Crystal structure of potassium bismuth hexathiodiphosphate, $KBiP_2S_6$

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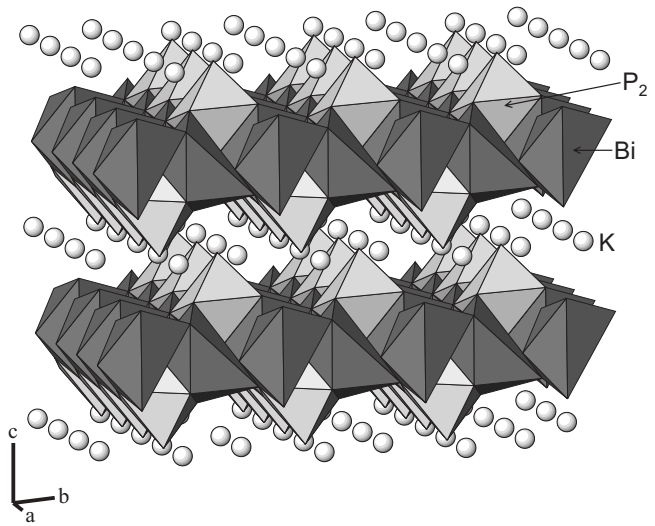

Abstract

$BiKP_2S_6$, monoclinic, $P12_11$ (No. 4), a = 6.6200(6) Å, b = 7.4058(7) Å, c = 9.9002(9) Å, β = 92.108(1)°, V = 485.0 Å^3, Z = 2, $R_{gt}(F)$ = 0.027, $wR_{ref}(F^2)$ = 0.060, T = 293 K.

Source of material

All manipulations were carried out under Ar atmosphere. For the synthesis of $KBiP_2S_6$ stoichiometric amounts of the corresponding high purity (99.99%) elements, supplied by Aldrich, were mixed an sealed in quartz tubes after evacuation. The mixture was them heated at 1123 K for two weeks. The reacted matter was slowly cooled (0.4 K/min) to room temperature.

Experimental details

The absolute configuration was tested and the $wR(F^2)$ values for the two possible orientations were 0.0586 and 0.1907. The first one represents the absolute structure of the crystal studied. The corresponding Flack parameter is 0.012(7).

Discussion

In the course of our work on chalcophosphate [1,2] we have preparated the quaternary bismuth hexathiodiphosphate $KBiP_2S_6$. The title compound has a complicated layered structure, which contains the ethane-like $[P_2S_6]^{4-}$ ligand. $KBiP_2S_6$ is structurally related to $Na_{0.16}Bi_{1.28}P_2S_6$ [3] and $KBiP_2Se_6$ [4]. The structure is characterized by layers of condensed S_6 distorted octahedra alternately centered by P_2 pairs and Bi atoms. The staircase layers of $[BiP_2S_6]^{1-}$ groups in the a-b plane are held together by a single layer of K^+ ions. The bond lengths in the hexathiodiphosphate $[P_2S_6]^{4-}$ are d(P—P) = 2.219(3) Å and d(P—S) in the range from 1.962(3) Å to 2.058(3) Å. The ethane-like $[P_2S_6]^{4-}$ ligand chelates to 4 Bi atoms, the bond lengths d(Bi—S) range from 2.706(2) Å to 3.143(2) Å.

Table 1. Data collection and handling.

Crystal:	red dark prism, size 0.075 × 0.075 × 0.2 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	201.48 cm^{-1}
Diffractometer, scan mode:	Siemens SMART CCD, φ/ω
$2\theta_{max}$:	56°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	3908, 2071
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 1901
$N(param)_{refined}$:	91
Programs:	SHELXL-97 [5], ATOMS [6]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Bi	2a	0.79399(4)	0.77391(6)	0.98012(3)	0.0245(2)	0.0188(1)	0.0223(2)	–0.0012(2)	0.0009(1)	–0.0048(2)
K	2a	0.7017(3)	0.0236(3)	0.5016(2)	0.032(1)	0.035(1)	0.026(1)	–0.0025(9)	–0.001(1)	0.0003(9)
P(1)	2a	0.6876(3)	0.3148(2)	0.8258(2)	0.017(1)	0.014(1)	0.013(1)	–0.0003(7)	–0.0014(8)	0.0005(7)
P(2)	2a	0.7956(3)	0.5409(3)	0.7003(2)	0.015(1)	0.0139(9)	0.014(1)	–0.0008(8)	–0.0017(8)	0.0004(8)
S(1)	2a	0.6585(3)	0.4287(3)	0.0136(2)	0.026(1)	0.020(1)	0.013(1)	–0.0044(9)	0.0015(9)	–0.0015(8)
S(2)	2a	0.9127(3)	0.1262(3)	0.8259(2)	0.019(1)	0.0153(9)	0.020(1)	0.0016(8)	–0.0028(9)	–0.0003(9)
S(3)	2a	0.4251(3)	0.2268(2)	0.7458(2)	0.018(1)	0.020(1)	0.020(1)	–0.0050(7)	–0.0033(8)	–0.0004(8)
S(4)	2a	0.0521(3)	0.6229(3)	0.8071(2)	0.015(1)	0.023(1)	0.019(1)	–0.0013(8)	–0.0010(8)	–0.0024(9)
S(5)	2a	0.5845(3)	0.7341(2)	0.7305(2)	0.021(1)	0.019(1)	0.021(1)	0.0043(8)	–0.0048(8)	–0.0008(8)
S(6)	2a	0.8230(4)	0.4592(3)	0.5134(2)	0.029(1)	0.031(1)	0.013(1)	–0.004(1)	0.0017(9)	–0.0020(9)

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Crystal structure of di(*N*-lithiummethylamino)bis(dimethylamino)silane, $Si(NLiCH_3)_2(N(CH_3)_2)_2$

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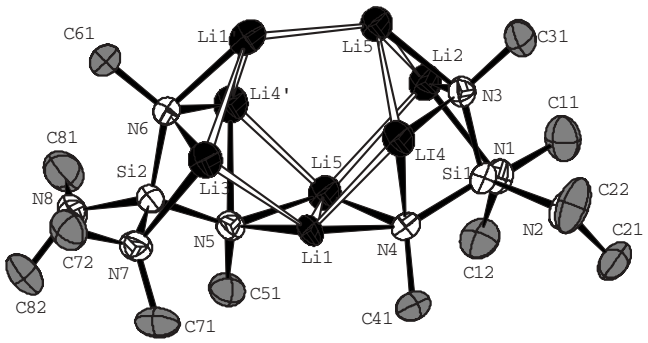

Abstract

$C_{12}H_{36}Li_4N_8Si_2$, monoclinic, *C*12/*c*1 (No. 15), a = 19.468(4) Å, b = 12.870(3) Å, c = 20.568(4) Å, β = 117.88(3)°, V = 4555.3 Å^3, Z = 8, $R_{gt}(F)$ = 0.052, $wR_{ref}(F^2)$ = 0.148, T = 293 K.

Source of material

$Si(NLiCH_3)_2(N(CH_3)_2)_2$ was obtained by reacting silicon tetrachloride first with lithiated dimethylamine and subsequently with lithiated monomethylamine in hexane. Transparent colourless crystals were grown from hexane solution at 238 K. All products are sensitive to air and moisture, so that they are to be handled under dry and oxygen free argon.

Experimental details

All non-hydrogen atoms were refined anisotropically, hydrogen atoms were calculated isotropically with fixed positions.

Table 1. Data collection and handling.

Crystal:	colorless irregular, size 0.2 × 0.5 × 1.0 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	1.66 cm^{-1}
Diffractometer, scan mode:	Stoe IPDS II, ω
$2\theta_{max}$:	45°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	11253, 2991
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 2209
$N(param)_{refined}$:	237
Programs:	SHELXS-97 [3], SHELXL-97 [4], DIAMOND [5]

Discussion

$Si(NLiCH_3)_2(N(CH_3)_2)_2$ crystallizes monoclinic in the space group *C*2/*c* and is, in contrast to dimeric $Si(NLiR)_2(N(CH_3)_2)_2$, R = CMe_3 [1], $SiMe_3$ [2], tetrameric in the solid state. In each tetramer eight lithium atoms cluster together to form the structure motive of realgar, As_4S_4. d(Li—Li) = 239.3(8) pm (shortest), 280.7(8) pm (longest). Together with half of the nitrogen atoms a topological interesting Li_8N_8-skeleton is built up: d(Li—N) = 201.5(6) pm (shortest), 229.6(6) pm (longest).

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(11A)	8*f*	0.3325	0.3281	0.1592	0.127
H(11B)	8*f*	0.3975	0.2853	0.1417	0.127
H(11C)	8*f*	0.4202	0.3389	0.2175	0.127
H(12A)	8*f*	0.2921	0.2274	0.2337	0.116
H(12B)	8*f*	0.3739	0.2583	0.2974	0.116
H(12C)	8*f*	0.3485	0.1414	0.2850	0.116
H(21A)	8*f*	0.1800	0.1646	0.0112	0.117
H(21B)	8*f*	0.2332	0.2353	0.0780	0.117
H(21C)	8*f*	0.1935	0.1367	0.0905	0.117
H(22A)	8*f*	0.2179	0.0532	–0.0282	0.154
H(22B)	8*f*	0.2560	–0.0371	0.0287	0.154
H(22C)	8*f*	0.3064	0.0277	0.0021	0.154
H(31A)	8*f*	0.4333	0.0804	0.0468	0.115
H(31B)	8*f*	0.5119	0.1266	0.1071	0.115
H(31C)	8*f*	0.4338	0.1865	0.0844	0.115
H(41A)	8*f*	0.2916	–0.1140	0.2292	0.098
H(41B)	8*f*	0.2491	–0.0671	0.1497	0.098
H(41C)	8*f*	0.2670	0.0033	0.2179	0.098
H(51A)	8*f*	0.3897	–0.0767	0.3651	0.098
H(51B)	8*f*	0.4572	–0.1229	0.4373	0.098
H(51C)	8*f*	0.3883	–0.1942	0.3845	0.098
H(61A)	8*f*	0.6997	–0.2643	0.4142	0.131
H(61B)	8*f*	0.6795	–0.3110	0.3369	0.131
H(61C)	8*f*	0.6569	–0.3716	0.3902	0.131
H(71A)	8*f*	0.3888	–0.4223	0.3614	0.125
H(71B)	8*f*	0.3675	–0.4519	0.2802	0.125
H(71C)	8*f*	0.3628	–0.3358	0.3008	0.125
H(72A)	8*f*	0.5073	–0.5167	0.3923	0.119
H(72B)	8*f*	0.5687	–0.4712	0.3710	0.119
H(72C)	8*f*	0.4948	–0.5281	0.3116	0.119
H(81A)	8*f*	0.6423	–0.2374	0.5684	0.147
H(81B)	8*f*	0.5976	–0.1484	0.5124	0.147
H(81C)	8*f*	0.6654	–0.2074	0.5074	0.147
H(82A)	8*f*	0.5745	–0.3531	0.5598	0.132
H(82B)	8*f*	0.5349	–0.4255	0.4907	0.132
H(82C)	8*f*	0.4890	–0.3311	0.4995	0.132

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Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Si(1)	8*f*	0.36463(5)	0.08144(7)	0.15744(5)	0.0394(5)	0.0428(5)	0.0399(6)	0.0076(4)	0.0130(4)	0.0019(4)
Si(2)	8*f*	0.52367(5)	–0.26924(7)	0.37585(5)	0.0432(6)	0.0449(6)	0.0419(6)	–0.0021(4)	0.0201(4)	0.0076(4)
N(1)	8*f*	0.3791(2)	0.1951(2)	0.2110(2)	0.056(2)	0.044(2)	0.054(2)	0.008(1)	0.020(2)	–0.001(1)
N(4)	8*f*	0.3617(2)	–0.0248(2)	0.2050(2)	0.032(1)	0.051(2)	0.049(2)	0.004(1)	0.018(1)	0.004(1)
N(3)	8*f*	0.4469(2)	0.0635(2)	0.1491(1)	0.044(2)	0.048(2)	0.040(2)	0.005(1)	0.020(1)	0.006(1)
N(2)	8*f*	0.2835(2)	0.1034(2)	0.0742(2)	0.050(2)	0.059(2)	0.049(2)	0.017(1)	0.006(2)	–0.002(2)
N(5)	8*f*	0.4644(2)	–0.1642(2)	0.3461(2)	0.049(2)	0.046(2)	0.042(2)	0.003(1)	0.026(1)	0.005(1)
N(6)	8*f*	0.5865(2)	–0.2501(2)	0.3412(2)	0.035(2)	0.048(2)	0.049(2)	0.003(1)	0.018(1)	0.010(1)
N(7)	8*f*	0.4721(2)	–0.3844(2)	0.3343(2)	0.052(2)	0.045(2)	0.065(2)	–0.008(1)	0.032(2)	0.001(1)
N(8)	8*f*	0.5680(2)	–0.2897(3)	0.4693(2)	0.061(2)	0.069(2)	0.045(2)	–0.009(2)	0.018(2)	0.016(2)
C(11)	8*f*	0.3826(3)	0.2954(3)	0.1797(3)	0.103(4)	0.048(2)	0.089(3)	0.001(2)	0.033(3)	0.001(2)
C(12)	8*f*	0.3455(3)	0.2065(4)	0.2611(3)	0.085(3)	0.077(3)	0.078(3)	0.017(2)	0.045(3)	–0.013(2)
C(21)	8*f*	0.2170(2)	0.1651(4)	0.0625(3)	0.052(2)	0.095(3)	0.073(3)	0.023(2)	0.017(2)	0.010(2)
C(22)	8*f*	0.2643(3)	0.0306(4)	0.0141(3)	0.099(4)	0.097(4)	0.059(3)	0.035(3)	–0.009(3)	–0.018(3)
C(31)	8*f*	0.4574(3)	0.1191(4)	0.0919(3)	0.081(3)	0.089(3)	0.068(3)	0.020(2)	0.041(2)	0.029(2)
C(41)	8*f*	0.2857(2)	–0.0531(3)	0.2000(2)	0.044(2)	0.071(3)	0.079(3)	0.003(2)	0.027(2)	0.009(2)
C(51)	8*f*	0.4211(2)	–0.1371(3)	0.3868(2)	0.074(3)	0.075(3)	0.063(3)	0.008(2)	0.045(2)	0.003(2)
C(61)	8*f*	0.6623(2)	–0.3039(4)	0.3734(3)	0.050(2)	0.111(4)	0.105(4)	0.026(2)	0.040(3)	0.053(3)
C(71)	8*f*	0.3908(3)	–0.3999(4)	0.3177(3)	0.070(3)	0.083(3)	0.106(4)	–0.025(2)	0.050(3)	–0.007(3)
C(72)	8*f*	0.5144(3)	–0.4838(3)	0.3540(3)	0.100(4)	0.051(2)	0.096(4)	0.004(2)	0.053(3)	0.006(2)
C(81)	8*f*	0.6229(3)	–0.2144(4)	0.5185(3)	0.098(3)	0.110(3)	0.080(2)	–0.020(2)	0.036(2)	0.012(2)
C(82)	8*f*	0.5392(3)	–0.3553(4)	0.5081(3)	0.121(4)	0.087(3)	0.069(3)	–0.009(3)	0.055(3)	0.019(3)
Li(1)	8*f*	0.3987(3)	–0.1729(4)	0.2367(3)	0.042(3)	0.048(3)	0.045(3)	0.002(2)	0.019(3)	–0.002(2)
Li(2)	4*e*	1/2	0.1487(6)	1/4	0.045(4)	0.054(5)	0.046(5)	0	0.016(4)	0
Li(3)	4*e*	1/2	–0.3343(6)	1/4	0.051(5)	0.048(4)	0.054(5)	0	0.024(4)	0
Li(4)	8*f*	0.4228(3)	–0.0935(4)	0.1441(3)	0.052(3)	0.045(3)	0.052(3)	0.004(3)	0.023(3)	–0.003(3)
Li(5)	8*f*	0.4514(3)	–0.0151(4)	0.3089(3)	0.043(3)	0.052(3)	0.048(3)	–0.002(2)	0.018(3)	0.000(3)

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Refinement of the crystal structure of trimercury(II) orthoborate, $Hg_3(BO_3)_2$

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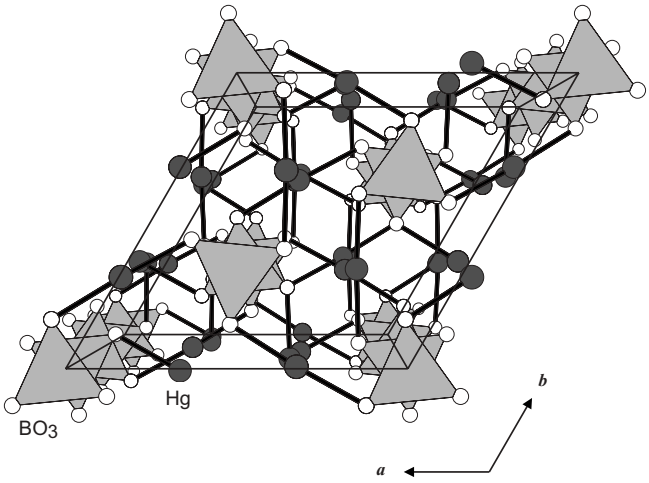

Abstract

$B_2Hg_3O_6$, trigonal, $R\bar{3}c$ (No. 167), a = 8.8936(9) Å, c = 13.052(3) Å, V = 894.1 Å^3, Z = 6, $R_{gt}(F)$ = 0.021, $wR_{ref}(F^2)$ = 0.053, T = 293 K.

Source of material

Stoichiometric amounts of B_2O_3 (Merck, p. A.) and HgO (Merck, p. A.) were heated in a sealed and evacuated silica tube at 723 K for two days which yielded a light-orange polycrystalline product. Application of a temperature gradient 773 K → 723 K for two days led to the formation of colourless single crystals with mostly pinacoidal habit and a length of up to 2 mm at the colder zone of the tube.

Discussion

$Hg_3(BO_3)_2$ has been structurally determined in a previous work by Rietveld refinement of X-ray powder data [1], using the structure of the isotypic $Eu_3(BO_3)_2$ [2] as a starting model. $Ca_3(BO_3)_2$ is another member of this structural family [3,4]. Hg(II) compounds normally show a unique crystal chemistry with a pronounced linear coordination [5,6] of the metal atom in comparison with e.g. the given Eu and Ca compounds . Since the previous model determined by the Rietveld refinement reveals an eight-fold coordinate Hg atom with more or less similar Hg—O distances, it seemed reasonable to refine the structure with higher accuracy on the basis of single crystal data.

$Hg_3(BO_3)_2$ is composed of columns of mercury atoms extended parallel to [001] and which are almost coincident with the 3_1 axis. The nearly planar borate anions are situated on trigonal prismatic holes around the threefold axes and are linked with the metal atoms via short Hg—O distances, as emphasized by the bold sticks in the figure. In contrast to the previous model, Hg shows the expected linear coordination with two very short Hg—O distances of 2.033(4) Å and an ∠O–Hg–O angle of 176.6(2)°. The two next nearest O atoms show significantly longer distances of 2.675(4) Å; the coordination around the Hg atom is augmented by four O atoms with long distances of 3.027(4) Å and 3.044 Å. The geometry of the BO_3^{3-} group deviates only slightly from that of an equilateral triangle and lies with a B—O distance of 1.375(4) Å and an ∠O–B–O angle of 119.98(2)° within the scope of the expected values [7].

Table 1. Data collection and handling.

Crystal:	colourless pinacoid, size 0.22 × 0.33 × 0.38 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	770.51 cm^{-1}
Diffractometer, scan mode:	Siemens SMART CCD, ω
$2\theta_{max}$:	60.92°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	3135, 309
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 307
$N(param)_{refined}$:	19
Programs:	SHELXL-97 [8], HABITUS [9], ATOMS [10]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Hg	18*e*	0.35247(5)	0	1/4	0.0117(2)	0.0101(2)	0.0184(2)	$U_{22}/2$	0.00037(4)	$2U_{13}$
B	12*c*	0	0	0.3873(6)	0.009(2)	U_{11}	0.012(3)	$U_{11}/2$	0	0
O	36*f*	0.1776(5)	0.0738(5)	0.1111(3)	0.010(2)	0.010(2)	0.027(2)	0.005(2)	–0.003(1)	0.002(1)

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Crystal structure of dithiocyanatotetra(dimethylformamide)manganese(II), $Mn(NCS)_2[OCHN(CH_3)_2]_4$

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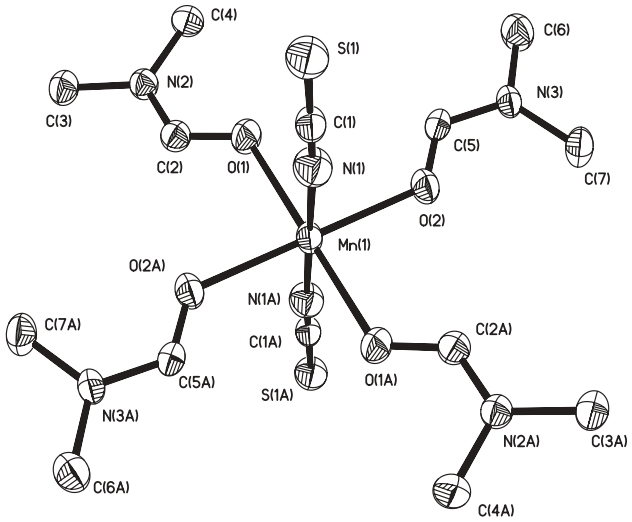

Abstract

$C_{14}H_{28}MnN_6O_4S_2$, triclinic, $P\bar{1}$ (No. 2), a = 7.27(2) Å, b = 9.55(2) Å, c = 9.68(2) Å, α = 82.12(3)°, β = 68.90(3)°, γ = 67.61(2)°, V = 580.0 Å^3, Z = 1, $R_{gt}(F)$ = 0.069, $wR_{ref}(F^2)$ = 0.190, T = 298 K.

Source of material

0.4534 g $Na_4Mn(NCS)_6(H_2O)_9$ (0.690 mmol) was dissolved in 10 ml dimethylformamide and the transparent colorless single crystal was obtained after the solution was allowed to stand at room temperature for a week.

Experimental details

The relative large standard deviations of the lattice parameters might be due to the low quality of the crystal.

Discussion

The structure of the title complex consists of divalent manganese cation coordinated by two thiocyanate anions and four neutral dimethylformamide molecules. The divalent manganese cation is coordinated by two N atoms from the two thiocyanate anions and four O atoms from four dimethylformamide molecules. The bond distance of Mn—N is 2.227(5) Å and the Mn—O bond distances are 2.225(5) Å and 2.182(4) Å. The Mn—N bond distance is close to the Mn—N bond distances of other complexes dealing with divalent manganese cation and thiocyanate ligand [1-4]. The angle of N–Mn–N is 180.0(2)° and the angles dealing with N–Mn–O range from 89.4(2)° to 90.6(2)°, while the angles of O–Mn–O are in the range of 89.2(2)° to 180.0°. The bond distances and the angles indicate that the divalent manganese cation is located at the inversion center in a little distorted octahedral environment. The neutral complexes are connected to each other through intermolecular forces to form a one-dimensional chain along c axis and then the one-dimensional chains pile up in parallel way to form the three-dimensional crystal structure.

Table 1. Data collection and handling.

Crystal:	colorless prism, size 0.15 × 0.23 × 0.32 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	7.78 cm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD, φ/ω
$2\theta_{max}$:	52.72°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	3093, 2210
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 1527
$N(param)_{refined}$:	124
Programs:	SHELXS-97 [5], SHELXL-97 [6]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(2)	2*i*	0.6266	0.3115	0.2198	0.060
H(3A)	2*i*	0.4832	0.2579	–0.0662	0.093
H(3B)	2*i*	0.6056	0.1508	0.0349	0.093
H(3C)	2*i*	0.6801	0.2803	–0.0552	0.093
H(4A)	2*i*	0.1892	0.4156	0.0389	0.090
H(4B)	2*i*	0.1815	0.5477	0.1234	0.090
H(4C)	2*i*	0.1098	0.4166	0.2124	0.090
H(5)	2*i*	0.0488	0.6935	0.4777	0.057
H(6A)	2*i*	–0.3999	1.0071	0.6191	0.106
H(6B)	2*i*	–0.3523	0.8409	0.5772	0.106
H(6C)	2*i*	–0.2517	0.9450	0.4599	0.106
H(7A)	2*i*	–0.2489	1.0315	0.7603	0.095
H(7B)	2*i*	–0.0030	0.9855	0.6927	0.095
H(7C)	2*i*	–0.1017	0.8817	0.8115	0.095

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Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mn(1)	1*h*	1/2	1/2	1/2	0.0411(5)	0.0414(5)	0.0424(5)	–0.0055(3)	–0.0122(4)	–0.0099(3)
N(1)	2*i*	0.3564(6)	0.3512(5)	0.6646(5)	0.065(2)	0.064(3)	0.061(2)	–0.026(2)	–0.014(2)	0.000(2)
N(2)	2*i*	0.4228(5)	0.3555(4)	0.1221(4)	0.047(2)	0.050(2)	0.046(2)	–0.012(2)	–0.017(2)	–0.006(2)
N(3)	2*i*	–0.1131(5)	0.8655(4)	0.6126(4)	0.041(2)	0.045(2)	0.050(2)	–0.004(1)	–0.010(1)	–0.014(2)
O(1)	2*i*	0.3790(5)	0.4549(4)	0.3363(3)	0.058(2)	0.068(2)	0.053(2)	–0.012(2)	–0.023(1)	–0.020(2)
O(2)	2*i*	0.2124(4)	0.6965(3)	0.5844(4)	0.046(2)	0.053(2)	0.064(2)	0.000(1)	–0.018(1)	–0.019(2)
S(1)	2*i*	0.1779(2)	0.1533(2)	0.8574(2)	0.0656(8)	0.0657(8)	0.0629(7)	–0.0291(6)	–0.0131(6)	–0.0006(6)
C(1)	2*i*	0.2827(6)	0.2706(5)	0.7433(5)	0.045(2)	0.046(2)	0.051(2)	–0.007(2)	–0.015(2)	–0.013(2)
C(2)	2*i*	0.4878(7)	0.3698(5)	0.2272(5)	0.049(2)	0.048(2)	0.053(2)	–0.012(2)	–0.021(2)	–0.005(2)
C(3)	2*i*	0.5596(8)	0.2524(6)	–0.0016(6)	0.063(3)	0.062(3)	0.059(3)	–0.014(2)	–0.020(2)	–0.017(2)
C(4)	2*i*	0.2074(7)	0.4412(6)	0.1244(6)	0.050(2)	0.060(3)	0.071(3)	–0.012(2)	–0.028(2)	–0.009(2)
C(5)	2*i*	0.0538(6)	0.7444(5)	0.5508(5)	0.051(2)	0.044(2)	0.047(2)	–0.013(2)	–0.015(2)	–0.014(2)
C(6)	2*i*	–0.2946(8)	0.9192(6)	0.5630(6)	0.058(3)	0.070(3)	0.075(3)	–0.004(2)	–0.027(2)	–0.015(3)
C(7)	2*i*	–0.1170(8)	0.9480(6)	0.7291(5)	0.068(3)	0.056(3)	0.055(3)	–0.008(2)	–0.018(2)	–0.018(2)

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Crystal structure of erbium vanadium tantal boride, $Er(V_{0.77}Ta_{0.23})VB_6$

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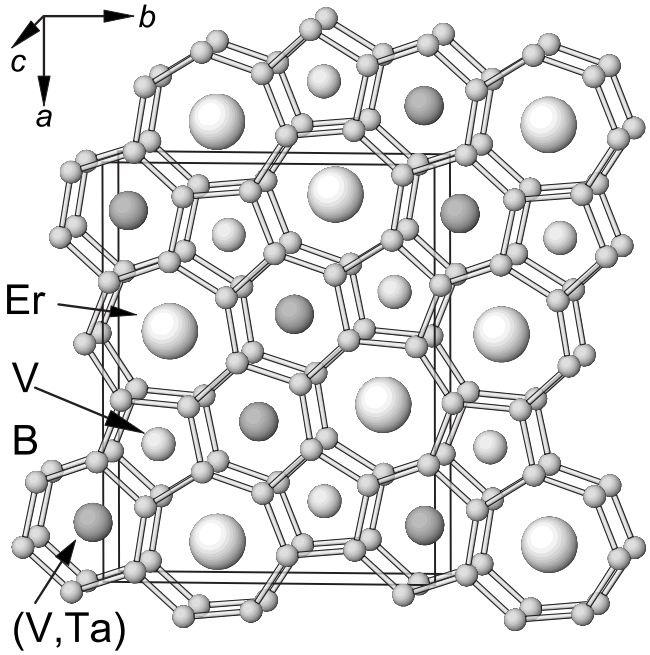

Abstract

$B_6ErTa_{0.23}V_{1.77}$, orthorhombic, *Pbam* (No. 55), $a = 11.280(2)$ Å, $b = 8.940(2)$ Å, $c = 3.390(1)$ Å, $V = 341.9$ Å^3, $Z = 4$, $R_{gt}(F) = 0.034$, $wR_{obs}(F) = 0.034$, $T = 293$ K.

Source of material

The title compound was obtained as by-product during systematic investigation in ternary Er–V–B system. A pellet pressed from erbium filings (99.9 %), vanadium powder (99.5 %), and crystalline boron (99.99 %) in ratio of 2:1:6 was wrapped in tantalum foil, sealed in quartz ampoule and sintered at 1270 K. Needle-shaped crystal were formed on contact surfaces of the pellet and tantalum foil. The presence of tantalum in the crystal was suspected during the structure refinement and was confirmed by EDAX. A detected atomic ratio between vanadium and sum of erbium with tantalum of 1.27(2) : 1 agrees with values of 1.44(1) : 1 obtained from crystal structure refinement.

Experimental details

The lattice parameters of $Er(V_{0.77}Ta_{0.23})VB_6$ were determined from least-square procedure of 1978 reflections measured during the data collection.

Discussion

The crystal structure of $Er(V_{0.77}Ta_{0.23})VB_6$ adopts Y_2ReB_6 type [1]. The boron atoms form two-dimensional planar nets of condensed five-, six-, and seven-membered rings. All prismatically coordinated centers between two slabs are filled by metals, according to the atomic radii, the largest Er and the smallest V atoms occupy the centers of heptagonal and pentagonal prisms, respectively. The hexagonal prisms contain statistically distributed Ta (intermediate size) and V atoms. Coordination polyhedra around Er, (Ta,V), and V atoms have 23, 20, and 17 vertices, respectively. Each boron atom is trigonal prismatically coordinated by metal atoms. The environment is completed by three additional boron neighbors, which are situated in the same plane as the central atom. The B—B bond lengths vary between 1.74(2) Å and 1.85(2) Å and agree very well with average distance of 1.776 Å in α-rhombohedral boron [2]. The shortest contacts between another pairs of atoms are d(Er—Ta,V) = 3.391(2) Å, d(Er—V) = 3.046(3) Å, d(Er—B) = 2.631(1) Å, d(Ta,V—V) = 2.764(3) Å, d(Ta,V—B) = 2.426(1) Å, and d(V—B) = 2.254(9) Å. Ternary compounds with Y_2ReB_6 structure type are observed in numerous rare-earth transition metal boron systems: RE_2MB_6 (RE = Y, Gd–Tm; M = Ru, Re, Os), RE_2MB_6 (RE = Yb, Lu; M = Ru, Os), Lu_2FeB_6, Yb_2AlB_6, U_2MB_6 (M = Mo, W, Re, Os) [3]; Sc_2ReB_6 [4]; RE_2MoB_6 (RE = Er, Tm, Yb, Lu) [4,5]; $Lu_{1.34}V_{1.66}B_6$ [6]; Lu_2WB_6 [7]. Nevertheless, a formation of isotypic phases was not detected during systematic investigation of ternary Er–V–B [8] and Ta–V–B [9] systems. $Er(V_{0.77}Ta_{0.23})VB_6$ is the first quasi-ternary representative of Y_2ReB_6 type and the third example of described structure, where transition metal atoms have hexagonal-prismatic environment. Recently reported borides Zr_2CrB_6 and $ZrCr_2B_6$ contain in the centers of hexagonal prisms Cr and statistically distributed Cr and Zr atoms, respectively [10].

Table 1. Data collection and handling.

Crystal:	metallic needle, size 0.02 × 0.03 × 0.08 mm
Wavelength:	Mo K_α radiation (0.7107 Å)
μ:	377.5 cm^{-1}
Diffractometer, scan mode:	Rigaku Mercury CCD, φ/ω
$2\theta_{max}$:	64.06°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	2542, 565
Criterion for F_{obs}, $N(hkl)_{gt}$:	$F_{obs} > 4\,\sigma(F_{obs})$, 545
$N(param)_{refined}$:	38
Programs:	WinCSD [11], ATOMS [12]

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Table 2. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	*x*	*y*	*z*	U_{iso}
B(1)	4*g*	0.237(1)	0.202(1)	0	0.005(2)
B(2)	4*g*	0.213(1)	0.518(2)	0	0.004(2)
B(3)	4*g*	0.081(1)	0.241(2)	0	0.005(2)
B(4)	4*g*	0.067(1)	0.447(2)	0	0.005(2)
B(5)	4*g*	0.320(1)	0.371(2)	0	0.006(2)
B(6)	4*g*	0.024(1)	0.907(2)	0	0.007(2)

Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Er	4*h*	0.91475(5)	0.32152(6)	1/2	0.0040(3)	0.0021(2)	0.0037(3)	–0.0005(2)	0	0
V/Ta(1) [a]	4*h*	0.37194(1)	0.55391(1)	1/2	0.0050(5)	0.0041(5)	0.0047(5)	–0.0012(4)	0	0
V(2)	4*h*	0.1840(2)	0.3555(2)	1/2	0.0052(8)	0.0030(8)	0.0044(8)	0.0022(7)	0	0

a: V/Ta(1) = 0.768(3)V + 0.232Ta

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The crystal structure of cerium decanickel tetraphosphide, $CeNi_{10}P_4$

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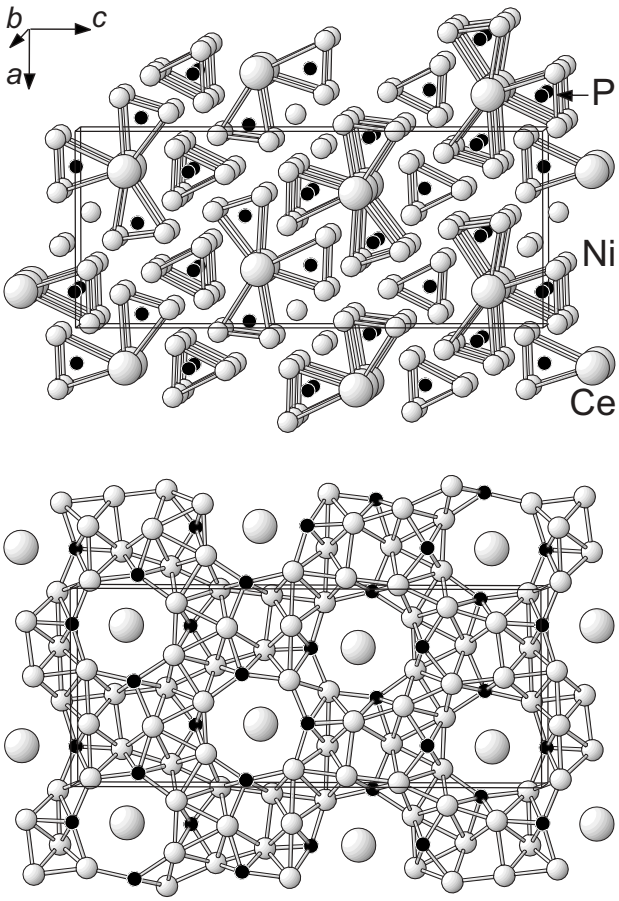

Abstract

$CeNi_{10}P_4$, orthorhombic, *Pnma* (No. 62), $a = 9.263(1)$ Å, $b = 3.6654(5)$ Å, $c = 22.092(3)$ Å, $V = 750.1$ Å^3, $Z = 4$, $R_{gt}(F) = 0.030$, $wR_{ref}(F^2) = 0.068$, $T = 293$ K.

Source of material

The title compound was prepared from cerium filings (99.99 %), nickel powder (99.99 %), and red phosphorus (99.99 %). A mixture of starting components with nominal composition of $Ce_8Ni_{67}P_{25}$ was pressed into a small pellet (~ 1 g) and sealed inside a carbon-glass crucible in evacuated silica tube. A sintering was carried out by heating up to 1273 K within 24 h, treatment at this temperature for the next 20 h and slow cooling to the room temperature (1 K/min). Needle-like single crystals with metallic lustre were formed on the surface of the pellet. The crystals showed tendency to form twinned agglomerates along needle direction (equivalent to the crystallographic [010] direction). The crystals are stable on the air and against diluted hydrochloric acid.

Experimental details

Lattice constants were refined from 1478 reflections (in the selected 2θ interval of 25° – 45°) obtained during the data collection. The intensities of the reflections were corrected for absorption by using multi-scan routine.

Discussion

The crystal structure of $CeNi_{10}P_4$ adopts the $LaNi_{10}P_4$ type (Pearson symbol *oP*60) [1]. The reported composition corresponds to the formely detected ternary phase ~ $CeNi_{11}P_5$ observed during systematic investigation of the ternary Ce–Ni–P system at 870 K [2].

All atoms in the structure of $CeNi_{10}P_4$ are situated on mirror planes, which are extended perpendicular [010] (figure, top). Phosphorus atoms are trigonal prismatically surrounded by metal species. Such trigonal prisms are partially condensed to three-membered "propellers" [3]. Neighbouring building blocks are displaced with respect to each one by half of translation period along [010]. A detailed discussion of $LaNi_{10}P_4$ structure type and its relationship to another two-layered compounds with metal-nonmetal ratio close to 2 : 1 can be found elsewhere [1,3].

Alternatively the structure of $CeNi_{10}P_4$ can be described as three-dimensional network built up from Ni and P atoms with infinite channels along [010] direction filled by rare-earth atoms (figure, bottom). The interatomic distances within this network cover the intervals of 2.214(2) Å – 2.451(2) Å for *d*(Ni—P) and 2.421(2) Å – 2.790(2) Å for *d*(Ni—Ni). The shortest Ce—P, Ce—Ni, and Ce—Ce contacts are of 3.014(2) Å, 3.222(1) Å, and 3.665(1) Å, respectively. No interaction between phosphorus atoms was found in the structure of $CeNi_{10}P_4$.

Table 1. Data collection and handling.

Crystal:	metallic needle, size 0.012 × 0.012 × 0.125 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	311.65 cm^{-1}
Diffractometer, scan mode:	Rigaku Mercury CCD, ω/φ
$2\theta_{max}$:	57.4°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	5631, 1104
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 980
$N(param)_{refined}$:	91
Programs:	SHELXL-97 [4], ATOMS [5]

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Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ce	4*c*	0.19962(5)	1/4	0.89228(2)	0.0100(2)	0.0084(2)	0.0060(2)	0	–0.0001(2)	0
Ni(1)	4*c*	0.0165(1)	1/4	0.69305(5)	0.0129(5)	0.0086(5)	0.0057(5)	0	–0.0004(4)	0
Ni(2)	4*c*	0.0351(1)	1/4	0.03817(5)	0.0095(5)	0.0105(5)	0.0078(6)	0	–0.0008(4)	0
Ni(3)	4*c*	0.0493(1)	1/4	0.58265(5)	0.0132(5)	0.0084(5)	0.0078(6)	0	0.0033(4)	0
Ni(4)	4*c*	0.0822(1)	1/4	0.46992(5)	0.0084(4)	0.0108(5)	0.0066(5)	0	–0.0010(4)	0
Ni(5)	4*c*	0.1602(1)	1/4	0.28380(5)	0.0085(4)	0.0096(5)	0.0067(5)	0	0.0009(4)	0
Ni(6)	4*c*	0.2963(1)	1/4	0.17115(5)	0.0085(5)	0.0133(5)	0.0130(6)	0	–0.0022(4)	0
Ni(7)	4*c*	0.3083(1)	1/4	0.03457(5)	0.0093(4)	0.0076(5)	0.0123(6)	0	–0.0003(4)	0
Ni(8)	4*c*	0.3261(1)	1/4	0.59813(5)	0.0133(5)	0.0093(5)	0.0064(5)	0	–0.0020(4)	0
Ni(9)	4*c*	0.4030(1)	1/4	0.70287(5)	0.0116(4)	0.0084(5)	0.0058(5)	0	0.0002(4)	0
Ni(10)	4*c*	0.4236(1)	1/4	0.27850(5)	0.0075(4)	0.0102(5)	0.0073(5)	0	–0.0007(4)	0
P(1)	4*c*	0.0274(2)	1/4	0.3693(1)	0.0094(8)	0.0078(9)	0.007(1)	0	0.0004(7)	0
P(2)	4*c*	0.0635(2)	1/4	0.1396(1)	0.0090(8)	0.0086(9)	0.005(1)	0	0.0009(7)	0
P(3)	4*c*	0.2038(2)	1/4	0.7553(1)	0.0093(8)	0.0071(9)	0.009(1)	0	0.0007(7)	0
P(4)	4*c*	0.3141(2)	1/4	0.5004(1)	0.0081(8)	0.0079(9)	0.007(1)	0	–0.0015(7)	0

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Crystal structure of tristrontium tetranitridochromate(VI), $Sr_3[CrN_4]$

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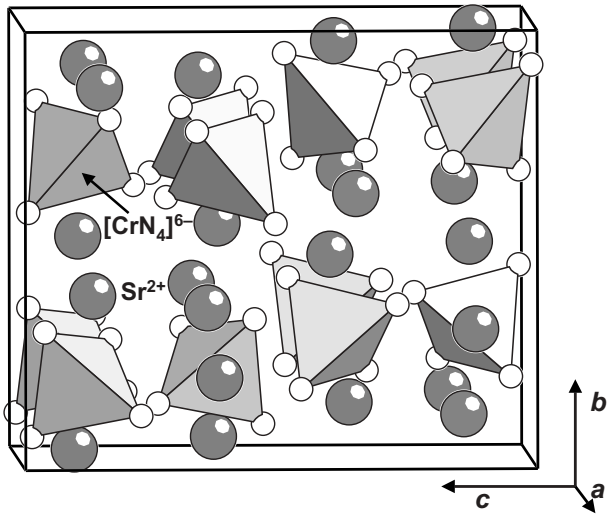

Abstract

CrN_4Sr_3, orthorhombic, *Pbca* (No. 61), $a = 10.199(1)$ Å, $b = 9.566(1)$ Å, $c = 11.169(2)$ Å, $V = 1089.6$ Å^3, $Z = 8$, $R(P) = 0.082$, $R(I) = 0.053$, $T = 293$ K.

Source of material

$Sr_3[CrN_4]$ was obtained as a brown powder from reaction of Sr_2N and CrN in the molar ratio 3 : 2 in nitrogen atmosphere at 1170 K for 20 h. Chemical analyses confirm the composition: 72.3(14) wt% Sr, 13.9(4) wt% Cr, 15.5(1) wt% N ≡ $Sr_{3.09(6)}Cr_{1.00(3)}N_{4.11(3)}$.

Experimental details

The unit cell parameters were determined from the least-squares refinement of the 2θ values of 57 reflections in the range $7° < 2\theta < 79°$ (X-ray powder data, LaB_6 standard, $a = 4.15695(6)$ Å). N atoms were refined with common U_{iso}.

Discussion

$Sr_3[CrN_4]$ is isotypic to $Ba_3[CrN_4]$ [1], the low temperature modification of $Ba_3[MN_4]$ (M = Mo, W) [2] as well to the related ordered ($Ca_2Sr[WN_4]$ [3]) and the substitutionally disordered ($(Ba,Sr)_3[MN_4]$ [4]) phases. Interestingly, $Sr_3[MoN_4]$ was reported to crystallize in a monoclinic distortion variant of the $Ba_3[CrN_4]$ structure [5]. No indication for such a distortion could be extracted from the X-ray powder diffraction data in the present study.

The crystal structure of $Sr_3[CrN_4]$ comprises isolated $[CrN_4]^{6-}$ tetrahedra with distances d(Cr—N) in the range of 1.700(7) Å – 1.789(7) Å comparable to those of 1.725 Å – 1.784 Å in $Ba_3[CrN_4]$ [1]. As in the mentioned Mo and W containing phases these tetrahedra are arranged in the motif of a hexagonal close packing. In $Sr_3[CrN_4]$ the Sr^{2+} ions are five- and six-fold coordinated by N with d(Sr—N) = 2.453 Å ($Sr_3[MoN_4]$: d(Sr—N) = 2.43 Å [5]). Magnetic susceptibility measurements revealed diamagnetism which is consistent with Cr^{6+}.

Table 1. Data collection and handling.

Powder:	brown
Wavelength:	Cu K_α radiation (1.54059 Å)
μ:	65.6 cm^{-1}
Diffractometer, scan mode:	Huber image plate Guinier, ω/θ
$2\theta_{max}$, stepwidth:	100°, 0.005°
$N(points)_{measured}$:	17600
$N(hkl)_{measured}$:	556
$N(param)_{refined}$:	35
Programs:	CSD [6], DIAMOND [7]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
Sr(1)	8*c*	0.02778(9)	0.12894(1)	0.14518(8)	0.0056(7)
Sr(2)	8*c*	0.12810(8)	0.47161(1)	0.10452(8)	0.0030(7)
Sr(3)	8*c*	0.21984(1)	0.30365(1)	0.38670(1)	0.0061(7)
Cr	8*c*	0.40045(1)	0.3054(2)	0.11224(2)	0.0049(5)
N(1)	8*c*	0.9946(6)	0.3795(8)	0.2694(6)	0.0050(7)
N(2)	8*c*	0.3506(7)	0.4306(8)	0.0102(6)	0.0050
N(3)	8*c*	0.0048(7)	0.1857(7)	0.4657(6)	0.0050
N(4)	8*c*	0.2684(7)	0.2225(7)	0.1721(6)	0.0050

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Crystal structure of hexamethanolo-iron diiodide, $Fe(HOCH_3)_6I_2$

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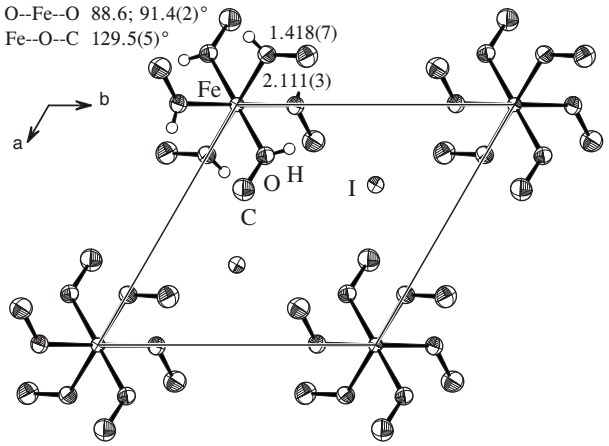

Abstract

$C_6H_{24}FeI_2O_6$, trigonal, $P\bar{3}$ (No. 147), $a = 8.2947(8)$ Å, $c = 7.0884(6)$ Å, $V = 422.4$ Å^3, $Z = 1$, $R_{gt}(F) = 0.023$, $wR_{ref}(F^2) = 0.065$, $T = 193$ K.

Source of material

Iron diiodide (0.31 g), prepared from iron and iodine [1], was dissolved in 2.0 mL of anhydrous methanol. After addition of 10 mL of anhydrous diethylether the title compound crystallized in the course of two hours. After decantation the crystals were dried in a stream of dry argon.

Experimental details

$Fe(HOCH_3)_6I_2$ is isotypic to $Ca(HOCH_3)_6Br_2$ [2]. As noted for the latter, merohedral twinning occurs. However, contrary to [2], we do not find (001) as a twinning plane, but twins of twins with the twinning planes (110) and (120). The domains of the (120)-twinning are very small, as evidenced by the refinement results: assuming macroscopic twinning along (120) (superposition of F^2 values) resulted in $R_{gt}(F) = 0.035$; superposition of F values yielded $R_{gt}(F) = 0.023$. However, for another crystal the F^2 superposition was slightly better. The four components of the reported crystal had volume fractions of 0.61(1), 0.13 (110)-twin, 0.22 (120) and 0.04 (210). If all four components had the same volume fractions, their superposition would feign the space group $P6/mmm$, which is a supergroup of $P\bar{3}$.

Discussion

The methyl groups and iodide ions are arranged like in a hexagonal closest-packing. One eighth of the octahedral voids are occupied by Fe^{2+} ions together with the O atoms linking them to the methyl groups. Another description relates the structure to the CdI_2 type, in which $Fe(OCH_3)_6^{2+}$ ions take the positions of the cadmium ions.

Table 1. Data collection and handling.

Crystal:	colourless hexagonal prism, size 0.13 × 0.24 × 0.34 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	45.61 cm^{-1}
Diffractometer, scan mode:	Stoe IPDS 2; $\Delta\varphi = 1°$, $\omega = 0° - 180°$ at $\varphi = 30°$, $\omega = 0° - 98°$ at $\varphi = 120°$
$2\theta_{max}$:	57.26°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	5978, 730
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 726
$N(param)_{refined}$:	37
Program:	SHELX-97 [3]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(1)	6*g*	0.19(1)	0.28(1)	0.20(1)	0.04(2)
H(2)	6*g*	0.4335	0.3229	0.3337	0.16
H(3)	6*g*	0.4297	0.1717	0.1905	0.16
H(4)	6*g*	0.2967	0.1055	0.3717	0.16

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Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Fe	1*a*	0	0	0	0.0196(3)	U_{11}	0.0294(6)	$U_{11}/2$	0	0
I	2*d*	1/3	2/3	0.23363(7)	0.0259(2)	U_{11}	0.0450(2)	$U_{11}/2$	0	0
O	6*g*	0.2127(5)	0.2083(5)	0.1675(6)	0.033(2)	0.024(2)	0.050(2)	0.016(1)	–0.017(2)	–0.010(2)
C	6*g*	0.3541(8)	0.202(1)	0.2741(8)	0.043(4)	0.045(3)	0.056(4)	0.022(3)	–0.029(3)	–0.009(3)

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Crystal structure of sodium cadmium diaqua *catena*-[monoboro-diphosphate]-hydrate, $NaCd(H_2O)_2[BP_2O_8] \cdot 0.8H_2O$

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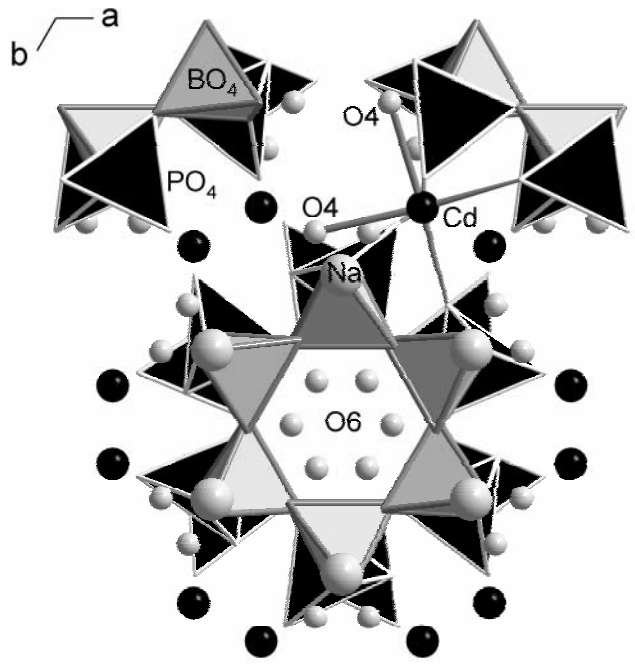

Abstract

$BCdH_6NaO_{10.8}P_2$, hexagonal, $P6_122$ (No. 178), $a = 9.713(1)$ Å, $c = 16.136(3)$ Å, $V = 1318.4$ Å^3, $Z = 6$, $R_{gt}(F) = 0.047$, $wR_{ref}(F^2) = 0.105$, $T = 273$ K.

Source of material

$NaCd(H_2O)_2[BP_2O_8] \cdot 0.8H_2O$ was prepared under mild hydrothermal conditions. A mixture of 0.459 g $CdCl_2 \cdot 2.5H_2O$, 1.900 g $Na_2B_4O_7 \cdot 10H_2O$, 6.436 g $NaBO_2 \cdot 4H_2O$, and 5 ml (85%) H_3PO_4 was heated at 363 K in deionized water (10 ml) under stirring until the components were completely dissolved. The clear solution (pH = 2.0) was transferred to a teflon autoclave (internal volume 27 ml) with filling degree 70% and heated at 443 K for four days. All the starting materials were of analytical grade without further purification. The chemical composition of the title compound was confirmed by ICP-AES analysis.

Discussion

A considerable number of borophosphates has been characterized in the past few years; however no cadmium based compounds have been reported so far. Here we report the first Cd-based borophosphate, $NaCd(H_2O)_2[BP_2O_8] \cdot 0.8H_2O$. Its crystal structure belongs to the family of borophosphate-hydrates with the general formula $M_x^I M_y^{II}(H_2O)_2[BP_2O_8] \cdot zH_2O$ (M^I = Li, Na, K, Rb, Cs; M^{II} = Mg, Mn, Fe, Co, Ni, Zn, Cu; $x = 0.35 - 1$, $y = 1 - 1.3$, $z = 0.2 - 1$) [1,2].

The crystal structure of the title compound contains infinite one-dimensional anionic tetrahedral ribbons $^1_\infty\{[BP_2O_8]^{3-}\}$, which form helical arrangements around the 6_1 screw axis. The spiral ribbons are built up from four-membered rings in which BO_4 and PO_4 groups alternate. Each BO_4 belongs to two adjacent four-membered rings of tetrahedra along the ribbon in such a way that all vertices of the BO_4 tetrahedra participate in bridging functions with PO_4 tetrahedra. The free loops of the borophosphate helices are occupied by Na^+ cations, which are surrounded by six oxygen atoms from adjacent phosphate groups (O2) and water molecules ($O4_{H_2O}$, $O6_{H_2O}$) in an irregular environment. The double helix $^1_\infty\{Na[BP_2O_8]^{2-}\}$ is completed by forming a central channel running along the 6_1 screw axis. The channel is filled with disordered water molecules ($O6_{H_2O}$), resulting in the formula $\{Na[BP_2O_8]^{2-} \cdot 0.8H_2O\}$. The Cd^{2+} ions are coordinated to four oxygen atoms of PO_4 groups (O2, O5) and two water molecules ($O4_{H_2O}$), resulting in an octahedral coordination $Cd(O_P)_4(O_{H_2O})_2$ connecting neighboring ribbons. Bond lengths and angles within the anionic partial structure are consistent with related borophosphates [3-6].

Table 1. Data collection and handling.

Crystal:	colorless hexagonal bipyramid, size 0.08 × 0.08 × 0.09 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	29.48 cm^{-1}
Diffractometer, scan mode:	Brucker SMART CCD, ω/φ
$2\theta_{max}$:	56.46°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	8039, 1072
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 1072
$N(param)_{refined}$:	77
Programs:	SHELXL-97 [7], DIAMOND [8]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	Occ.	x	y	z	U_{iso}
O(6)	6*a*	0.80	0.889(6)	0	0	0.23(3)
B	6*b*		0.1525(7)	2x	1/4	0.015(2)
H(1)	12*c*		0.94(2)	–0.15(1)	0.231(9)	0.05
H(2)	12*c*		0.61(2)	0.17(1)	0.048(8)	0.05
H(3)	12*c*		0.8094	0.2446	0.0332	0.05

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Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cd	6*b*	0.45073(4)	2*x*	1/4	0.0140(3)	0.0116(4)	0.0136(3)	$U_{22}/2$	–0.0039(2)	0
P	12*c*	0.8376(2)	0.2224(2)	0.2509(1)	0.0109(8)	0.0108(8)	0.0080(8)	0.0035(6)	0.0021(7)	0.0032(8)
Na	6*b*	0.8116(6)	2*x*	1/4	0.078(4)	0.111(7)	0.027(3)	$U_{22}/2$	–0.003(3)	0
O(1)	12*c*	0.8151(6)	0.2284(6)	0.3462(3)	0.012(2)	0.016(3)	0.008(2)	0.008(2)	0.001(2)	0.002(2)
O(2)	12*c*	0.8691(7)	0.3791(6)	0.2171(3)	0.017(3)	0.014(2)	0.018(2)	0.010(2)	–0.003(2)	0.002(2)
O(3)	12*c*	0.9821(6)	0.1968(6)	0.2368(3)	0.014(2)	0.016(3)	0.011(2)	0.007(2)	–0.001(2)	–0.005(2)
O(4)	12*c*	0.6978(7)	0.1854(8)	0.0546(4)	0.014(3)	0.026(3)	0.033(3)	0.005(3)	–0.003(2)	0.010(3)
O(5)	12*c*	0.6981(7)	0.0793(7)	0.2116(3)	0.010(3)	0.023(3)	0.020(3)	0.005(2)	–0.003(2)	0.000(2)

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Crystal structure of the α-modification of caesium gallium(III) monohydrogen triphosphate, α-$CsGaHP_3O_{10}$

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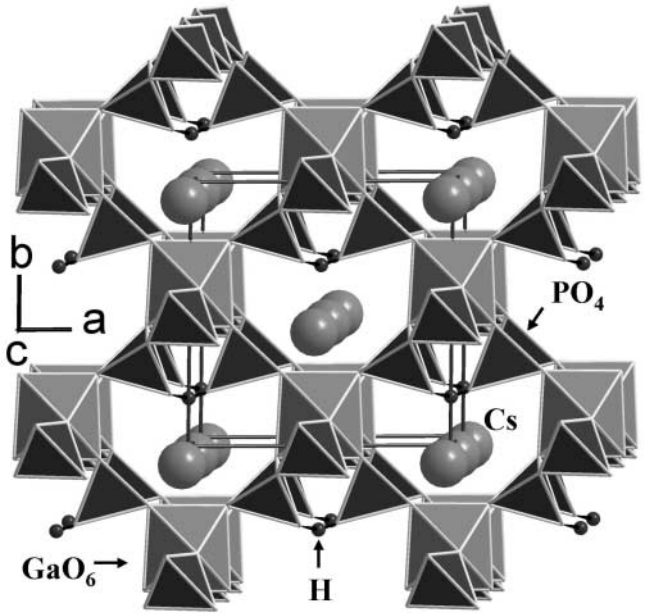

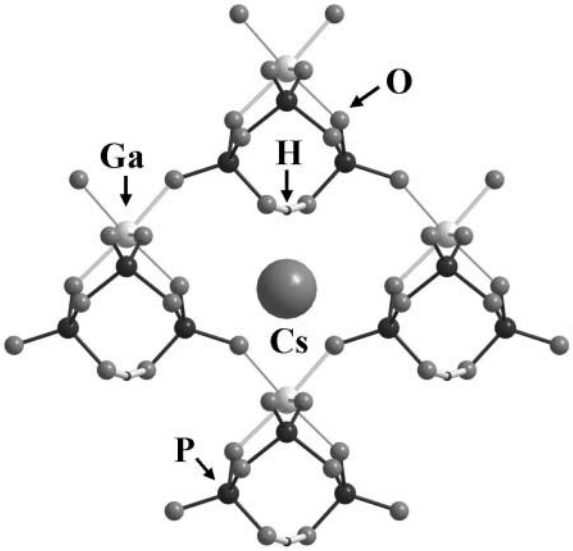

Abstract

$CsGaHO_{10}P_3$, monoclinic, $C121$ (No. 5), a = 9.061(1) Å, b = 8.7105(9) Å, c = 6.2195(8) Å, β = 111.993(6)°, V = 455.2 Å^3, Z = 2, $R_{gt}(F)$ = 0.018, $wR_{ref}(F^2)$ = 0.046, T = 295 K.

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Source of material

The title compound was synthesized in aqueous solution by two steps. In the first step, the reaction was carried out with the mixture of $GaCl_3$(1.046 metal gallium dissolved in 5 ml 37% HCl), CsCl (2.525 g) and an excess of HCl (molar ratio Ga : Cs = 1 : 1). The mixture was heated to the boiling point. While it was cooled down and evaporated in air for several days, transparent colorless crystals were obtained. After filtering from liquid, they were identified to be $CsGaCl_4$ [1], and it was confirmed by X-ray powder diffraction. On the second step, the reaction was made with the mixture of $CsGaCl_4$ (3.44 g), $Cs(OH) \cdot H_2O$ (1.679 g) and 5 ml 85% H_3PO_4 (molar ratio 1:1:7). The starting materials were all of analytical grade. The mixture was heated (open system) to the boiling point on stove and kept heating for three days to evaporate the solvent. Three modifications of crystals of $CsGaHP_3O_{10}$ were obtained in the reaction product. The α-modification showed in block shape; 3M-modification in thick plate and 1M-modification in thin plate. All of them were colorless and transparent. The 2O-modification reported by Anisimova (1995) as III-$CsGaHP_3O_{10}$ was not found in these products indicating that it should have different synthetic conditions or a different stability temperature range.

Experimental details

The position of the H atom was determined from a difference Fourier map.

Discussion

In 1987, Chudinova et al. reported [2] a series of caesium gallium phosphate compounds, namely $Cs_2GaH_3(P_2O_7)_2$, $Gs_3Ga_3P_{12}O_{36}$ and $CsGaHP_3O_{10}$, and claimed that the formulae $CsGaHP_3O_{10}$ contains four modifications from powder diffraction data. By comparing the powder diffraction patterns of different phases, the authors assumed that phase I and III should have some common structural characteristics. Later in 1995, Anisimova et al. synthesized the modification III, reported its crystal structure and claimed that III-$CsGaHP_3O_{10}$ was the most stable one among the four modifications [3]. Although several kinds of caesium gallium phosphate structures are available [4-7], the structures of the other three modifications of $CsGaHP_3O_{10}$ have not been reported until now. Here we report one of them. According to our systematic structural researches, modifications of $CsGaHP_3O_{10}$ should belong to different polymorphs and polytypes. We name them as α-, 1M-, 2O-, 3M-modifications, respectively. The α-modification and 1M-modification belong to monoclinic system with space groups of $C2$ and $P2/n$ respectively [8]. The 2O-modification belongs to orthorhombic system with $Pca2_1$ [2].

The crystal structures of the four $CsGaHP_3O_{10}$ modifications have a common building unit, i.e. a triphosphate [HPO_3-O–PO_2–O-HPO_3] group. In each unit, each PO_4 tetrahedron shares two further O-corners with two GaO_6 octahedra. Thus, three-membered phosphate tetrahedra groups linked with GaO_6 octahedra lead to a three-dimensional framework structure in the α-modification and a two-dimensional layer structure in the 1M-, 2O-, 3M-modifications.

In the title structure, [HPO_3-O–PO_2–O-HPO_3] groups stretch in a chiral chain mode along *c* axis and link with GaO_6 octahedra via O-corners to modification a three dimensional framework structure. It is isotypic to $CsMnHP_3O_{10}$ [9]. Caesium cations are distributed within the channels of eight-membered ring as cross-section which formed by alternating GaO_6 octahedra (4×) and phosphate tetrahedra (4×), running along the *c* axis. Caesium has coordination number of 10 with the distances from 3.033 Å to 3.667 Å. The Ga—O bond distances within the coordination octahedra range from 1.931 Å to 1.979 Å. The P—O bond distances (ranging from 1.578 Å to 1.632 Å) for bridging P–O–P oxygen are apparently larger than the P—O bond distances in the structure (ranging from 1.491 Å to 1.510 Å in PO_4 tetrahedra).

Table 1. Data collection and handling.

Crystal:	transparent colorless block, size 0.12 × 0.12 × 0.15 mm
Wavelength:	Mo K_α radiation (0.71069 Å)
μ:	75.29 cm^{-1}
Diffractometer, scan mode:	Rigaku AFC7-CCD, 500 images, $\Delta\varphi = 0.6°$, 60-ω scan, $\Delta\omega = 0.6°$, $\chi = 90°$
$2\theta_{max}$:	64.5°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	3897, 1363
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 1362
$N(param)_{refined}$:	71
Programs:	SHELXL-97 [10], DIAMOND [11]

Table 2. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	*x*	*y*	*z*	U_{iso}
H(1)	2*a*	1/2	0.6831	0	0.05

Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cs(1)	2*b*	0	0.94671(2)	1/2	0.0540(2)	0.0154(2)	0.0208(2)	0	–0.0032(1)	0
Ga(1)	2*a*	0	0.61078(4)	0	0.0076(1)	0.0065(2)	0.0066(2)	0	0.0026(1)	0
P(1)	2*b*	0	0.5143(1)	1/2	0.0107(3)	0.0088(4)	0.0058(4)	0	0.0038(3)	0
P(2)	4*c*	0.81768(7)	0.32891(7)	0.1061(1)	0.0081(2)	0.0081(3)	0.0087(3)	–0.0015(2)	0.0034(2)	0.0005(2)
O(1)	4*c*	0.8349(2)	0.4551(2)	0.9508(3)	0.0118(7)	0.0091(8)	0.0102(8)	–0.0039(7)	0.0031(6)	0.0007(7)
O(2)	4*c*	0.6489(2)	0.2762(2)	0.0339(4)	0.0106(7)	0.0114(9)	0.0193(9)	–0.0061(7)	0.0052(6)	–0.0006(7)
O(3)	4*c*	0.8574(2)	0.4045(2)	0.3617(4)	0.0179(8)	0.019(1)	0.0088(9)	–0.0078(7)	0.0062(7)	–0.0018(7)
O(4)	4*c*	0.9480(2)	0.6062(3)	0.6613(3)	0.0162(7)	0.0138(9)	0.0064(7)	0.0041(7)	0.0059(6)	0.0005(7)
O(5)	4*c*	0.4376(2)	0.7013(3)	0.1440(4)	0.0178(8)	0.015(1)	0.024(1)	0.0055(7)	0.0121(8)	0.0072(7)

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Crystal structure of the 1M-modification of caesium gallium(III) monohydrogen triphosphate, 1M-$CsGaHP_3O_{10}$

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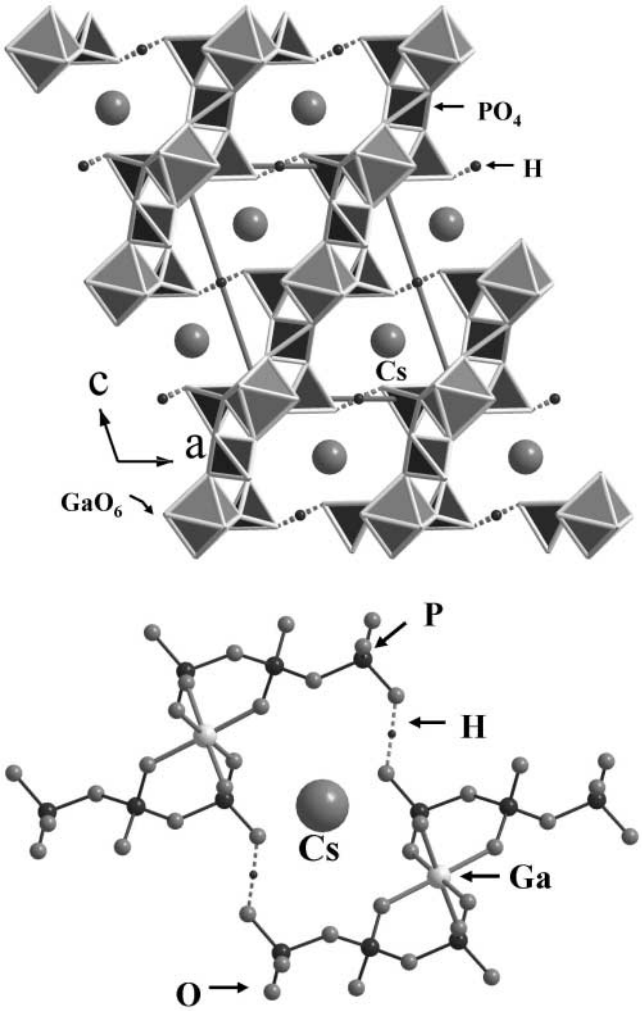

Abstract

$CsGaHO_{10}P_3$, monoclinic, $P12_1/n1$ (No. 13), a = 8.843(1) Å, b = 4.9523(5) Å, c = 11.084(1) Å, β = 108.793(6)°, V = 459.5 Å^3, Z = 2, $R_{gt(F)}$ = 0.042, $wR_{ref(F^2)}$ = 0.123, T = 295 K.

Source of material

The title compound was synthesized in aqueous solution by two steps. In the first step, the reaction was carried out with a mixture of $GaCl_3$ (1.046 metal gallium dissolved in 5 ml 37% HCl), CsCl (2.525 g) and an excess of 37% HCl (molar ratio Ga : Cs = 1 : 1). The mixture was heated to the boiling point. The resulting reaction product ($CsGaCl_4$ [1]) was used as reactant for the next step, which was made with a mixture of $CsGaCl_4$ (3.444 g), $Cs(OH) \cdot H_2O$ (1.679 g) and 5 ml 85% H_3PO_4 (molar ratio 1:1:7). The starting materials were all of analytical grade. The mixture was heated (open system) to the boiling point and kept heating for three days to evaporate the solvent. Three modifications of $CsGaHP_3O_{10}$ crystals were obtained in the reaction product. The one with a shape of thin plate corresponds to the title compound and was used for the structure determination.

Experimental details

The positions of the H atom was determined from a difference Fourier map.

Discussion

In 1987, Chudinova et al. synthesized a series of caesium gallium phosphates with the common chemical formula $CsGaHP_3O_{10}$ and identified four modifications from their powder patterns [2]. Later in 1995, Anisimova et al. [3] reported the crystal structure of the so called modification III. According to our recent systematic structural investigations, the four modifications of $CsGaHP_3O_{10}$ belong to the polymorphs series α [4], 1M, 2O and 3M. Here we report on the crystal structure of the 1M-modification.

1M-$CsGaHP_3O_{10}$ is isotypic to $(NH_4)AlHP_3O_{10}$ [5]: three-membered [HPO_3-O–PO_2–O-HPO_3] groups stretch in a chain mode along the c axis and link with GaO_6 octahedra via O-corners to form a two-dimensional layer structure parallel ($\bar{1}01$). The layers are connected by hydrogen bonds. Caesium occupies positions between the layers and is ten-fold coordinated by oxygen. The Cs—O distances range from 3.098 Å to 3.490 Å. The Ga—O bond distances within the coordination octahedra range from 1.920 Å to 1.949 Å. The P—O bond distances (ranging from 1.571 Å to 1.606 Å) for P–O–P bridging oxygen are apparently larger than the (terminal) P—O distances (ranging from 1.489 Å to 1.520 Å). The crystal structures of the four $CsGaHP_3O_{10}$ polymorphs have a common building unit, i.e. the triphosphate group [HPO_3-O–PO_2–O-HPO_3]. Within this group the central PO_4 shares two further O-corners with two GaO_6 octahedra. This lead to an overall three-dimensional framework structure in the α-modification and a two-dimensional layer structure in the 1M-, 2O-, 3M-modifications. The thickness of one layer is about $d_{(\bar{1}01)}$ = 7.902 Å. While in the 2O-modification, the structure consists of two layers normal to the c axis, leading to a c axis of 15.722(1) Å, which is about 2 times larger compared with that of the 1M-modification. Line-up directions of the three-membered phosphate

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groups in the neighbouring successive layers are paralleled to each other in the 1M-modification and normal to each other in the 2O-modification, respectively. The cell parameters of the 3M-modification were indexed as $a = 11.741(3)$ Å, $b = 4.952(1)$, $c = 23.705(3)$, $\beta = 90.03(1)°$ and this c axis is about 3 times larger compared with that of the 1M-modification. It is assumed that its structure within one unit cell should consist of a sequence of three layers normal to the c axis.

Table 1. Data collection and handling.

Crystal:	transparent colorless thin plate, size 0.05 × 0.15 × 0.20 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	74.58 cm^{-1}
Diffractometer, scan mode:	Rigaku AFC7-CCD, 400 images, $\Delta\varphi = 0.6°$, 60-ω scan, $\Delta\omega = 0.6°$, $\chi = 90°$
$2\theta_{max}$:	64.48°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	7193, 1456
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 1204
$N(param)_{refined}$:	72
Programs:	SHELXL-97 [6], DIAMOND [7]

Table 2. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{iso}
H(1)	2*d*	1/2	0	0	0.05

Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cs(1)	2*f*	3/4	0.5095(1)	1/4	0.1553(8)	0.0293(3)	0.0462(3)	0	0.0667(4)	0
Ga(1)	2*c*	0	1/2	0	0.0146(3)	0.0116(3)	0.0108(3)	–0.0010(2)	0.0008(2)	–0.0005(2)
P(1)	4*g*	0.7723(1)	0.0010(2)	0.99350(8)	0.0115(4)	0.0126(4)	0.0144(4)	0.0005(3)	0.0027(3)	0.0006(3)
P(2)	2*e*	1/4	0.7411(3)	1/4	0.0174(5)	0.0118(5)	0.0108(4)	0	–0.0021(4)	0
O(1)	4*g*	0.9102(3)	0.1877(5)	0.0539(2)	0.016(1)	0.012(1)	0.015(1)	–0.0018(8)	0.0013(8)	0.0014(8)
O(2)	4*g*	0.8142(3)	0.7074(5)	0.0039(2)	0.018(1)	0.013(1)	0.023(1)	–0.0002(9)	0.0057(9)	0.0021(9)
O(3)	4*g*	0.1043(3)	0.5861(6)	0.1787(2)	0.025(1)	0.021(1)	0.012(1)	–0.008(1)	0.0001(9)	–0.0029(9)
O(4)	4*g*	0.2013(4)	0.9341(7)	0.3438(3)	0.031(2)	0.029(2)	0.019(1)	0.016(1)	–0.007(1)	–0.008(1)
O(5)	4*g*	0.6386(4)	0.0550(8)	0.0487(4)	0.020(1)	0.040(2)	0.045(2)	–0.002(1)	0.017(1)	–0.011(2)

Acknowledgments. This project was supported by the Fund for Distinguished Young Scholars from the NNSF of China, Fund of the 863 project from the DOST of China, and the Fund from the NNSF of China. JXM and JTZ are indebted to the financial support from the Max-Planck-Gesellschaft.

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Crystal structure of caesium gallium(III) *catena*-[monohydrogen-monoborate-bis(monophosphate)], $CsGa[BP_2O_8(OH)]$

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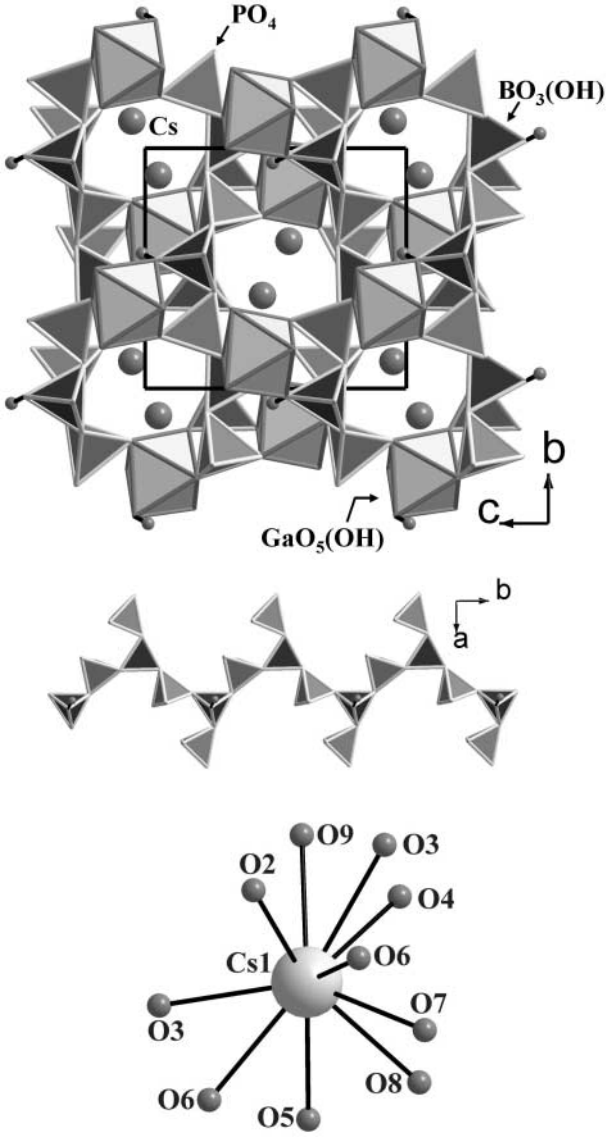

Abstract

$BCsGaHO_9P_2$, monoclinic, $P12_1/c1$ (No. 14), $a = 9.259(1)$ Å, $b = 8.6462(9)$ Å, $c = 9.615(1)$ Å, $\beta = 103.059(6)°$, $V = 749.8$ Å^3, $Z = 4$, $R_{gt}(F) = 0.050$, $wR_{ref}(F^2) = 0.104$, $T = 295$ K.

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Source of material

$CsGa[BP_2O_8(OH)]$ was synthesized under mild hydrothermal conditions. The reactions were carried out with mixtures of $Cs(OH) \cdot H_2O$ (1.679 g), $GaCl_3$ (0.35 g metal gallium dissolved in 2 ml 37% HCl), H_3BO_3 (0.618 g), LiH_2PO_4 (3.118 g) and 2 ml 85% H_3PO_4 with molar ratio of Cs : Ga : B : Li : P = 2 : 1 : 2 : 6 : 12. The mixture was filled in a teflon autoclave with about 20 ml in volume. The degree of filling was about 50%. The autoclave was placed in an oven with subsequent heating at 443 K for 7 days. All starting materials were of analytical grade purity. The composition was confirmed by chemical analysis (ICP) with Cs : Ga : B : P = 0.9(1):1.02(1):0.91(2):2.00(3). The Li content was below the detective limit of the analytical method.

Experimental details

The position of the H atom was determined from a difference Fourier map.

Discussion

In our recent investigations on Ga-containing borophosphates, mild hydrothermal conditions have been proved to be efficient in preparing new compounds with different structures, such as $NaGa[BP_2O_7(OH)_3]$, $KGa[BP_2O_7(OH)_3]$, $(NH_4)Ga[BP_2O_8(OH)]$ and $RbGa[BP_2O_8(OH)]$ [1-4]. The title compound was also synthesized under mild hydrothermal conditions.

The crystal structure of the title compound is isotypic to $CsFe[BP_2O_8(OH)]$ [5] and contains isolated $GaO_5(OH)$ octahedra sharing common O-corners with five phosphate tetrahedra and a common (OH)-corner with a hydrogenborate group to form a three dimensional framework structure. The anionic partial structure consists of open-branched vierer-single chains $[BP_2O_8(OH)]^{4-}$, which are formed by alternating hydrogenborate and phosphate tetrahedra sharing common O-corners. The $[BP_2O_8(OH)]_n$ chains run along the *b* axis and are connected via $GaO_5(OH)$ octahedra sharing common corners. The caesium cations are distributed in a zigzag arrangement within the open channels with an elliptical cross-section and running along the *a* axis. Caesium has ten oxygen neighbours with distances ranging from 3.070 Å to 3.308 Å. The Ga—O and Ga—OH bond distances in the Ga-coordinaton-octahedron range from 1.909 Å to 2.117 Å. The P—O bond distances range from 1.512 Å to 1.572 Å, and those of B—O from 1.458 Å to 1.490 Å. Bond lengths and angles of hydrogenborate and phosphate tetrahedra within the anionic chains are in the same ranges as observed in other borophosphates [1-4].

Table 1. Data collection and handling.

Crystal:	colorless transparente prism, size 0.04 × 0.05 × 0.08 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	89.09 cm^{-1}
Diffractometer, scan mode:	Rigaku AFC7-CCD, 400 images, $\Delta\varphi = 0.6°$, 60-ω scan, $\Delta\omega = 0.6°$, $\chi = 90°$
$2\theta_{max}$:	64.92°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	6603, 2402
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2060
$N(param)_{refined}$:	127
Programs:	SHELXL-97 [6], DIAMOND [7]

Table 2. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	*x*	*y*	*z*	U_{iso}
H(1)	4*e*	0.1234	0.9385	0.5114	0.05

Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cs(1)	4*e*	0.30327(6)	0.61291(6)	0.44906(5)	0.0251(2)	0.0197(2)	0.0195(2)	–0.0004(2)	0.0024(2)	0.0035(2)
Ga(1)	4*e*	0.29621(7)	0.15438(8)	0.57305(7)	0.0075(3)	0.0078(3)	0.0052(3)	0.0004(2)	0.0007(2)	0.0000(2)
P(1)	4*e*	0.4294(2)	0.0738(2)	0.3005(2)	0.0062(6)	0.0067(6)	0.0056(6)	0.0009(5)	0.0013(5)	0.0005(5)
P(2)	4*e*	0.0829(2)	0.2689(2)	0.2869(2)	0.0072(7)	0.0075(6)	0.0081(7)	0.0009(5)	0.0011(5)	0.0009(5)
B(1)	4*e*	0.8407(7)	0.4589(7)	0.1955(7)	0.008(3)	0.003(3)	0.008(3)	0.000(2)	0.002(2)	0.002(2)
O(1)	4*e*	0.0792(5)	0.0987(5)	0.2361(5)	0.014(2)	0.007(2)	0.015(2)	–0.001(2)	0.001(2)	–0.002(2)
O(2)	4*e*	0.4187(5)	0.1657(5)	0.4325(5)	0.013(2)	0.015(2)	0.006(2)	–0.005(2)	0.007(2)	–0.005(2)
O(3)	4*e*	0.3077(5)	0.9436(5)	0.2769(5)	0.007(2)	0.014(2)	0.015(2)	–0.002(2)	0.002(2)	–0.003(2)
O(4)	4*e*	0.9171(5)	0.3189(5)	0.2568(5)	0.006(2)	0.011(2)	0.015(2)	0.002(2)	0.002(2)	0.001(2)
O(5)	4*e*	0.1465(5)	0.2822(6)	0.4459(5)	0.016(2)	0.012(2)	0.009(2)	0.006(2)	–0.001(2)	–0.001(2)
O(6)	4*e*	0.4021(5)	0.1709(5)	0.1660(5)	0.015(2)	0.009(2)	0.007(2)	0.004(2)	0.001(2)	0.002(2)
O(7)	4*e*	0.5785(5)	0.9973(5)	0.3123(5)	0.008(2)	0.014(2)	0.010(2)	0.005(2)	0.003(2)	0.006(2)
O(8)	4*e*	0.1622(5)	0.3713(5)	0.1997(5)	0.014(2)	0.012(2)	0.012(2)	–0.003(2)	0.007(2)	–0.001(2)
O(9)	4*e*	0.1767(6)	0.9670(5)	0.4604(5)	0.019(2)	0.012(2)	0.004(2)	–0.004(2)	0.001(2)	0.001(2)

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Crystal structure of yttrium borosilicide, $Y_5Si_{2-x}B_8$ (x = 0.13)

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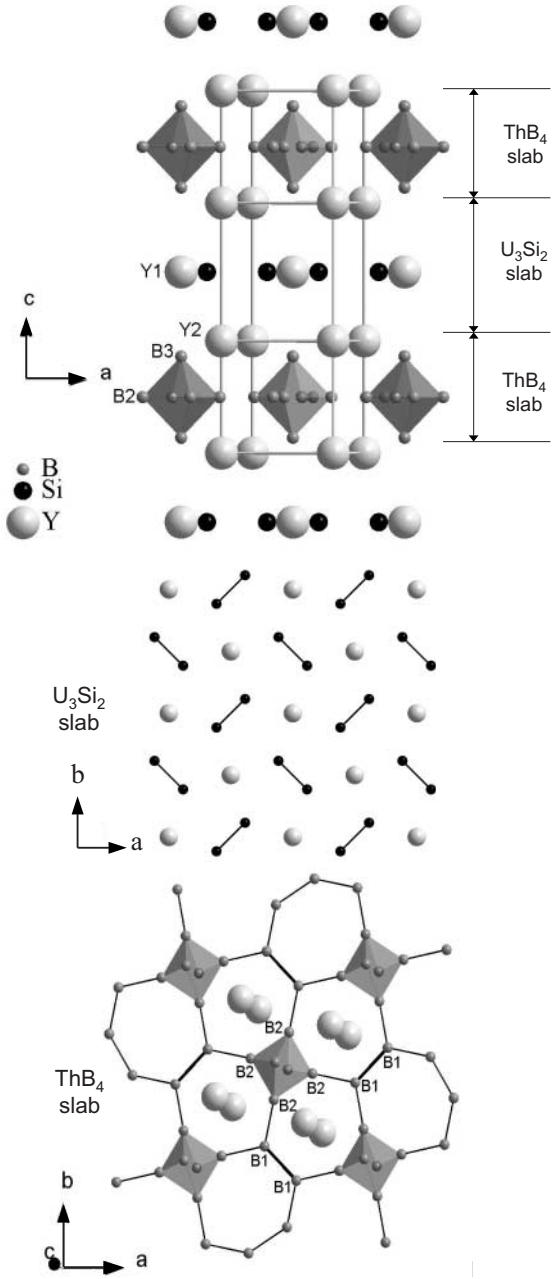

Abstract

$B_8Si_{1.87}Y_5$, tetragonal, *P4/mbm* (No. 127), a = 7.2234(2) Å, c = 8.0961(3) Å, V = 422.4 Å^3, Z = 2, $R_{gt}(F)$ = 0.040, $wR_{ref}(F^2)$ = 0.095, T = 293 K.

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Source of material

Suitable amounts of powder and freshly filed chips of the constituents in the nominal atomic percentage Y:Si:B=5:2:8 were mixed together and pressed into pellets. Samples melting was performed in an arc furnace using a non-consumable thoriated tungsten electrode under Ti/Zr-gettered argon atmosphere. To ensure homogeneity, the samples were turned over and re-melted several times. Shiny black platelet-like single crystals could be extracted from molten samples after crushing and used for structure determination.

Discussion

The ternary compound $Y_5Si_{2-x}B_8$ belongs to the family of rare earth borosilicides $R_5Si_2B_8$ (R = Sm, Gd, Tb, Dy), which we have recently discovered [1, 2]. This family of compounds crystallizes in the new structure type $Gd_5Si_2B_8$. The structure determination concludes to the occurrence of two yttrium (Y1, Y2) and three boron (B1, B2, B3) independent positions. On the other hand, there is only one silicon position, which has been found slightly deficient (τ = 0.935(9)). The structure $Y_5Si_2B_8$ can be easily described as an intergrowth structure of ThB_4 [3] and U_3Si_2 [4] related slabs of composition YB_4 and Y_3Si_2, following each other along the [001] direction (top figure). For example, the structure composition is confirmed by the resulting equation: $2YB_4 + Y_3Si_2 = Y_5Si_2B_8$. The salient characteristic of the structure results from the occurrence of two ordered independent boron and silicon sublattices. The silicon atoms within the U_3Si_2 related slab form Si—Si pairs with a Si—Si distance of 2.358(4) Å (middle figure). The boron atoms within the ThB_4 related slab form distorted B_6 octahedra, which are built from four B2 (square basis) and two B3 atoms. These octahedra, which are inserted in yttrium cubes, are close to ideal local O_h symmetry, as shown by the inter-octahedral B2—B3 and B2—B2 distances which are quite similar (1.81(1) Å and 1.84(1) Å, respectively; ave. 1.83(1) Å). The last boron atoms, namely the B1 atoms, lie in the same z = 1/2 as the B2 squares to which they are connected. Each B1 atom is connected to another B1 atom and to two B2 atoms which belong to two different octahedra, i.e. each B1 atom is three-coordinated (sp^2 hybridisation). The B1—B2 and B1—B1 distances of 1.76(1) Å and 1.82(2) Å, respectively, are slightly shorter than the intra-octahedron ones. As a result, the boron sublattice can be described as made of B_6 octahedra which are linked together in the (a, b) plane through boron atoms which form B—B pairs (bottom figure). It is worth noting that the B—B pairs (z = 1/2) are situated almost straight up the Si—Si ones (z = 0). Finally, the B1 and B2 atoms generate a two-dimensional planar (2-D) network which can be described as made of fused squares and heptagons (bottom figure). The Y1 atoms are octahedrally surrounded by two boron and four silicon atoms, while the Y2 ones are twelve-coordinated by nine boron and three silicon atoms, but in a more complex arrangement.

Table 1. Data collection and handling.

Crystal:	shiny black platelet, size 0.036 × 0.052 × 0.052 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	341.70 cm^{-1}
Diffractometer, scan mode:	Kappa CCD-Nonius, $\theta/2\theta$
$2\theta_{max}$:	69.76°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	1730, 534
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 436
$N(param)_{refined}$:	28
Programs:	SIR97 [5], SHELXL-97 [6], DIAMOND [7]

Table 2. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	Occ.	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Y(1)	2*a*		0	0	0	0.0136(3)	U_{11}	0.0057(4)	0	0	0
Y(2)	8*k*		0.81897(4)	–*x*+1/2	0.72410(6)	0.0077(2)	U_{11}	0.0069(3)	–0.0004(2)	0.0002(1)	$-U_{13}$
Si	4*g*	0.935(9)	0.3846(2)	–*x*+1/2	0	0.0112(8)	U_{11}	0.009(1)	0.0001(8)	0	0
B(1)	4*h*		0.9109(8)	*x*+1/2	1/2	0.012(2)	U_{11}	0.010(4)	0.005(3)	0	0
B(2)	8*j*		0.6724(7)	0.4597(8)	1/2	0.009(2)	0.010(2)	0.004(2)	–0.002(2)	0	0
B(3)	4*e*		0	0	0.337(1)	0.009(2)	U_{11}	0.010(3)	0	0	0

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Crystal structure of 4-(2-oxobenzothiazolin-3-yl)butanoic acid, $C_{11}H_{11}NO_3S$

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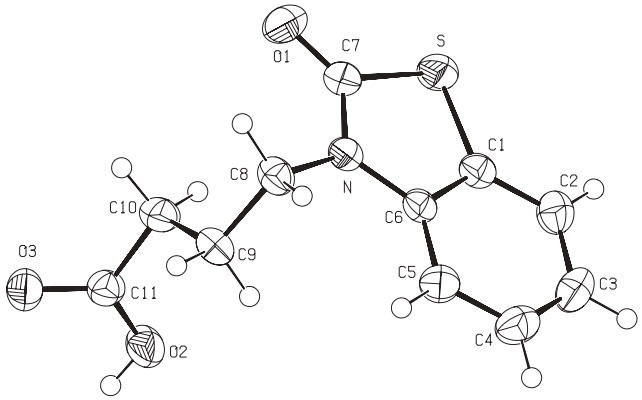

Abstract

$C_{11}H_{11}NO_3S$, triclinic, $P\bar{1}$ (No. 2), $a = 7.240(1)$ Å, $b = 7.495(2)$ Å, $c = 10.427(1)$ Å, $\alpha = 83.89(1)°$, $\beta = 85.74(1)°$, $\gamma = 71.16(1)°$, $V = 532.0$ Å^3, $Z = 2$, $R_{gt}(F) = 0.035$, $wR_{ref}(F^2) = 0.096$, $T = 293$ K.

Source of material

For the synthesis, 10.0 mmol ethyl 4-(2-oxobenzothiazolin-3-yl)-butanoate in concentrated hydrochloric acid (50 ml) was stirred at room temperature for 2 hours, then refluxed for 4 hours. The reaction mixture was cooled, poured into 100 g ice-water, and stirred for 1 hour. The precipitate was collected by filtration, washed with water, dried and crystallised from water.

Discussion

The benzene ring defined by C1–C2–C3–C4–C5–C6 atoms is planar. Torsion angles of C1–C2–C3–C4, C6–C5–C4–C3 and C1–C6–C5–C4 are 0.4(3)°, 0.1(3)° and 0.3(3)°, respectively. The thiazolon ring defined by C1–C6–N–C7–S atoms is planar. Torsion angles of C7–S–C1–C6 and C6–N–C7–S are 0.6(1)° and 1.2(2)°, respectively. The dihedral angle between these two planes is 0.99(8)° implying that they are co-planar. The torsion angles of C7–N–C6–C5, N–C6–C1–C2, C7–S–C1–C2 and S2–C1–C2–C3 are 178.8(2)°, 179.2(2)°, –178.6(2)° and 179.1(2)°, respectively. O1 and C8 atoms are also at this plane. Torsion angles of C6–N–C7–O1, C1–S–C7–O1, C8–N–C6–C1 and C8–N–C7–O1 are –179.0(2)°, 179.2(2)°, –179.0(2)° and –0.7(3)°, respectively. C9 atom lies below 1.351(3) Å from thiazolon plane. Torsion angles of C7–N–C8–C9, C6–N–C8–C9 and N–C8–C9–C10 are 103.8(2)°, –78.0(2)° and –68.5(2)°, respectively. The bond lengths and angles in the 4-(2-oxobenzothiazolin-3-yl)butanoic acid are all in accord with similar structures in the literature [1-3]. The bond lengths of C—C are between 1.378(3) Å – 1.522(3) Å. The bond lengths of C7=O1, C11—O2 and C11=O3 are 1.214(2) Å, 1.262(2) Å and 1.263(2) Å, respectively. The bond lengths of C7—S and C1—S are 1.782(2) Å and 1.743(2) Å, respectively. The bond lengths of C6—N, C7—N and C8—N are 1.395(2) Å, 1.368(2) Å and 1.464(2) Å, respectively.

Table 1. Data collection and handling.

Crystal:	white needle, size 0.06 × 0.27 × 0.48 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	2.94 cm^{-1}
Diffractometer, scan mode:	Enraf-Nonius CAD-4, $\omega/2\theta$
$2\theta_{max}$:	52.58°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	2300, 2130
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 1786
$N(param)_{refined}$:	147
Programs:	SHELXS-97 [4] SHELXL-97 [5], ORTEP-III [6]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(2)	2*i*	–0.4244	–0.0414	0.5929	0.070
H(8A)	2*i*	–0.1139	0.5419	0.6207	0.041
H(8B)	2*i*	–0.2521	0.5945	0.7436	0.041
H(5)	2*i*	–0.3345	0.4424	0.9429	0.046
H(4)	2*i*	–0.3352	0.3370	1.1597	0.053
H(9A)	2*i*	–0.4118	0.4711	0.6134	0.042
H(9B)	2*i*	–0.3442	0.3186	0.7301	0.042
H(10A)	2*i*	–0.1531	0.2997	0.4823	0.048
H(10B)	2*i*	–0.0717	0.1516	0.5994	0.048
H(2A)	2*i*	0.2404	0.0690	1.1354	0.048
H(3)	2*i*	–0.0519	0.1549	1.2552	0.054

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Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S	2*i*	0.32516(6)	0.16590(7)	0.85628(5)	0.0272(2)	0.0507(3)	0.0421(3)	–0.0099(2)	–0.0009(2)	–0.0008(2)
O(2)	2*i*	–0.3456(2)	0.0043(2)	0.6171(1)	0.0589(9)	0.0509(9)	0.0424(8)	–0.0339(7)	–0.0150(6)	0.0080(6)
O(3)	2*i*	–0.3910(2)	0.1564(2)	0.4210(1)	0.0590(9)	0.0510(8)	0.0337(7)	–0.0311(7)	–0.0082(6)	0.0022(6)
O(1)	2*i*	0.2322(2)	0.3345(2)	0.6211(1)	0.0448(8)	0.069(1)	0.0399(8)	–0.0219(7)	0.0058(6)	0.0044(7)
N	2*i*	–0.0148(2)	0.3698(2)	0.7785(1)	0.0288(7)	0.0354(8)	0.0317(8)	–0.0138(6)	–0.0040(6)	–0.0008(6)
C(6)	2*i*	–0.0443(2)	0.3184(2)	0.9091(2)	0.0309(8)	0.0297(8)	0.0310(8)	–0.0143(7)	–0.0032(7)	–0.0042(7)
C(1)	2*i*	0.1269(2)	0.2062(2)	0.9673(2)	0.0297(8)	0.0310(9)	0.0354(9)	–0.0108(7)	–0.0014(7)	–0.0053(7)
C(11)	2*i*	–0.3165(3)	0.1242(3)	0.5303(2)	0.0350(9)	0.0347(9)	0.0354(9)	–0.0138(7)	0.0006(7)	–0.0047(7)
C(8)	2*i*	–0.1711(3)	0.4898(2)	0.6966(2)	0.0362(9)	0.0313(9)	0.0382(9)	–0.0133(7)	–0.0091(7)	0.0015(7)
C(5)	2*i*	–0.2193(3)	0.3681(3)	0.9809(2)	0.0314(9)	0.043(1)	0.039(1)	–0.0094(8)	0.0010(7)	–0.0052(8)
C(4)	2*i*	–0.2187(3)	0.3048(3)	1.1104(2)	0.043(1)	0.049(1)	0.042(1)	–0.0148(9)	0.0107(8)	–0.0088(9)
C(9)	2*i*	–0.2984(2)	0.3820(3)	0.6545(2)	0.0300(9)	0.036(1)	0.041(1)	–0.0119(7)	–0.0069(7)	–0.0038(8)
C(10)	2*i*	–0.1901(3)	0.2362(3)	0.5611(2)	0.039(1)	0.048(1)	0.042(1)	–0.0243(9)	0.0025(8)	–0.0088(9)
C(7)	2*i*	0.1740(3)	0.3046(3)	0.7310(2)	0.0339(9)	0.040(1)	0.0361(9)	–0.0184(8)	–0.0007(7)	–0.0032(7)
C(2)	2*i*	0.1258(3)	0.1438(3)	1.0969(2)	0.042(1)	0.040(1)	0.037(1)	–0.0109(8)	–0.0083(8)	0.0006(8)
C(3)	2*i*	–0.0487(3)	0.1949(3)	1.1678(2)	0.058(1)	0.047(1)	0.0299(9)	–0.018(1)	0.0018(8)	–0.0003(8)

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Crystal structure of 2,3,8,9,10,11-hexahydro-7*H*-dibenzo[*de*,*h*]quinolin-7-one, $C_{16}H_{15}NO$

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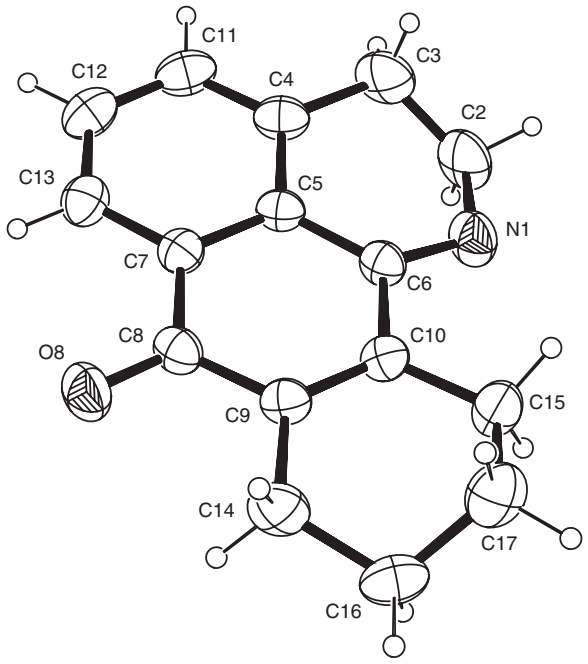

Abstract

$C_{16}H_{15}NO$, monoclinic, $P12_1/a1$ (No. 14), $a = 7.085(1)$ Å, $b = 18.587(3)$ Å, $c = 9.080(2)$ Å, $\beta = 95.30(2)°$, $V = 1190.5$ Å^3, $Z = 4$, $R_{gt}(F) = 0.068$, $wR_{ref}(F^2) = 0.239$, $T = 293$ K.

Source of material

A solution of [*de*,*h*]quinolin-7-one (500 mg, 2.14 mmol) in acetic acid (150 ml) was catalytically hydrogenated over platinum oxide (300 mg) at 65 psi and room temperature. After 2 days, the mixture was filtered through Celite and concentrated to give a brown residue. After work up and purification by Si-gel flash cromatography (4:1 hexane-ethyl acetate, v/v), 2,3,8,9,10,11-hexahydro-7*H*-dibenzo[*de*,*h*]-quinolin-7-one was obtained (270 mg, yield 53%), which crystallized from MeOH as yellow needles.

Discussion

The structure of the molecule is largely planar including aromatic ring C4–C5–C7–C13–C12–C11 with imine and carbonyl bond lengths of *d*(N1—C6) = 1.297(4) Å and *d*(C8—O8) = 1.235(3) Å, respectively. However, the partial reduction of the second aromatic ring is reflected in the dihedral angle ∠C14–C16–C17–C15 of –66(1)°. The structure shows a disorder on two carbon positions (namely split positions C16/C18 and C17/C19) of the 7a,11a-cyclohexene ring. Only C16 and C17 atoms with corresponding attached H atoms are shown in the figure. This disorder is not observed for the methylenes on C2 and C3 atoms. On the other hand, the distance *d*(C9—C10) = 1.353(4) Å is similar to the carbon-carbon distances observed in the aromatic ring C4–C5–C7–C13–C12–C11.

Table 1. Data collection and handling.

Crystal:	yellow prism, size 0.16 × 0.24 × 1.2 mm
Wavelength:	Cu K_α radiation (1.54184 Å)
μ:	6.47 cm^{-1}
Diffractometer, scan mode:	Enraf Nonius CAD4, $\omega/2\theta$
$2\theta_{max}$:	145.82°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	2566, 2369
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 1547
$N(param)_{refined}$:	182
Programs:	SHELXS-97 [1], SHELXL-97 [2], ORTEP-3 [3], WinGX [4]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	Occ.	*x*	*y*	*z*	U_{iso}
H(2A)	4*e*		0.9021	–0.1638	0.2423	0.111
H(2B)	4*e*		0.7185	–0.1822	0.1404	0.111
H(3A)	4*e*		0.7115	–0.2129	0.3915	0.105
H(3B)	4*e*		0.5348	–0.1699	0.3220	0.105
H(11)	4*e*		0.6692	–0.1691	0.6518	0.089
H(12)	4*e*		0.7138	–0.0771	0.8208	0.088
H(13)	4*e*		0.7605	0.0381	0.7419	0.078
H(14A)	4*e*		0.9022	0.2023	0.3396	0.092
H(14B)	4*e*		0.6871	0.2048	0.2808	0.092
H(15A)	4*e*		0.6620	0.0333	0.0015	0.086
H(15B)	4*e*		0.8808	0.0479	0.0187	0.086
H(16A)	4*e*	0.65	0.8519	0.2381	0.0820	0.100
H(16B)	4*e*	0.65	0.9904	0.1720	0.1063	0.100
H(17A)	4*e*	0.65	0.7451	0.1501	–0.0911	0.104
H(17B)	4*e*	0.65	0.5943	0.1548	0.0254	0.104
H(18A)	4*e*	0.35	0.5919	0.1847	0.0981	0.112
H(18B)	4*e*	0.35	0.7558	0.2402	0.0785	0.112
H(19A)	4*e*	0.35	0.9595	0.1422	0.0438	0.111
H(19B)	4*e*	0.35	0.7943	0.1488	–0.0831	0.111

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Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	Occ.	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
N(1)	4*e*		0.7611(4)	–0.0764(1)	0.1654(3)	0.098(2)	0.055(2)	0.071(2)	0.004(1)	0.007(2)	–0.013(1)
C(2)	4*e*		0.7698(7)	–0.1510(2)	0.2200(5)	0.127(4)	0.051(2)	0.097(3)	0.002(2)	0.004(3)	–0.020(2)
C(3)	4*e*		0.6697(6)	–0.1666(2)	0.3514(5)	0.106(3)	0.047(2)	0.111(3)	–0.006(2)	0.013(2)	–0.005(2)
C(4)	4*e*		0.7022(4)	–0.1113(2)	0.4682(4)	0.061(2)	0.049(2)	0.086(2)	0.001(1)	0.009(2)	0.009(2)
C(5)	4*e*		0.7390(4)	–0.0408(1)	0.4210(3)	0.048(1)	0.046(1)	0.065(2)	0.001(1)	0.007(1)	0.002(1)
C(6)	4*e*		0.7532(4)	–0.0268(2)	0.2651(3)	0.054(2)	0.046(2)	0.062(2)	0.003(1)	0.007(1)	–0.006(1)
C(7)	4*e*		0.7579(4)	0.0149(2)	0.5249(3)	0.049(1)	0.055(2)	0.058(2)	0.003(1)	0.008(1)	–0.002(1)
C(8)	4*e*		0.7842(4)	0.0889(2)	0.4742(3)	0.053(2)	0.048(2)	0.068(2)	0.003(1)	0.007(1)	–0.009(1)
O(8)	4*e*		0.8007(4)	0.1394(1)	0.5629(3)	0.098(2)	0.060(1)	0.073(2)	–0.001(1)	0.007(1)	–0.017(1)
C(9)	4*e*		0.7844(4)	0.1023(2)	0.3156(3)	0.054(2)	0.043(1)	0.066(2)	0.005(1)	0.010(1)	0.002(1)
C(10)	4*e*		0.7655(4)	0.0486(2)	0.2145(3)	0.052(1)	0.051(2)	0.059(2)	0.004(1)	0.010(1)	0.002(1)
C(11)	4*e*		0.6928(5)	–0.1229(2)	0.6187(4)	0.068(2)	0.064(2)	0.092(3)	0.005(2)	0.015(2)	0.028(2)
C(12)	4*e*		0.7175(5)	–0.0676(2)	0.7205(4)	0.070(2)	0.082(2)	0.070(2)	0.010(2)	0.015(2)	0.020(2)
C(13)	4*e*		0.7473(4)	0.0008(2)	0.6736(4)	0.062(2)	0.072(2)	0.061(2)	0.005(1)	0.009(1)	–0.001(2)
C(14)	4*e*		0.8057(6)	0.1798(2)	0.2720(4)	0.091(2)	0.047(2)	0.091(3)	–0.000(2)	0.007(2)	0.006(2)
C(15)	4*e*		0.7608(6)	0.0626(2)	0.0527(4)	0.086(2)	0.072(2)	0.059(2)	0.004(2)	0.014(2)	0.003(2)
C(16)	4*e*	0.65	0.861(1)	0.1880(4)	0.1123(8)	0.091(4)	0.065(4)	0.097(5)	–0.004(4)	0.015(4)	0.029(3)
C(17)	4*e*	0.65	0.724(1)	0.1421(7)	0.012(1)	0.101(6)	0.083(5)	0.074(5)	0.014(6)	0.001(6)	0.024(4)
C(18)	4*e*	0.35	0.728(3)	0.1917(7)	0.110(2)	0.13(1)	0.062(7)	0.092(9)	0.009(8)	0.027(9)	0.022(6)
C(19)	4*e*	0.35	0.823(3)	0.138(1)	0.021(2)	0.13(2)	0.08(1)	0.061(8)	–0.00(1)	0.02(1)	0.025(7)

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Crystal structure of Boc-L-Ile-ΔPhe-Ile-OCH_3, $C_{27}H_{41}N_3O_6 \cdot H_2O$

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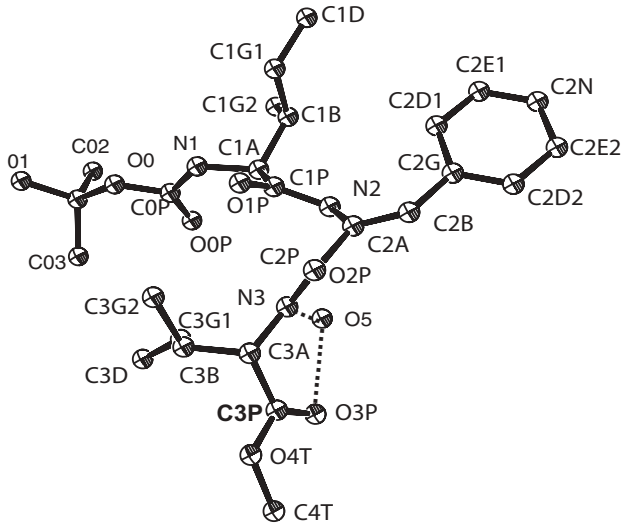

Abstract

$C_{27}H_{43}N_3O_7$, orthorhombic, $P2_12_12$ (No. 18), a = 12.202(1) Å, b = 27.790(1) Å, c = 9.128(1) Å, V = 3095.2 Å^3, Z = 4, $R_{gt}(F)$ = 0.054, $wR_{ref}(F^2)$ = 0.180, T = 293 K.

Source of material

The title peptide *N*-butyloxycarbonyl-isoleucyl-dehydrophenylalanine-isoleucine has been synthesised using the mixed anhydride coupling and the azalactone method according to [1] and [2], respectively. The peptide was crystallised from its solution in acetone-water mixture (4:1) by slow evaporation.

Experimental details

The two H atoms attached to O5 could not be located.

Discussion

The peptide Boc-L-ILe-ΔPhe-L-Ile-OCH_3 was synthesised as part of the program on peptide design with α,β-dehydro-residues [3].

The structure contains a peptide and a hydrogen bonded water molecule. It adopts a poorly folded conformation with φ,ψ torsion angles: φ_1 = –124.9(3)°, ψ_1 = 162.4(2)°, φ_2 = 51.0(3)°, ψ_2 = 36.8(3)°, φ_3 = –117.9(3)°, ψ_3^T = 167.3(2)°. The structure of the peptide does not form an intramolecular hydrogen bond. However, two intra residue hydrogen bonds are present that determine the conformation of (*i*+3) substituted Ile in the structure. The water molecule is also involved in an intermolecular hydrogen bond with carbonyl oxygen atom of ΔPhe. There are two more intermolecular hydrogen bonds involving NH groups of first two amino acids and carbonyl oxygen atoms of symmetry related last two amino acids in the structure.

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Table 1. Data collection and handling.

Crystal:	colourless prism, size 0.3 × 0.4 × 0.6 mm
Wavelength:	Cu K_α radiation (1.54180 Å)
μ:	6.59 cm^{-1}
Diffractometer, scan mode:	Enraf Nonius CAD4, $\omega/2\theta$
$2\theta_{max}$:	150.64°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	3311, 3306
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 3181
$N(param)_{refined}$:	335
Programs:	SHELXS-97 [4], SHELXL-97 [5]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	*x*	*y*	*z*	U_{iso}
H(01A)	4*c*	1.1675	0.9932	1.5315	0.08
H(01B)	4*c*	1.2735	1.0021	1.6245	0.08
H(01C)	4*c*	1.1965	0.9586	1.6616	0.08
H(02A)	4*c*	1.4492	0.9301	1.4723	0.08
H(02B)	4*c*	1.3862	0.9013	1.5937	0.08
H(02C)	4*c*	1.4168	0.9555	1.6195	0.08
H(03A)	4*c*	1.2464	0.9776	1.2904	0.08
H(03B)	4*c*	1.3670	0.9581	1.2902	0.08
H(03C)	4*c*	1.3389	1.0061	1.3721	0.08
H(1)	4*c*	1.1336	0.8340	1.4521	0.08
H(1A)	4*c*	1.2488	0.7936	1.2258	0.08
H(1B)	4*c*	1.2404	0.7172	1.3302	0.08
H(1GA)	4*c*	1.1431	0.7574	1.5820	0.08
H(1GB)	4*c*	1.0794	0.7263	1.4671	0.08
H(1DA)	4*c*	1.1220	0.6800	1.6699	0.08
H(1DB)	4*c*	1.2471	0.6903	1.6469	0.08
H(1DC)	4*c*	1.1827	0.6592	1.5324	0.08
H(1GC)	4*c*	1.3957	0.7637	1.3777	0.08
H(1GD)	4*c*	1.3751	0.7274	1.5064	0.08
H(1GE)	4*c*	1.3434	0.7818	1.5246	0.08
H(2)	4*c*	1.1543	0.7335	1.0920	0.08
H(2B)	4*c*	0.9142	0.6826	0.9356	0.08
H(2DA)	4*c*	1.0925	0.6611	1.2376	0.08
H(2DB)	4*c*	0.9913	0.6071	0.8536	0.08
H(2EA)	4*c*	1.1733	0.5882	1.2934	0.08
H(2EB)	4*c*	1.0678	0.5335	0.9123	0.08
H(2N)	4*c*	1.1693	0.5262	1.1270	0.08
H(3)	4*c*	1.0498	0.8111	0.9367	0.08
H(3A)	4*c*	0.8458	0.8447	0.8644	0.08
H(3B)	4*c*	0.9098	0.9248	0.9044	0.08
H(3GA)	4*c*	1.0705	0.8942	1.0841	0.08
H(3GB)	4*c*	1.0962	0.8878	0.9197	0.08
H(3GC)	4*c*	0.8708	0.9215	1.1523	0.08
H(3GD)	4*c*	0.9042	0.8671	1.1596	0.08
H(3GE)	4*c*	0.7986	0.8826	1.0739	0.08
H(3DA)	4*c*	1.0648	0.9738	0.9929	0.08
H(3DB)	4*c*	1.1578	0.9482	0.9036	0.08
H(3DC)	4*c*	1.1594	0.9469	1.0753	0.08
H(4TA)	4*c*	0.9645	0.9287	0.4808	0.08
H(4TB)	4*c*	0.8592	0.9007	0.4313	0.08
H(4TC)	4*c*	0.9702	0.8732	0.4517	0.08

Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(01)	4*c*	1.226(1)	0.9779(2)	1.584(1)	0.22(1)	0.087(3)	0.144(6)	–0.030(5)	0.008(7)	–0.058(4)
C(02)	4*c*	1.3946(8)	0.9322(3)	1.548(2)	0.179(9)	0.132(6)	0.25(1)	–0.058(6)	–0.10(1)	–0.022(8)
C(03)	4*c*	1.313(1)	0.9746(3)	1.347(1)	0.186(8)	0.099(4)	0.149(7)	–0.038(5)	–0.005(7)	0.010(4)
C(0)	4*c*	1.2895(6)	0.9470(2)	1.4827(7)	0.132(5)	0.071(2)	0.108(4)	–0.048(3)	–0.002(4)	–0.023(3)
O(0)	4*c*	1.2214(3)	0.9057(1)	1.4571(4)	0.090(2)	0.064(1)	0.081(2)	–0.025(1)	0.018(2)	–0.027(1)
C(0P)	4*c*	1.2518(3)	0.8694(1)	1.3690(4)	0.052(2)	0.061(2)	0.061(2)	–0.016(1)	0.011(1)	–0.015(1)
O(0P)	4*c*	1.3277(3)	0.8704(1)	1.2845(5)	0.094(2)	0.093(2)	0.118(3)	–0.044(2)	0.057(2)	–0.031(2)
N(1)	4*c*	1.1846(2)	0.83195(8)	1.3874(3)	0.038(1)	0.050(1)	0.046(1)	–0.0058(8)	0.0072(9)	–0.0105(9)
C(1A)	4*c*	1.1942(2)	0.78808(8)	1.3028(2)	0.029(1)	0.049(1)	0.035(1)	–0.0021(8)	0.0024(8)	–0.0055(9)
C(1B)	4*c*	1.2333(2)	0.7448(1)	1.3965(3)	0.033(1)	0.059(1)	0.046(1)	0.009(1)	–0.007(1)	–0.004(1)
C(1G2)	4*c*	1.1501(3)	0.7309(1)	1.5136(4)	0.061(2)	0.071(2)	0.051(1)	0.016(1)	0.003(1)	0.014(1)
C(1D)	4*c*	1.1780(6)	0.6860(2)	1.5984(6)	0.113(4)	0.095(3)	0.087(3)	0.025(3)	0.006(3)	0.037(3)
C(1G1)	4*c*	1.3475(3)	0.7554(2)	1.4569(5)	0.050(2)	0.098(3)	0.081(2)	0.012(2)	–0.027(2)	–0.013(2)
C(1P)	4*c*	1.0851(2)	0.77740(8)	1.2286(2)	0.029(1)	0.0419(9)	0.0321(9)	0.0002(8)	–0.0004(8)	0.0038(8)
O(1P)	4*c*	0.9988(2)	0.79462(7)	1.2674(2)	0.0326(9)	0.064(1)	0.0415(8)	0.0090(7)	0.0023(7)	–0.0010(7)
N(2)	4*c*	1.0916(2)	0.74551(7)	1.1150(2)	0.027(1)	0.0415(8)	0.0397(9)	–0.0003(7)	–0.0046(7)	–0.0018(7)
C(2A)	4*c*	0.9978(2)	0.73181(8)	1.0344(3)	0.029(1)	0.043(1)	0.040(1)	0.0002(8)	–0.0070(9)	0.0019(9)
C(2B)	4*c*	0.9746(2)	0.6865(1)	0.9966(3)	0.043(1)	0.045(1)	0.057(1)	–0.004(1)	–0.017(1)	–0.001(1)
C(2G)	4*c*	1.0318(3)	0.64182(9)	1.0382(4)	0.050(2)	0.044(1)	0.065(2)	–0.005(1)	–0.016(1)	0.003(1)
C(2D1)	4*c*	1.0882(3)	0.6357(1)	1.1715(4)	0.069(2)	0.048(1)	0.074(2)	–0.007(1)	–0.027(2)	0.011(1)
C(2D2)	4*c*	1.0272(5)	0.6034(1)	0.9428(6)	0.105(3)	0.052(2)	0.095(3)	0.009(2)	–0.043(3)	–0.009(2)
C(2E1)	4*c*	1.1373(4)	0.5921(1)	1.2044(6)	0.075(2)	0.064(2)	0.104(3)	–0.004(2)	–0.031(2)	0.031(2)
C(2E2)	4*c*	1.0748(6)	0.5594(2)	0.9760(8)	0.135(4)	0.052(2)	0.123(4)	0.016(2)	–0.031(4)	–0.009(2)
C(2N)	4*c*	1.1330(5)	0.5548(2)	1.1062(8)	0.103(3)	0.056(2)	0.131(4)	0.018(2)	–0.030(3)	0.017(2)
C(2P)	4*c*	0.9259(2)	0.77173(8)	0.9753(3)	0.032(1)	0.041(1)	0.039(1)	0.0019(8)	–0.0069(9)	–0.0011(8)
O(2P)	4*c*	0.8263(2)	0.76643(7)	0.9689(3)	0.030(1)	0.056(1)	0.069(1)	–0.0006(7)	–0.0122(9)	0.0051(9)
N(3)	4*c*	0.9795(2)	0.81051(8)	0.9291(2)	0.033(1)	0.0444(9)	0.0406(9)	0.0047(8)	–0.0003(8)	0.0066(8)
C(3A)	4*c*	0.9244(2)	0.85187(9)	0.8665(3)	0.047(1)	0.048(1)	0.036(1)	0.014(1)	0.003(1)	0.0039(9)
C(3B)	4*c*	0.9403(5)	0.8977(1)	0.9595(4)	0.160(5)	0.051(2)	0.048(2)	0.039(2)	–0.020(2)	–0.007(1)
C(3G1)	4*c*	1.0574(9)	0.9082(2)	0.988(1)	0.222(9)	0.073(3)	0.168(7)	–0.018(4)	–0.116(7)	–0.010(4)
C(3G2)	4*c*	0.8721(8)	0.8917(2)	1.0994(5)	0.243(9)	0.121(4)	0.048(2)	0.107(6)	0.017(3)	0.002(2)
C(3D)	4*c*	1.113(1)	0.9466(6)	0.990(3)	0.17(1)	0.34(2)	0.74(7)	–0.00(2)	0.01(2)	0.35(4)
C(3P)	4*c*	0.9617(2)	0.85891(9)	0.7093(3)	0.042(1)	0.046(1)	0.036(1)	0.0049(9)	0.0030(9)	0.0018(9)
O(3P)	4*c*	1.0387(2)	0.83898(9)	0.6540(2)	0.062(1)	0.076(1)	0.048(1)	0.022(1)	0.013(1)	0.0067(9)
O(4)	4*c*	0.8979(2)	0.88975(9)	0.6396(2)	0.067(1)	0.080(1)	0.0421(9)	0.028(1)	0.005(1)	0.0194(9)
C(4)	4*c*	0.9252(4)	0.8989(2)	0.4881(3)	0.084(3)	0.086(2)	0.041(1)	0.023(2)	0.006(2)	0.021(1)
O(5)	4*c*	1.2153(3)	0.8068(2)	0.8712(5)	0.055(2)	0.143(3)	0.112(3)	0.006(2)	–0.003(2)	0.051(3)

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Crystal structure of 14β-hydroxy-3,4-dimethoxy-5β,17-dimethyl-morphinan-6-one, $C_{20}H_{27}NO_4$

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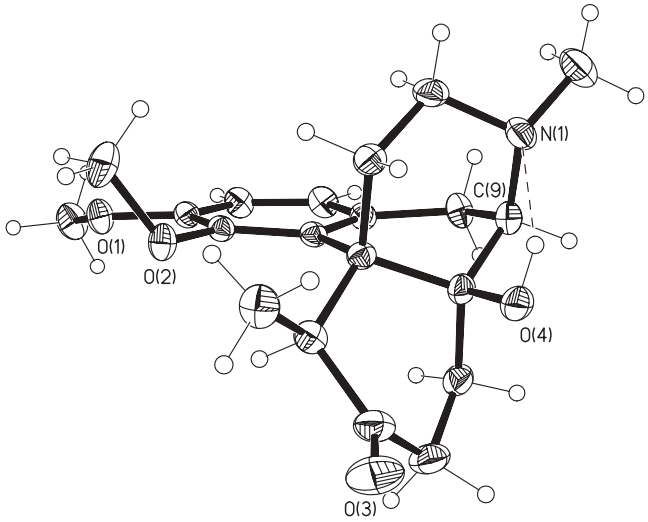

Abstract

$C_{20}H_{27}NO_4$, monoclinic, $P12_11$ (No. 4), a = 12.689(6) Å, b = 7.539(2) Å, c = 19.490(3) Å, β = 105.87(3)°, V = 1793.4 Å^3, Z = 4, $R_{gt}(F)$ = 0.032, $wR_{ref}(F^2)$ = 0.081, T = 218 K.

Source of material

The title compound was prepared from 5-methyloxycodone [1] by 4-5-ring opening with activated zinc and ammonium chloride in refluxing ethanol [2], followed by *O*-methylation with dimethyl sulfate under phase transfer conditions (40% tetrabutylammonium hydroxide, dichloromethane) [3]. Suitable crystals were grown by slow evaporation of a solution in a mixture of CH_2Cl_2/MeOH.

Discussion

The title complex crystallizes with two molecules in the asymmetric unit of a chiral space group. Only one of these nearly congruent molecules is shown in the figure. The hydrogen atoms of the hydroxyl groups at O4 and O8 were refined isotropically, and they are orientated in direction to the nitrogen atom of each molecule (dashed line). The N···H distances are 2.158 Å for N1···H4O and 2.168 Å for N2···H8O, and the angles ∠C9–N1···H4O and ∠C09–N2···H(8O) are around 76°. The molecules are intermolecular connected by weak hydrogen bonds above 2.5 Å for O···H distances.

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Table 1. Data collection and handling.

Crystal:	colorless prism, size 0.55 × 0.6 × 0.7 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	0.88 cm^{-1}
Diffractometer, scan mode:	Bruker P4, ω
$2\theta_{max}$:	49°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	4263, 3714
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 3482
$N(param)_{refined}$:	468
Programs:	SHELXS-97 [4], SHELXL-97 [5], SHELXTL [6]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(4O)	2*a*	0.029(3)	0.729(6)	–0.004(2)	0.07(1)
H(1)	2*a*	0.4943	1.0080	0.0119	0.047
H(2)	2*a*	0.6411	0.8734	0.0932	0.045
H(5)	2*a*	0.2813	0.6669	0.1893	0.043
H(7A)	2*a*	0.1811	1.0115	0.2030	0.064
H(7B)	2*a*	0.0589	1.0087	0.1541	0.064
H(8A)	2*a*	0.1329	1.1041	0.0710	0.050
H(8B)	2*a*	0.2505	1.0293	0.1111	0.050
H(9)	2*a*	0.1165	0.9899	–0.0475	0.047
H(10A)	2*a*	0.3011	0.9527	–0.0653	0.050
H(10B)	2*a*	0.2851	1.0889	–0.0074	0.050
H(15A)	2*a*	0.2536	0.4310	0.0414	0.043
H(15B)	2*a*	0.1282	0.4839	0.0240	0.043
H(16A)	2*a*	0.2777	0.6075	–0.0508	0.051
H(16B)	2*a*	0.1760	0.4818	–0.0828	0.051
H(17A)	2*a*	0.1959	0.8050	–0.1557	0.089
H(17B)	2*a*	0.0754	0.8767	–0.1657	0.089
H(17C)	2*a*	0.0949	0.6738	–0.1793	0.089
H(18A)	2*a*	0.7666	0.6863	0.1552	0.076
H(18B)	2*a*	0.7889	0.6240	0.2355	0.076
H(18C)	2*a*	0.7356	0.8120	0.2119	0.076
H(19A)	2*a*	0.4404	0.3106	0.1054	0.082
H(19B)	2*a*	0.4411	0.2480	0.1831	0.082
H(19C)	2*a*	0.5459	0.3409	0.1700	0.082
H(20A)	2*a*	0.1787	0.4330	0.2135	0.074
H(20B)	2*a*	0.2443	0.3727	0.1590	0.074
H(20C)	2*a*	0.1173	0.4137	0.1313	0.074
H(8O)	2*a*	0.048(2)	0.881(5)	0.519(2)	0.054(9)
H(01)	2*a*	0.4832	0.5898	0.4778	0.043
H(02)	2*a*	0.5456	0.7164	0.3878	0.047
H(05)	2*a*	0.1167	0.9492	0.3216	0.040
H(07A)	2*a*	–0.0089	0.6165	0.3091	0.050
H(07B)	2*a*	–0.0763	0.6241	0.3665	0.050
H(08A)	2*a*	0.0774	0.5115	0.4370	0.045
H(08B)	2*a*	0.1516	0.5944	0.3915	0.045
H(09)	2*a*	0.1701	0.6139	0.5560	0.042
H(01A)	2*a*	0.3691	0.6477	0.5654	0.044

Table 2. Continued.

Atom	Site	*x*	*y*	*z*	U_{iso}
H(01B)	2*a*	0.2980	0.5147	0.5086	0.044
H(01C)	2*a*	0.2306	1.1791	0.4709	0.038
H(01D)	2*a*	0.1231	1.1279	0.4930	0.038
H(01E)	2*a*	0.3369	0.9912	0.5575	0.043
H(01F)	2*a*	0.2696	1.1163	0.5956	0.043
H(01G)	2*a*	0.3508	0.7911	0.6618	0.079
H(01H)	2*a*	0.2415	0.7126	0.6739	0.079
H(01I)	2*a*	0.2717	0.9148	0.6909	0.079
H(01J)	2*a*	0.6137	0.9210	0.3240	0.079

Table 2. Continued.

Atom	Site	*x*	*y*	*z*	U_{iso}
H(01K)	2*a*	0.5572	0.9769	0.2440	0.079
H(01L)	2*a*	0.5312	0.7897	0.2725	0.079
H(01M)	2*a*	0.3749	1.2784	0.4057	0.069
H(01N)	2*a*	0.2932	1.3743	0.3400	0.069
H(01O)	2*a*	0.3979	1.2750	0.3299	0.069
H(02A)	2*a*	0.0092	1.1966	0.3010	0.063
H(02B)	2*a*	0.1183	1.2472	0.3598	0.063
H(02C)	2*a*	0.0093	1.2099	0.3821	0.063

Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(1)	2*a*	0.6320(1)	0.6113(3)	0.18073(8)	0.0249(7)	0.050(1)	0.0398(8)	–0.0023(8)	–0.0022(6)	0.0038(8)
O(2)	2*a*	0.4247(1)	0.5088(2)	0.16915(8)	0.0345(8)	0.0356(9)	0.0428(8)	0.0004(7)	0.0080(6)	0.0109(8)
O(3)	2*a*	0.0593(2)	0.7009(4)	0.2016(1)	0.077(1)	0.082(2)	0.080(1)	–0.004(1)	0.056(1)	–0.007(1)
O(4)	2*a*	0.0417(1)	0.7879(3)	0.0352(1)	0.0266(7)	0.058(1)	0.0466(9)	0.0045(8)	0.0064(7)	–0.010(1)
N(1)	2*a*	0.1331(2)	0.7374(3)	–0.07530(9)	0.0348(9)	0.058(2)	0.0308(9)	0.001(1)	0.0024(7)	–0.006(1)
C(1)	2*a*	0.4809(2)	0.9178(4)	0.0417(1)	0.040(1)	0.040(2)	0.038(1)	–0.009(1)	0.0119(9)	0.004(1)
C(3)	2*a*	0.5500(2)	0.7000(3)	0.1317(1)	0.029(1)	0.034(1)	0.029(1)	–0.001(1)	0.0033(8)	–0.004(1)
C(2)	2*a*	0.5691(2)	0.8361(4)	0.0896(1)	0.027(1)	0.046(2)	0.039(1)	–0.008(1)	0.0072(9)	–0.001(1)
C(4)	2*a*	0.4422(2)	0.6464(3)	0.1268(1)	0.032(1)	0.028(1)	0.027(1)	–0.001(1)	0.0070(8)	–0.002(1)
C(5)	2*a*	0.2111(2)	0.6410(4)	0.1535(1)	0.031(1)	0.042(2)	0.035(1)	–0.005(1)	0.0089(9)	–0.001(1)
C(6)	2*a*	0.1260(2)	0.7604(4)	0.1728(1)	0.046(1)	0.057(2)	0.043(1)	–0.004(1)	0.020(1)	–0.010(1)
C(7)	2*a*	0.1318(2)	0.9570(4)	0.1606(2)	0.059(2)	0.050(2)	0.054(2)	0.007(2)	0.020(1)	–0.017(2)
C(8)	2*a*	0.1723(2)	1.0004(4)	0.0957(1)	0.042(1)	0.034(1)	0.045(1)	0.008(1)	0.006(1)	–0.006(1)
C(9)	2*a*	0.1681(2)	0.8920(4)	–0.0283(1)	0.032(1)	0.044(2)	0.038(1)	0.006(1)	0.0026(9)	0.002(1)
C(10)	2*a*	0.2840(2)	0.9626(4)	–0.0194(1)	0.041(1)	0.042(2)	0.036(1)	–0.001(1)	0.0031(9)	0.009(1)
C(11)	2*a*	0.3734(2)	0.8698(3)	0.0369(1)	0.034(1)	0.031(1)	0.030(1)	–0.000(1)	0.0065(8)	–0.000(1)
C(12)	2*a*	0.3515(2)	0.7364(3)	0.0820(1)	0.028(1)	0.028(1)	0.0263(9)	–0.003(1)	0.0049(8)	–0.0051(9)
C(13)	2*a*	0.2313(2)	0.6854(3)	0.0779(1)	0.027(1)	0.029(1)	0.031(1)	–0.002(1)	0.0074(8)	–0.004(1)
C(14)	2*a*	0.1539(2)	0.8429(4)	0.0448(1)	0.027(1)	0.037(1)	0.036(1)	0.003(1)	0.0041(8)	–0.003(1)
C(15)	2*a*	0.2012(2)	0.5277(3)	0.0249(1)	0.029(1)	0.035(1)	0.041(1)	–0.004(1)	0.0048(9)	–0.009(1)
C(16)	2*a*	0.2023(2)	0.5812(4)	–0.0502(1)	0.036(1)	0.049(2)	0.040(1)	–0.003(1)	0.007(1)	–0.018(1)
C(17)	2*a*	0.1241(2)	0.7765(6)	–0.1503(1)	0.051(1)	0.090(3)	0.034(1)	–0.006(2)	0.006(1)	–0.003(2)
C(18)	2*a*	0.7396(2)	0.6898(5)	0.1972(1)	0.029(1)	0.065(2)	0.049(1)	–0.009(1)	–0.004(1)	–0.002(2)
C(19)	2*a*	0.4664(2)	0.3381(4)	0.1558(2)	0.049(2)	0.034(2)	0.076(2)	0.005(1)	0.010(1)	0.012(2)
C(20)	2*a*	0.1855(2)	0.4475(4)	0.1654(1)	0.048(1)	0.049(2)	0.054(1)	–0.005(1)	0.018(1)	0.009(1)
O(5)	2*a*	0.4583(1)	0.9895(3)	0.30655(9)	0.0497(9)	0.046(1)	0.0542(9)	0.0100(9)	0.0334(8)	0.0109(9)
O(6)	2*a*	0.2787(1)	1.1118(2)	0.33750(8)	0.0352(8)	0.0285(9)	0.0372(8)	0.0030(7)	0.0065(6)	0.0032(7)
O(7)	2*a*	–0.1132(1)	0.9369(3)	0.3213(1)	0.0289(8)	0.070(2)	0.088(1)	0.005(1)	–0.0073(8)	–0.031(1)
O(8)	2*a*	0.0243(1)	0.8267(3)	0.48182(9)	0.0289(7)	0.051(1)	0.0444(9)	–0.0094(8)	0.0166(7)	–0.0181(9)
N(2)	2*a*	0.2157(1)	0.8639(3)	0.58583(9)	0.0355(9)	0.043(1)	0.0306(9)	–0.004(1)	0.0100(7)	–0.0055(9)
C(01)	2*a*	0.4425(2)	0.6813(3)	0.4500(1)	0.034(1)	0.029(1)	0.044(1)	0.008(1)	0.0094(9)	0.004(1)
C(02)	2*a*	0.4816(2)	0.7594(4)	0.3975(1)	0.032(1)	0.039(1)	0.053(1)	0.009(1)	0.021(1)	0.003(1)
C(03)	2*a*	0.4256(2)	0.9014(3)	0.3593(1)	0.033(1)	0.034(1)	0.037(1)	–0.001(1)	0.0147(9)	–0.001(1)
C(04)	2*a*	0.3294(2)	0.9623(3)	0.3732(1)	0.028(1)	0.027(1)	0.028(1)	0.002(1)	0.0040(8)	–0.0030(9)
C(05)	2*a*	0.0824(2)	0.9793(3)	0.3600(1)	0.027(1)	0.036(1)	0.035(1)	0.002(1)	0.0047(8)	–0.009(1)
C(06)	2*a*	–0.0230(2)	0.8697(4)	0.3447(1)	0.029(1)	0.052(2)	0.043(1)	–0.002(1)	0.003(1)	–0.022(1)
C(07)	2*a*	–0.0117(2)	0.6708(4)	0.3542(1)	0.035(1)	0.048(2)	0.045(1)	–0.014(1)	0.013(1)	–0.019(1)
C(08)	2*a*	0.0915(2)	0.6191(4)	0.4128(1)	0.039(1)	0.033(1)	0.045(1)	–0.011(1)	0.018(1)	–0.013(1)
C(09)	2*a*	0.2043(2)	0.7125(3)	0.5363(1)	0.037(1)	0.033(1)	0.038(1)	–0.007(1)	0.0163(9)	–0.002(1)
C(010)	2*a*	0.3092(2)	0.6404(3)	0.5213(1)	0.040(1)	0.031(1)	0.041(1)	0.001(1)	0.013(1)	0.004(1)
C(011)	2*a*	0.3446(2)	0.7348(3)	0.4626(1)	0.029(1)	0.026(1)	0.032(1)	0.000(1)	0.0068(8)	–0.003(1)
C(012)	2*a*	0.2830(2)	0.8736(3)	0.4216(1)	0.0240(9)	0.025(1)	0.0295(9)	–0.0034(9)	0.0066(8)	–0.0075(9)
C(013)	2*a*	0.1708(2)	0.9288(3)	0.4329(1)	0.0242(9)	0.026(1)	0.032(1)	0.0002(9)	0.0079(8)	–0.008(1)
C(014)	2*a*	0.1238(2)	0.7706(3)	0.4664(1)	0.0256(9)	0.034(1)	0.035(1)	–0.006(1)	0.0125(8)	–0.009(1)
C(015)	2*a*	0.1930(2)	1.0822(3)	0.4881(1)	0.026(1)	0.030(1)	0.038(1)	–0.002(1)	0.0084(8)	–0.010(1)
C(016)	2*a*	0.2632(2)	1.0200(4)	0.5609(1)	0.028(1)	0.040(1)	0.038(1)	–0.005(1)	0.0085(9)	–0.017(1)
C(017)	2*a*	0.2750(2)	0.8166(5)	0.6593(1)	0.058(2)	0.063(2)	0.035(1)	0.000(2)	0.010(1)	–0.006(1)
C(018)	2*a*	0.5472(2)	0.9132(4)	0.2850(1)	0.061(2)	0.052(2)	0.059(2)	0.005(2)	0.042(1)	0.001(2)
C(019)	2*a*	0.3413(2)	1.2731(4)	0.3547(2)	0.051(1)	0.028(1)	0.059(2)	–0.001(1)	0.013(1)	0.004(1)
C(020)	2*a*	0.0520(2)	1.1764(4)	0.3498(1)	0.037(1)	0.042(2)	0.042(1)	0.008(1)	0.002(1)	–0.005(1)

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Crystal structure of 1,3,3,4,6,6-hexaferrocenyl-hexa-4,5-dien-1-yne, $C_{66}H_{54}Fe_6$

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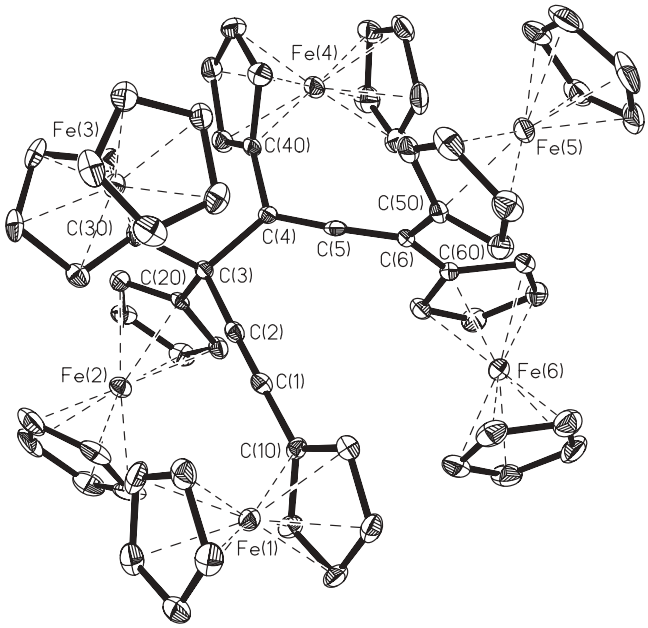

Abstract

$C_{66}H_{54}Fe_6$, monoclinic, $P12_1/c1$ (No. 14), a = 12.4201(4) Å, b = 20.0247(6) Å, c = 19.8328(3) Å, β = 93.054(2)°, V = 4925.6 Å^3, Z = 4, $R_{gt}(F)$ = 0.039, $wR_{ref}(F^2)$ = 0.074, T = 223 K.

Source of material

The title compound was obtained in low yield by attempted synthesis of tetraferrocenylallene [1] from triferrocenylallenylium tetrafluoroborate [2] with lithioferrocene.

Discussion

The title compound crystallizes in a centrosymmetric space group with one molecule in the asymmetric unit. The hexadienyne chain lies nearly in a plane with a small deviation, shown by the low torsion angle C2–C3–C4–C5 of 4.5(5)°. The bond distances of the alkyne with 1.182(4) Å (C1—C2) and the allene with 1.312(4) Å and 1.317(4) Å (C4—C5 and C5—C6) are in a normal range [3]. The geometric features of the allene group deviate only marginally from the idealized state. The bond angle C4–C5–C6 is slightly bended with an angle of 175.1(3)°. The angles with the ferrocenyl subsituents are in the range of 120° (120.0(3)° for ∠C3–C4–C40 and 123.2(3)° for ∠C50–C6–C60) and the dihedral angle between the planes C3–C4–C40 and C50–C6–C60 is 88.0(3)°.

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Table 1. Data collection and handling.

Crystal:	brown prism, size 0.06 × 0.08 × 0.2 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	17.65 cm^{-1}
Diffractometer, scan mode:	Kappa CCD, φ/ω
$2\theta_{max}$:	48°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	14358, 7737
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 5431
$N(param)_{refined}$:	649
Programs:	SHELXS-97 [4], SHELXL-97 [5], SHELXTL [6]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(11)	4*e*	0.2462	0.3171	0.7665	0.037
H(12)	4*e*	0.2020	0.4228	0.7028	0.040
H(13)	4*e*	0.1375	0.5083	0.7842	0.040
H(14)	4*e*	0.1348	0.4545	0.8986	0.035
H(15)	4*e*	–0.0500	0.2887	0.8549	0.048
H(16)	4*e*	–0.0063	0.2652	0.7343	0.044
H(17)	4*e*	–0.0452	0.3709	0.6676	0.046
H(18)	4*e*	–0.1094	0.4578	0.7464	0.049
H(19)	4*e*	–0.1167	0.4065	0.8616	0.049
H(21)	4*e*	0.3130	0.3624	1.0612	0.034
H(22)	4*e*	0.2795	0.3896	1.1822	0.042
H(23)	4*e*	0.1765	0.2950	1.2300	0.040
H(24)	4*e*	0.1427	0.2089	1.1387	0.033
H(25)	4*e*	0.0098	0.3477	0.9831	0.053
H(26)	4*e*	0.0911	0.4532	1.0321	0.062
H(27)	4*e*	0.0521	0.4582	1.1547	0.061
H(28)	4*e*	–0.0573	0.3579	1.1812	0.060
H(29)	4*e*	–0.0838	0.2881	1.0760	0.061
H(31)	4*e*	0.0110	0.2282	0.9705	0.034
H(32)	4*e*	–0.0929	0.1230	0.9928	0.041
H(33)	4*e*	0.0390	0.0382	1.0420	0.040
H(34)	4*e*	0.2230	0.0903	1.0505	0.031
H(35)	4*e*	0.2302	0.1675	0.8473	0.043
H(36)	4*e*	0.0306	0.1703	0.8192	0.050
H(37)	4*e*	–0.0466	0.0584	0.8449	0.047
H(38)	4*e*	0.1067	–0.0151	0.8885	0.045
H(39)	4*e*	0.2775	0.0523	0.8885	0.037
H(41)	4*e*	0.4290	0.0696	0.9912	0.042
H(42)	4*e*	0.4667	0.0026	1.0971	0.049
H(43)	4*e*	0.4422	0.0775	1.1960	0.047
H(44)	4*e*	0.3863	0.1915	1.1530	0.038
H(45)	4*e*	0.6367	0.2503	1.0807	0.059
H(46)	4*e*	0.6579	0.1694	0.9857	0.064
H(47)	4*e*	0.7061	0.0567	1.0360	0.055
H(48)	4*e*	0.7121	0.0694	1.1628	0.049
H(49)	4*e*	0.6727	0.1890	1.1898	0.056
H(51)	4*e*	0.5468	0.2890	0.7841	0.044

Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
H(52)	4*e*	0.5066	0.2035	0.6925	0.053
H(53)	4*e*	0.4442	0.0975	0.7470	0.053
H(54)	4*e*	0.4442	0.1179	0.8720	0.040
H(55)	4*e*	0.7812	0.1870	0.8943	0.054
H(56)	4*e*	0.7983	0.2231	0.7746	0.061
H(57)	4*e*	0.7275	0.1299	0.6987	0.076
H(58)	4*e*	0.6716	0.0365	0.7737	0.079
H(59)	4*e*	0.7050	0.0715	0.8942	0.066
H(61)	4*e*	0.7058	0.2957	0.8851	0.037

Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
H(62)	4*e*	0.7909	0.3838	0.9619	0.042
H(63)	4*e*	0.6583	0.4144	1.0475	0.045
H(64)	4*e*	0.4887	0.3490	1.0235	0.037
H(65)	4*e*	0.4307	0.3923	0.8158	0.054
H(66)	4*e*	0.6217	0.4171	0.7851	0.057
H(67)	4*e*	0.6974	0.5028	0.8666	0.060
H(68)	4*e*	0.5544	0.5325	0.9463	0.056
H(69)	4*e*	0.3898	0.4639	0.9146	0.053

Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Fe(1)	4*e*	0.05966(4)	0.38198(2)	0.79082(2)	0.0238(3)	0.0279(3)	0.0253(3)	–0.0007(2)	0.0016(2)	0.0069(2)
Fe(2)	4*e*	0.11467(4)	0.33952(3)	1.10572(2)	0.0298(3)	0.0286(3)	0.0287(3)	0.0061(3)	0.0051(2)	–0.0036(2)
Fe(3)	4*e*	0.09940(4)	0.11137(2)	0.93545(2)	0.0259(3)	0.0258(3)	0.0232(2)	–0.0041(2)	0.0022(2)	–0.0021(2)
Fe(4)	4*e*	0.54742(4)	0.12747(3)	1.09146(2)	0.0239(3)	0.0362(4)	0.0331(3)	0.0061(3)	0.0018(2)	0.0080(2)
Fe(5)	4*e*	0.61396(4)	0.16099(3)	0.80569(2)	0.0256(3)	0.0304(3)	0.0414(3)	–0.0010(3)	0.0116(2)	–0.0062(2)
Fe(6)	4*e*	0.58401(4)	0.40185(3)	0.91691(2)	0.0287(3)	0.0254(3)	0.0361(3)	–0.0025(3)	0.0045(2)	0.0016(2)
C(1)	4*e*	0.2065(3)	0.3187(2)	0.9072(2)	0.020(2)	0.029(2)	0.028(2)	0.004(2)	–0.000(2)	0.000(2)
C(2)	4*e*	0.2181(3)	0.2799(2)	0.9519(2)	0.016(2)	0.025(2)	0.028(2)	–0.000(2)	–0.000(2)	–0.005(2)
C(3)	4*e*	0.2368(3)	0.2327(2)	1.0092(1)	0.019(2)	0.021(2)	0.021(2)	0.002(2)	0.002(1)	0.001(1)
C(4)	4*e*	0.3551(2)	0.2051(2)	1.0063(1)	0.018(2)	0.015(2)	0.024(2)	–0.002(2)	–0.001(2)	–0.003(1)
C(5)	4*e*	0.4202(3)	0.2277(2)	0.9616(2)	0.025(2)	0.014(2)	0.032(2)	0.005(2)	–0.003(2)	0.001(2)
C(6)	4*e*	0.4926(3)	0.2486(2)	0.9203(2)	0.020(2)	0.017(2)	0.036(2)	0.002(2)	0.009(2)	0.002(2)
C(10)	4*e*	0.1939(3)	0.3668(2)	0.8537(2)	0.022(2)	0.024(2)	0.026(2)	–0.005(2)	–0.000(2)	0.003(2)
C(11)	4*e*	0.2187(3)	0.3565(2)	0.7848(2)	0.026(2)	0.032(2)	0.034(2)	0.003(2)	0.005(2)	0.000(2)
C(12)	4*e*	0.1946(3)	0.4161(2)	0.7492(2)	0.032(2)	0.040(3)	0.029(2)	–0.008(2)	0.004(2)	0.010(2)
C(13)	4*e*	0.1577(3)	0.4641(2)	0.7948(2)	0.034(3)	0.023(2)	0.042(2)	–0.006(2)	0.002(2)	0.011(2)
C(14)	4*e*	0.1566(3)	0.4339(2)	0.8590(2)	0.033(2)	0.023(2)	0.030(2)	–0.004(2)	–0.001(2)	0.000(2)
C(15)	4*e*	–0.0570(3)	0.3190(2)	0.8188(2)	0.034(3)	0.049(3)	0.038(2)	–0.015(2)	0.003(2)	0.016(2)
C(16)	4*e*	–0.0322(3)	0.3057(2)	0.7512(2)	0.024(2)	0.038(3)	0.048(2)	–0.007(2)	–0.002(2)	–0.005(2)
C(17)	4*e*	–0.0539(3)	0.3651(2)	0.7141(2)	0.031(2)	0.055(3)	0.027(2)	–0.005(2)	–0.007(2)	0.008(2)
C(18)	4*e*	–0.0904(3)	0.4136(2)	0.7581(2)	0.026(2)	0.048(3)	0.050(2)	0.009(2)	–0.000(2)	0.012(2)
C(19)	4*e*	–0.0938(3)	0.3851(2)	0.8227(2)	0.029(2)	0.052(3)	0.041(2)	–0.002(2)	0.009(2)	0.001(2)
C(20)	4*e*	0.2282(2)	0.2724(2)	1.0757(1)	0.014(2)	0.023(2)	0.027(2)	0.005(2)	–0.001(1)	–0.001(2)
C(21)	4*e*	0.2757(3)	0.3355(2)	1.0910(2)	0.022(2)	0.028(2)	0.036(2)	–0.002(2)	0.004(2)	–0.007(2)
C(22)	4*e*	0.2570(3)	0.3508(2)	1.1590(2)	0.037(3)	0.032(2)	0.035(2)	0.001(2)	–0.007(2)	–0.013(2)
C(23)	4*e*	0.1991(3)	0.2979(2)	1.1856(2)	0.046(3)	0.033(2)	0.022(2)	0.013(2)	0.004(2)	–0.001(2)
C(24)	4*e*	0.1803(3)	0.2493(2)	1.1344(2)	0.028(2)	0.029(2)	0.027(2)	0.002(2)	0.004(2)	0.004(2)
C(25)	4*e*	0.0063(3)	0.3622(2)	1.0280(2)	0.038(3)	0.053(3)	0.043(2)	0.025(2)	–0.004(2)	–0.003(2)
C(26)	4*e*	0.0522(3)	0.4213(2)	1.0556(2)	0.060(3)	0.038(3)	0.057(3)	0.028(2)	0.004(2)	0.007(2)
C(27)	4*e*	0.0300(3)	0.4244(2)	1.1242(2)	0.054(3)	0.043(3)	0.055(3)	0.019(3)	0.004(2)	–0.016(2)
C(28)	4*e*	–0.0307(3)	0.3681(2)	1.1388(2)	0.033(3)	0.071(3)	0.048(3)	0.027(3)	0.019(2)	0.001(2)
C(29)	4*e*	–0.0461(3)	0.3287(2)	1.0799(2)	0.024(3)	0.058(3)	0.070(3)	0.014(2)	–0.003(2)	–0.007(2)
C(30)	4*e*	0.1506(3)	0.1776(2)	1.0080(1)	0.022(2)	0.029(2)	0.018(2)	–0.003(2)	0.007(1)	–0.003(2)
C(31)	4*e*	0.0403(3)	0.1884(2)	0.9887(2)	0.026(2)	0.030(2)	0.029(2)	0.002(2)	0.000(2)	–0.008(2)
C(32)	4*e*	–0.0185(3)	0.1294(2)	1.0013(2)	0.021(2)	0.048(3)	0.033(2)	–0.014(2)	0.006(2)	–0.009(2)
C(33)	4*e*	0.0558(3)	0.0819(2)	1.0289(2)	0.040(3)	0.036(2)	0.025(2)	–0.020(2)	0.007(2)	0.002(2)
C(34)	4*e*	0.1593(3)	0.1111(2)	1.0336(1)	0.027(2)	0.027(2)	0.024(2)	–0.005(2)	–0.002(2)	0.002(2)
C(35)	4*e*	0.1819(3)	0.1318(2)	0.8518(2)	0.045(3)	0.042(3)	0.022(2)	–0.008(2)	0.008(2)	–0.000(2)
C(36)	4*e*	0.0698(3)	0.1332(2)	0.8363(2)	0.050(3)	0.054(3)	0.020(2)	0.015(2)	0.000(2)	0.003(2)
C(37)	4*e*	0.0263(3)	0.0708(2)	0.8505(2)	0.028(2)	0.060(3)	0.030(2)	–0.006(2)	0.001(2)	–0.018(2)
C(38)	4*e*	0.1123(3)	0.0297(2)	0.8749(2)	0.039(3)	0.035(2)	0.037(2)	–0.007(2)	0.010(2)	–0.013(2)
C(39)	4*e*	0.2080(3)	0.0676(2)	0.8751(2)	0.027(2)	0.033(2)	0.034(2)	–0.003(2)	0.006(2)	–0.006(2)
C(40)	4*e*	0.3937(3)	0.1515(2)	1.0539(1)	0.016(2)	0.027(2)	0.028(2)	0.005(2)	0.001(1)	0.007(2)
C(41)	4*e*	0.4243(3)	0.0855(2)	1.0355(2)	0.034(2)	0.033(2)	0.036(2)	0.003(2)	0.001(2)	–0.002(2)
C(42)	4*e*	0.4462(3)	0.0478(2)	1.0950(2)	0.036(3)	0.030(2)	0.058(2)	0.005(2)	0.002(2)	0.013(2)
C(43)	4*e*	0.4322(3)	0.0898(2)	1.1503(2)	0.029(2)	0.053(3)	0.037(2)	0.007(2)	0.004(2)	0.021(2)
C(44)	4*e*	0.4004(3)	0.1540(2)	1.1263(2)	0.027(2)	0.036(2)	0.032(2)	0.004(2)	0.002(2)	0.004(2)
C(45)	4*e*	0.6546(3)	0.2048(2)	1.0852(2)	0.022(3)	0.042(3)	0.085(3)	–0.002(2)	0.003(2)	0.018(2)
C(46)	4*e*	0.6664(3)	0.1594(2)	1.0320(2)	0.025(3)	0.080(4)	0.057(3)	0.004(2)	0.013(2)	0.031(3)
C(47)	4*e*	0.6932(3)	0.0961(2)	1.0601(2)	0.030(3)	0.057(3)	0.051(2)	0.017(2)	0.012(2)	0.009(2)

Table 3. Continued.

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(48)	4*e*	0.6970(3)	0.1035(2)	1.1311(2)	0.030(3)	0.046(3)	0.045(2)	0.012(2)	–0.003(2)	0.009(2)
C(49)	4*e*	0.6743(3)	0.1705(2)	1.1463(2)	0.034(3)	0.053(3)	0.053(3)	–0.001(2)	–0.006(2)	–0.001(2)
C(50)	4*e*	0.4970(3)	0.2159(2)	0.8533(2)	0.019(2)	0.027(2)	0.034(2)	0.000(2)	0.006(2)	0.000(2)
C(51)	4*e*	0.5210(3)	0.2454(2)	0.7904(2)	0.045(3)	0.036(2)	0.031(2)	0.006(2)	0.010(2)	0.004(2)
C(52)	4*e*	0.4990(3)	0.1970(2)	0.7389(2)	0.049(3)	0.051(3)	0.033(2)	0.009(2)	0.004(2)	–0.003(2)
C(53)	4*e*	0.4638(3)	0.1374(2)	0.7693(2)	0.029(3)	0.051(3)	0.053(3)	–0.001(2)	–0.002(2)	–0.022(2)
C(54)	4*e*	0.4635(3)	0.1493(2)	0.8395(2)	0.019(2)	0.037(3)	0.044(2)	–0.001(2)	0.005(2)	–0.001(2)
C(55)	4*e*	0.7617(3)	0.1615(2)	0.8558(2)	0.027(3)	0.043(3)	0.064(3)	0.006(2)	0.003(2)	–0.012(2)
C(56)	4*e*	0.7709(3)	0.1820(2)	0.7888(2)	0.029(3)	0.050(3)	0.076(3)	–0.008(2)	0.022(2)	–0.005(2)
C(57)	4*e*	0.7317(3)	0.1298(3)	0.7462(2)	0.040(3)	0.087(4)	0.064(3)	0.001(3)	0.029(2)	–0.030(3)
C(58)	4*e*	0.7004(3)	0.0777(2)	0.7884(3)	0.041(3)	0.038(3)	0.120(4)	0.007(2)	0.020(3)	–0.030(3)
C(59)	4*e*	0.7189(3)	0.0971(2)	0.8559(2)	0.033(3)	0.040(3)	0.093(3)	0.015(2)	0.013(2)	0.002(3)
C(60)	4*e*	0.5667(3)	0.3023(2)	0.9433(2)	0.024(2)	0.024(2)	0.033(2)	0.004(2)	0.007(2)	0.007(2)
C(61)	4*e*	0.6734(3)	0.3161(2)	0.9216(2)	0.027(2)	0.025(2)	0.040(2)	0.003(2)	0.007(2)	0.001(2)
C(62)	4*e*	0.7214(3)	0.3658(2)	0.9648(2)	0.025(2)	0.033(2)	0.048(2)	–0.007(2)	–0.001(2)	0.001(2)
C(63)	4*e*	0.6468(3)	0.3831(2)	1.0126(2)	0.043(3)	0.034(2)	0.036(2)	–0.003(2)	0.001(2)	–0.003(2)
C(64)	4*e*	0.5517(3)	0.3458(2)	0.9994(2)	0.026(2)	0.033(2)	0.034(2)	0.007(2)	0.006(2)	–0.000(2)
C(65)	4*e*	0.4781(3)	0.4229(2)	0.8377(2)	0.050(3)	0.040(3)	0.044(2)	–0.005(2)	–0.012(2)	0.011(2)
C(66)	4*e*	0.5854(4)	0.4367(2)	0.8205(2)	0.060(3)	0.043(3)	0.038(2)	0.001(2)	0.006(2)	0.008(2)
C(67)	4*e*	0.6275(3)	0.4847(2)	0.8661(2)	0.050(3)	0.037(3)	0.062(3)	–0.015(2)	0.005(2)	0.017(2)
C(68)	4*e*	0.5476(3)	0.5014(2)	0.9109(2)	0.054(3)	0.026(2)	0.060(3)	0.003(2)	–0.001(2)	–0.002(2)
C(69)	4*e*	0.4554(3)	0.4629(2)	0.8930(2)	0.036(3)	0.040(3)	0.057(3)	0.012(2)	0.000(2)	0.006(2)

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Crystal structure of [1*R*,7,7-trimethylbicyclo[2.2.1]heptan-2,3-bis(2,6-diisopropylphen-1-yl)imine]nickeldibromide]—toluene (1:1), $C_{34}H_{48}Br_2N_2Ni \cdot C_7H_8$

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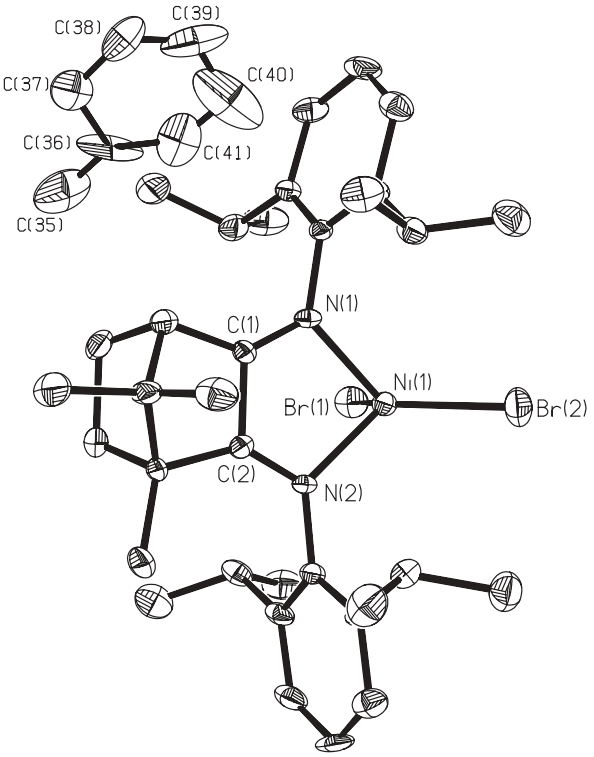

Abstract

$C_{41}H_{56}Br_2N_2Ni$, orthorhombic, $P2_12_12_1$ (No. 19), a = 10.121(2) Å, b = 17.115(2) Å, c = 22.835(2) Å, V = 3955.5 Å^3, Z = 4, $R_{gt}(F)$ = 0.037, $wR_{ref}(F^2)$ = 0.086, T = 218 K.

Source of material

The Ni-complex was obtained from 1*R*-camphorchinon-*N*,*N*′-bis(2,6-diisopropylphenyl)diimine [1] and (dimethoxyethane)-nickeldibromide.

Experimental details

The chiral compound crystallizes in the chiral space group $P2_12_12_1$ and the absolute structure was determined by the method of Flack (Flack parameter x = 0.025(15)).

Discussion

In the asymmetric unit is one molecule of the complex and one molecule of the solvent toluene. The Ni(II) cation has a distorted tetrahedral coordination with bond distances of 2.027(5) Å and 2.033(5) Å for Ni—N bonds and 2.294(2) Å and 2.328(2) Å for Ni—Br bonds. The smallest and greatest bond angle is ∠N1–Ni2–N2 with 82.8(2)° and ∠Br1–Ni1–Br2 with 123.5(1)°. The double bonds of the imino groups are located between N1–C1 and N2–C2 with bond distances of 1.272(8) Å and 1.274(8) Å. The solvent toluene is slightly disordered and was refined without hydrogen atoms.

Table 1. Data collection and handling.

Crystal:	brown prism, size 0.35 × 0.5 × 0.65 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	25.40 cm^{-1}
Diffractometer, scan mode:	Bruker P4, ω
$2\theta_{max}$:	40.98°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	3773, 3310
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 2759
$N(param)_{refined}$:	416
Programs:	SHELXS-97 [2], SHELXL-97 [3], SHELXTL [4]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(4A)	4*a*	1.0399	1.1343	0.4150	0.066
H(4B)	4*a*	0.9804	1.0564	0.3872	0.066
H(5A)	4*a*	0.9144	1.1256	0.3073	0.075
H(5B)	4*a*	0.9770	1.2031	0.3345	0.075
H(6)	4*a*	1.1167	1.1793	0.2503	0.054
H(8A)	4*a*	1.2658	1.0950	0.4457	0.078
H(8B)	4*a*	1.3495	1.0358	0.4073	0.078
H(8C)	4*a*	1.2191	1.0071	0.4391	0.078
H(9A)	4*a*	1.3571	1.0762	0.2739	0.095
H(9B)	4*a*	1.4323	1.1181	0.3260	0.095
H(9C)	4*a*	1.3884	1.1667	0.2703	0.095
H(10A)	4*a*	1.1622	1.2301	0.3798	0.113
H(10B)	4*a*	1.2687	1.2605	0.3344	0.113
H(10C)	4*a*	1.3140	1.2121	0.3900	0.113
H(13)	4*a*	1.1670	1.0934	0.0357	0.063
H(14)	4*a*	0.9492	1.1216	0.0159	0.072
H(15)	4*a*	0.7940	1.1110	0.0884	0.065
H(17)	4*a*	1.2993	1.0234	0.1690	0.051
H(18A)	4*a*	1.4493	0.9949	0.0943	0.101
H(18B)	4*a*	1.3483	1.0263	0.0468	0.101
H(18C)	4*a*	1.3148	0.9500	0.0832	0.101
H(19A)	4*a*	1.4512	1.1231	0.1435	0.093
H(19B)	4*a*	1.3192	1.1590	0.1693	0.093
H(19C)	4*a*	1.3449	1.1600	0.1008	0.093
H(20)	4*a*	0.8431	1.0432	0.2341	0.060
H(21A)	4*a*	0.6232	1.0123	0.2061	0.124
H(21B)	4*a*	0.7248	0.9616	0.1695	0.124
H(21C)	4*a*	0.6560	1.0351	0.1404	0.124

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Table 2. Continued.

Atom	Site	*x*	*y*	*z*	U_{iso}
H(22A)	4*a*	0.6847	1.1443	0.2409	0.132
H(22B)	4*a*	0.7223	1.1725	0.1770	0.132
H(22C)	4*a*	0.8269	1.1791	0.2283	0.132
H(25)	4*a*	1.4818	0.8011	0.4021	0.064
H(26)	4*a*	1.3378	0.7510	0.4718	0.072
H(27)	4*a*	1.1195	0.7880	0.4713	0.066
H(29)	4*a*	1.4047	0.9253	0.2842	0.056
H(30A)	4*a*	1.5787	0.8423	0.2541	0.102
H(30B)	4*a*	1.4465	0.7937	0.2617	0.102
H(30C)	4*a*	1.5576	0.7898	0.3104	0.102

Table 2. Continued.

Atom	Site	*x*	*y*	*z*	U_{iso}
H(31A)	4*a*	1.6210	0.9596	0.3127	0.107
H(31B)	4*a*	1.6033	0.9131	0.3722	0.107
H(31C)	4*a*	1.5181	0.9891	0.3601	0.107
H(32)	4*a*	0.9609	0.9111	0.3667	0.060
H(33A)	4*a*	0.8048	0.8116	0.3910	0.103
H(33B)	4*a*	0.9180	0.7628	0.4220	0.103
H(33C)	4*a*	0.9217	0.7761	0.3534	0.103
H(34A)	4*a*	0.8376	0.9255	0.4532	0.109
H(34B)	4*a*	0.9786	0.9641	0.4616	0.109
H(34C)	4*a*	0.9482	0.8811	0.4893	0.109

Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ni(1)	4*a*	1.1039(1)	0.90339(5)	0.23252(4)	0.0516(7)	0.0275(5)	0.0320(6)	–0.0003(5)	–0.0042(6)	–0.0009(4)
Br(1)	4*a*	0.88604(9)	0.86370(5)	0.24611(4)	0.0547(5)	0.0564(5)	0.0632(6)	–0.0149(5)	–0.0114(5)	–0.0011(4)
Br(2)	4*a*	1.2530(1)	0.83631(5)	0.17600(4)	0.0916(8)	0.0668(6)	0.0641(6)	0.0160(7)	0.0231(6)	–0.0113(5)
N(1)	4*a*	1.0867(5)	1.0199(3)	0.2187(3)	0.024(4)	0.033(4)	0.028(4)	–0.001(3)	–0.001(3)	0.012(3)
N(2)	4*a*	1.1686(5)	0.9388(4)	0.3125(2)	0.039(4)	0.030(4)	0.023(4)	0.004(3)	–0.005(3)	0.006(3)
C(1)	4*a*	1.1133(8)	1.0580(4)	0.2650(3)	0.040(5)	0.031(5)	0.025(5)	0.000(4)	–0.006(4)	–0.002(4)
C(2)	4*a*	1.1583(7)	1.0126(4)	0.3182(3)	0.029(5)	0.028(5)	0.033(5)	0.002(4)	0.002(4)	0.003(4)
C(3)	4*a*	1.1799(8)	1.0729(4)	0.3652(3)	0.060(6)	0.026(5)	0.025(5)	0.006(4)	–0.012(4)	–0.007(4)
C(4)	4*a*	1.0393(9)	1.1009(5)	0.3802(4)	0.082(8)	0.043(6)	0.041(5)	0.019(5)	0.003(5)	–0.007(5)
C(5)	4*a*	0.9942(9)	1.1483(5)	0.3246(4)	0.089(8)	0.036(6)	0.061(6)	0.023(5)	–0.029(6)	–0.012(5)
C(6)	4*a*	1.1132(9)	1.1409(4)	0.2827(3)	0.065(6)	0.034(5)	0.036(5)	0.006(5)	–0.011(5)	0.001(4)
C(7)	4*a*	1.2314(9)	1.1423(4)	0.3258(3)	0.083(7)	0.028(5)	0.039(5)	–0.001(5)	–0.029(6)	0.000(5)
C(8)	4*a*	1.261(1)	1.0506(4)	0.4193(3)	0.076(6)	0.046(5)	0.035(5)	0.001(6)	–0.012(5)	–0.012(4)
C(9)	4*a*	1.365(1)	1.1242(5)	0.2963(4)	0.080(8)	0.050(6)	0.059(6)	–0.025(6)	–0.015(6)	0.012(5)
C(10)	4*a*	1.245(1)	1.2182(4)	0.3607(4)	0.121(9)	0.037(5)	0.069(7)	–0.009(6)	–0.043(7)	–0.006(5)
C(11)	4*a*	1.0473(8)	1.0551(4)	0.1636(3)	0.045(6)	0.022(4)	0.025(5)	–0.001(4)	–0.007(5)	0.001(4)
C(12)	4*a*	1.1433(8)	1.0629(4)	0.1203(3)	0.058(7)	0.035(5)	0.021(5)	–0.005(4)	–0.012(5)	–0.001(4)
C(13)	4*a*	1.104(1)	1.0880(5)	0.0655(3)	0.063(7)	0.052(6)	0.042(6)	–0.016(5)	0.002(6)	0.005(5)
C(14)	4*a*	0.974(1)	1.1052(5)	0.0535(4)	0.093(9)	0.055(6)	0.032(6)	–0.010(6)	–0.029(6)	0.009(5)
C(15)	4*a*	0.8823(9)	1.0982(5)	0.0968(4)	0.046(6)	0.060(6)	0.057(6)	0.005(5)	–0.014(6)	0.017(5)
C(16)	4*a*	0.9146(9)	1.0726(4)	0.1534(3)	0.049(7)	0.036(5)	0.028(5)	0.004(4)	–0.005(5)	0.004(4)
C(17)	4*a*	1.2896(8)	1.0507(5)	0.1310(3)	0.051(7)	0.043(5)	0.032(5)	–0.004(5)	–0.003(4)	0.002(4)
C(18)	4*a*	1.3566(9)	1.0010(5)	0.0846(4)	0.060(7)	0.087(7)	0.054(6)	0.000(6)	0.011(5)	0.007(5)
C(19)	4*a*	1.3575(8)	1.1306(5)	0.1367(4)	0.049(6)	0.066(6)	0.072(6)	–0.006(6)	–0.008(5)	0.011(5)
C(20)	4*a*	0.8060(8)	1.0664(5)	0.1979(3)	0.048(6)	0.053(6)	0.050(6)	0.010(5)	–0.012(5)	0.003(4)
C(21)	4*a*	0.6919(9)	1.0140(6)	0.1765(5)	0.044(6)	0.116(9)	0.089(8)	–0.005(6)	–0.015(6)	0.040(7)
C(22)	4*a*	0.755(1)	1.1480(6)	0.2123(4)	0.101(8)	0.097(8)	0.065(7)	0.053(8)	–0.002(6)	0.008(6)
C(23)	4*a*	1.2143(8)	0.8873(4)	0.3587(3)	0.039(6)	0.032(5)	0.026(5)	0.001(4)	–0.005(4)	0.003(4)
C(24)	4*a*	1.3467(8)	0.8659(4)	0.3583(3)	0.059(7)	0.020(4)	0.036(5)	–0.001(5)	–0.018(5)	0.004(4)
C(25)	4*a*	1.3921(9)	0.8154(5)	0.4014(4)	0.055(6)	0.044(6)	0.061(6)	–0.005(5)	–0.020(6)	0.002(5)
C(26)	4*a*	1.307(1)	0.7858(5)	0.4431(4)	0.087(9)	0.035(5)	0.057(7)	0.005(6)	–0.040(7)	0.018(5)
C(27)	4*a*	1.177(1)	0.8075(5)	0.4422(3)	0.089(8)	0.048(6)	0.029(5)	–0.010(6)	–0.010(5)	0.008(5)
C(28)	4*a*	1.1254(9)	0.8577(4)	0.3997(3)	0.062(7)	0.031(5)	0.029(5)	–0.014(5)	–0.014(5)	0.002(4)
C(29)	4*a*	1.4502(8)	0.8929(4)	0.3139(4)	0.052(6)	0.040(5)	0.049(5)	0.011(5)	–0.002(5)	0.002(5)
C(30)	4*a*	1.5142(9)	0.8232(5)	0.2821(4)	0.078(7)	0.055(6)	0.071(6)	0.007(5)	0.006(5)	–0.009(6)
C(31)	4*a*	1.5581(9)	0.9433(5)	0.3423(4)	0.065(7)	0.058(6)	0.091(7)	–0.004(5)	–0.017(6)	–0.011(6)
C(32)	4*a*	0.9796(9)	0.8756(5)	0.3999(3)	0.059(7)	0.062(7)	0.031(5)	–0.010(5)	0.005(5)	0.009(5)
C(33)	4*a*	0.898(1)	0.7993(5)	0.3907(4)	0.068(7)	0.063(6)	0.075(6)	–0.023(6)	–0.012(6)	0.024(5)
C(34)	4*a*	0.932(1)	0.9152(5)	0.4561(4)	0.068(8)	0.089(7)	0.061(6)	–0.014(6)	0.014(5)	0.012(6)
C(35)	4*a*	1.479(2)	1.304(1)	0.4652(8)	0.31(3)	0.21(2)	0.15(2)	–0.12(2)	–0.08(2)	–0.02(2)
C(36)	4*a*	1.523(3)	1.234(1)	0.471(1)	0.35(4)	0.05(1)	0.24(3)	–0.13(2)	–0.22(3)	0.08(2)
C(37)	4*a*	1.451(2)	1.205(1)	0.5297(9)	0.18(2)	0.11(1)	0.15(2)	–0.04(1)	–0.06(1)	–0.03(1)
C(38)	4*a*	1.513(2)	1.131(2)	0.5396(8)	0.14(2)	0.21(2)	0.10(1)	–0.08(2)	0.01(1)	–0.04(2)
C(39)	4*a*	1.611(3)	1.090(2)	0.503(1)	0.27(3)	0.27(3)	0.13(2)	–0.15(3)	–0.08(2)	0.10(2)
C(40)	4*a*	1.661(3)	1.116(2)	0.447(2)	0.24(4)	0.16(2)	0.60(7)	–0.03(2)	–0.27(4)	–0.01(4)
C(41)	4*a*	1.609(2)	1.183(2)	0.443(1)	0.11(2)	0.22(3)	0.20(2)	–0.07(2)	–0.00(2)	–0.06(2)

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Crystal structure of nitrato-*O*,*O*′-bis(1,10-phenanthroline)nitritolead(II), $Pb(phen)_2(NO_3)_{1.5}(NO_2)_{0.5}$

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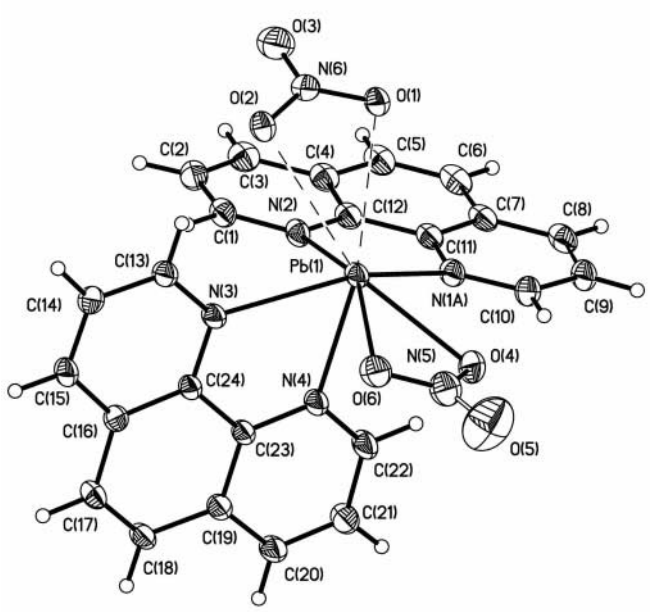

Abstract

$C_{24}H_{16}N_6O_{5.50}Pb$, triclinic, $P\bar{1}$ (No. 2), a = 7.805(2) Å, b = 11.332(2) Å, c = 13.184(3) Å, α = 94.934(3)°, β = 99.471(3)°, γ = 101.504(3)°, V = 1118.6 Å^3, Z = 2, $R_{gt}(F)$ = 0.028, $wR_{ref}(F^2)$ = 0.066, T = 110 K.

Source of material

The $[Pb(phen)_2(NO_3)_{1.5}(NO_2)_{0.5}]$ complex was prepared by the branch tube method: 1,10-phenanthroline (0.4 g, 2 mmol) was placed in one arm of the branched tube and a mixture of lead (II) acetate (0.36 g, 1 mmol), sodium nitrate (0.085 g, 1 mmol) and sodium nitrite (0.069 g, 1 mmol) in the other one. Methanol was carefully added to fill both arms, then the tube was sealed and the ligand-containing arm immersed in a bath at 333 K while the other was at ambient temperature. After 5 days, yellow crystals (mp 550 K) were deposited in the cooler arm. They were filtered off, washed with acetone and ether and air dried (0.499 g; yield 70%). Analysis (except for Pb): found – C 41.92%, H 2.23%, N 12.88%; calculated for $C_{24}H_{16}N_6O_{5.5}Pb$ – C 42.10%, H 2.34%, N 12.28 %.

Discussion

The interaction of divalent lead with biological materials has been studied extensively. Recent structural studies of lead(II) compounds [1] in particular have provided a basis for the evidence for coordination sphere distortions, which may be a consequence of the presence of stereoactive electron pairs. In relation to earlier work on mixed-anions complexes [2,3], it becomes as little surprise to find further examples of such complexes. We have particularly interested in the structural properties of the mixed-anions Pb(II) complexes.

The title compound showed the complex in the solid state to be a monomeric species. The Pb-atom is unsymmetrically six-coordinated by four nitrogen atoms of two 1,10-phenanthroline ligands and two oxygen atoms of NO_3^- anions. There are two crystallographically independent nitrate anions in the structure, one of them coordinates the lead atom and the other shares one crystallographic position with the nitrite anion. Final refinement showed that 50% of these positions in the crystal are occupied by nitrate and 50% of positions contain nitrite anions. The arrangement of two 1 ,10-phenanthroline ligands and NO_3^- anion suggest a gap in coordination geometry around the metal ion, occupied possibly by a stereoactive lone pair of electrons on lead(II). The observed shortening of the Pb—N bond on the side of Pb(II) ion opposite to the position of the putative lone pair (2.475 Å and 2.572 Å compared with 2.612 Å and 2.623 Å, adjacent to the lone pair) supports the presence of this feature. The coordination around the lead atom is hemidirected (i.e. the bonds to ligand atoms are distributed through only part of an encompassing globe) with a significant gap *trans* to the cleating 1,10-phenanthroline ligands. Hence, the geometry of the nearest coordination environment of lead atom is likely caused by the geometrical constraints of coordinated 1,10-phenantroline and nitrate anion and by the influence of a stereochemically active lone pair of electrons.

There are two lead(II) compounds related to the title compound, namely $Pb(phen)_2(NO_3)_2$] [4] and $[Pb(phen)_2(ClO_4)_2]$ [4]. The striking similarity among them is that the lone pair in the three compounds is active and also that they are monomeric species.

Table 1. Data collection and handling.

Crystal:	yellow prism, size 0.2 × 0.3 × 0.5 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	75.96 cm^{-1}
Diffractometer, scan mode:	Bruker SMART 1000 CCD, φ/ω
$2\theta_{max}$:	52.04°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	8791, 4275
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 4060
$N(param)_{refined}$:	334
Programs:	SHELXTL-plus [4], SHELXTL-97 [5], SADABS [6]

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Table 2. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	*x*	*y*	*z*	U_{iso}
H(1A)	2*i*	–0.0173	0.6633	0.0823	0.048
H(2A)	2*i*	–0.3162	0.5694	0.0534	0.051
H(3A)	2*i*	–0.4495	0.5173	0.1926	0.052
H(5A)	2*i*	–0.4261	0.5245	0.3861	0.053
H(6A)	2*i*	–0.2556	0.5763	0.5492	0.055
H(8A)	2*i*	0.0421	0.6656	0.6648	0.055
H(9A)	2*i*	0.3341	0.7648	0.6785	0.061
H(10A)	2*i*	0.4513	0.8042	0.5299	0.056
H(13A)	2*i*	0.3616	0.6619	0.0036	0.049
H(14A)	2*i*	0.3364	0.7315	–0.1575	0.051
H(15A)	2*i*	0.2714	0.9215	–0.1742	0.048
H(17A)	2*i*	0.2042	1.1126	–0.0895	0.046
H(18A)	2*i*	0.1691	1.2210	0.0556	0.046
H(20A)	2*i*	0.1696	1.2407	0.2484	0.057
H(21A)	2*i*	0.2097	1.1599	0.4020	0.067
H(22A)	2*i*	0.2868	0.9711	0.4053	0.066

Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	Occ.	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pb(1)	2*i*		0.37628(2)	0.74140(1)	0.26474(1)	0.0541(1)	0.0321(1)	0.02503(9)	0.01598(7)	0.01369(7)	0.00772(6)
C(1)	2*i*		–0.0714(7)	0.6453(4)	0.1403(3)	0.054(3)	0.042(2)	0.031(2)	0.021(2)	0.014(2)	0.007(2)
C(2)	2*i*		–0.2498(7)	0.5880(4)	0.1221(4)	0.053(3)	0.044(2)	0.036(2)	0.022(2)	0.010(2)	0.003(2)
C(3)	2*i*		–0.3283(7)	0.5588(4)	0.2036(4)	0.047(3)	0.043(2)	0.050(3)	0.025(2)	0.015(2)	0.005(2)
C(4)	2*i*		–0.2278(7)	0.5910(4)	0.3055(4)	0.050(3)	0.040(2)	0.039(2)	0.024(2)	0.015(2)	0.008(2)
C(5)	2*i*		–0.3043(7)	0.5639(5)	0.3944(4)	0.052(3)	0.046(3)	0.045(3)	0.024(2)	0.022(2)	0.011(2)
C(6)	2*i*		–0.2034(7)	0.5946(4)	0.4907(4)	0.060(3)	0.047(3)	0.046(3)	0.028(2)	0.028(2)	0.018(2)
C(7)	2*i*		–0.0227(7)	0.6530(4)	0.5054(3)	0.065(3)	0.035(2)	0.031(2)	0.024(2)	0.021(2)	0.010(2)
C(8)	2*i*		0.0882(8)	0.6844(4)	0.6043(4)	0.074(4)	0.043(3)	0.034(2)	0.025(2)	0.026(2)	0.012(2)
C(9)	2*i*		0.2599(9)	0.7414(5)	0.6122(4)	0.084(4)	0.050(3)	0.023(2)	0.020(3)	0.016(2)	0.006(2)
C(10)	2*i*		0.3293(8)	0.7661(5)	0.5230(3)	0.068(3)	0.045(3)	0.027(2)	0.011(2)	0.011(2)	0.006(2)
C(11)	2*i*		0.0574(7)	0.6816(4)	0.4188(3)	0.056(3)	0.034(2)	0.031(2)	0.021(2)	0.018(2)	0.009(2)
C(12)	2*i*		–0.0513(6)	0.6502(4)	0.3166(3)	0.052(3)	0.033(2)	0.030(2)	0.022(2)	0.015(2)	0.005(2)
C(13)	2*i*		0.3367(7)	0.7400(4)	–0.0024(3)	0.066(3)	0.035(2)	0.027(2)	0.015(2)	0.014(2)	0.005(2)
C(14)	2*i*		0.3211(7)	0.7805(4)	–0.0989(3)	0.064(3)	0.040(2)	0.026(2)	0.010(2)	0.015(2)	0.002(2)
C(15)	2*i*		0.2832(7)	0.8922(4)	–0.1085(3)	0.054(3)	0.044(2)	0.026(2)	0.012(2)	0.012(2)	0.012(2)
C(16)	2*i*		0.2621(6)	0.9631(4)	–0.0210(3)	0.038(2)	0.036(2)	0.028(2)	0.005(2)	0.011(2)	0.007(2)
C(17)	2*i*		0.2186(6)	1.0803(4)	–0.0253(4)	0.047(3)	0.040(2)	0.035(2)	0.014(2)	0.013(2)	0.017(2)
C(18)	2*i*		0.1984(7)	1.1439(4)	0.0602(3)	0.051(3)	0.034(2)	0.036(2)	0.014(2)	0.013(2)	0.013(2)
C(19)	2*i*		0.2197(6)	1.0993(4)	0.1584(3)	0.045(3)	0.033(2)	0.033(2)	0.013(2)	0.009(2)	0.008(2)
C(20)	2*i*		0.1998(8)	1.1637(4)	0.2501(4)	0.074(4)	0.036(2)	0.036(2)	0.026(2)	0.010(2)	0.004(2)
C(21)	2*i*		0.2234(9)	1.1167(5)	0.3398(4)	0.102(5)	0.045(3)	0.030(2)	0.037(3)	0.016(3)	0.004(2)
C(22)	2*i*		0.2686(9)	1.0031(5)	0.3410(4)	0.106(5)	0.042(3)	0.026(2)	0.036(3)	0.013(3)	0.006(2)
C(23)	2*i*		0.2620(6)	0.9847(4)	0.1653(3)	0.041(2)	0.030(2)	0.027(2)	0.008(2)	0.007(2)	0.009(2)
C(24)	2*i*		0.2815(6)	0.9157(4)	0.0737(3)	0.039(2)	0.031(2)	0.026(2)	0.008(2)	0.009(2)	0.008(2)
O(1)	2*i*		0.2482(5)	0.4737(3)	0.2723(2)	0.063(2)	0.042(2)	0.030(2)	0.011(2)	0.011(2)	0.009(1)
O(2)	2*i*		0.2467(5)	0.5126(3)	0.1155(2)	0.058(2)	0.048(2)	0.031(2)	0.011(2)	0.013(2)	0.012(1)
O(3)	2*i*		0.0344(6)	0.3824(4)	0.1519(4)	0.069(3)	0.053(2)	0.075(3)	0.013(2)	0.008(2)	0.011(2)
O(4)	2*i*		0.6139(5)	0.8841(3)	0.4095(3)	0.068(2)	0.053(2)	0.030(2)	0.009(2)	0.013(2)	0.008(2)
O(5)	2*i*	0.50	0.882(2)	0.972(1)	0.397(1)	0.083(8)	0.14(1)	0.12(1)	–0.020(8)	0.039(8)	–0.008(9)
O(6)	2*i*		0.6838(6)	0.8910(3)	0.2597(3)	0.088(3)	0.052(2)	0.036(2)	0.008(2)	0.028(2)	0.013(2)
N(1)	2*i*		0.2285(6)	0.7376(3)	0.4288(3)	0.057(2)	0.039(2)	0.027(2)	0.016(2)	0.015(2)	0.007(2)
N(2)	2*i*		0.0281(5)	0.6764(3)	0.2343(3)	0.046(2)	0.039(2)	0.028(2)	0.020(2)	0.010(2)	0.008(1)
N(3)	2*i*		0.3185(6)	0.8051(3)	0.0817(3)	0.058(2)	0.031(2)	0.029(2)	0.013(2)	0.013(2)	0.008(1)
N(4)	2*i*		0.2869(6)	0.9386(3)	0.2569(3)	0.064(3)	0.035(2)	0.026(2)	0.018(2)	0.010(2)	0.007(1)
N(5)	2*i*		0.7285(8)	0.9180(5)	0.3560(4)	0.082(4)	0.058(3)	0.044(3)	0.009(3)	0.020(3)	0.013(2)
N(6)	2*i*		0.1796(5)	0.4521(3)	0.1787(3)	0.039(2)	0.035(2)	0.040(2)	0.009(2)	0.010(2)	0.005(2)

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Crystal structure of 4-(3-chlorophenyl)-1-[4-(4-oxoquinazolin-3(4*H*)-yl)-butyl]piperazin-1-ium chloride trihydrate, $(C_{22}H_{26}ClN_4O)Cl \cdot 3H_2O$

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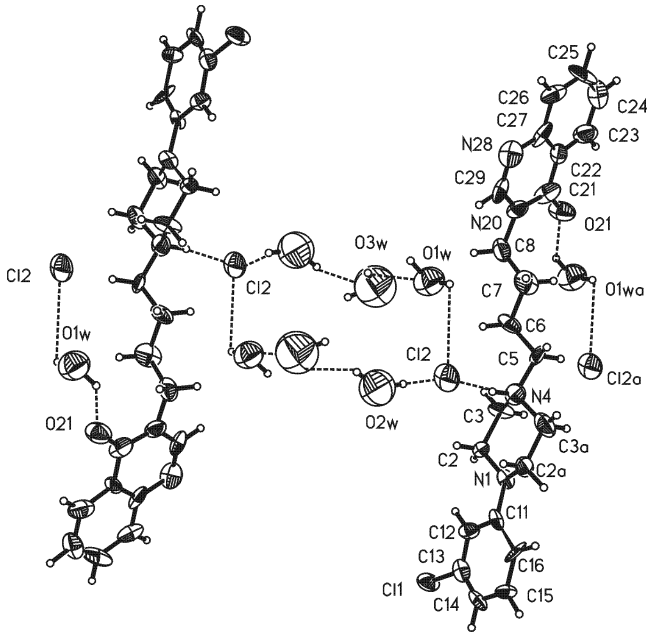

Abstract

$C_{22}H_{32}Cl_2N_4O_4$, triclinic, $P\bar{1}$ (No. 2), a = 7.081(1) Å, b = 13.247(3) Å, c = 13.923(3) Å, α = 102.90(3)°, β = 96.90(3)°, γ = 98.36(3)°, V = 1243.7 Å^3, Z = 2, $R_{gt}(F)$ = 0.066, $wR_{ref}(F^2)$ = 0.241, T = 293 K.

Source of material

The synthesis of the title compound has been described previously [1] as a part of our research program focused on serotonine $5HT_{1A}$ receptor ligands. The crystals for X-ray studies were obtained from 1-propanole : acetone (2 : 1) mixture by slow evaporation. As for all arylpiperazines of our interest, most of the obtained samples have been classified as plates of amorphous glass. Due to this kind of crystals, a very high quality measurements on a single-crystal diffractometer could not be performed.

Discussion

As a subsequent part of our research on long chain arylpiperazines as serotonin $5HT_{1A}$ and $5HT_{1A}$ receptor ligands, we now investigate the crystal structure of the title compound, which showed a distinct anxiolytic-like activity [1]. In functional *in vivo* studies it revealed an antagonistic activity at postsynaptic $5HT_{1A}$ receptors and behaved as agonist at presynaptic ones. This dual $5HT_{1A}/5HT_{2A}$ receptor ligand contains a flexible four methylene groups spacer, linking arylpiperazine and lactame moieties, and is structurally related to buspirone – approved anxiolytic drug [1]. The independent unit of the crystal is composed of the protonated main molecule, Cl^- ion, and three water moieties. As in previously studied structures of potential $5HT_{1A}$ and $5HT_{2A}$ receptor ligands [2-6], the main molecule incorporates two border cyclic moieties – arylpiperazine and quinazolinone – linked via butyric four-carbons aliphatic spacer. Both border rings – phenyl from arylpiperazine and quinazolinone – are planar within experimental error but definitely not coplanar. They are slightly inclined to each other at 4.1(2)°. The border cyclic moieties are almost perpendicular with dihedral angle of 79.3(2)°. The extended spacer adopts *trans-trans-trans-trans-trans* conformation. Ion $Cl2^-$ interacts with nitrogen from *chair*-conformed piperazine via H-bond as follows: N4–H4···Cl2 = 3.049(5) °A. In most of the studied derivatives (mainly arylopiperazines) with prospective activities to $5HT_{1A}$ and $5HT_{2A}$ receptors [2-5], one or two water molecules were usually localised. In the present structure, three water molecules were identified filling the space between long and flexible molecules in triclinic unit. However, respective hydrogen atoms found from $\Delta\rho$ map, were unquestionably located at just one oxygen atom, namely O1w. Remaining two atoms (O2w and O3w) are strongly disordered, being refined with isotropic temperature factors. Moreover, H atoms given in the figure (and in the Table 2) are only in roughly estimated positions. Merely, one water molecule with O1w atom is attached to the main molecule d(O1w–H1w1···O21^i) = 2.804(7) Å, i = (–1+x, y, z), via hydrogen bond. The hydrochlorides of the title compound are combined into infinite chain by the system of the following H-bonds net, involving Cl2 ion and all water oxygens: d(O1w–H1w2···Cl2) = 3.215 Å, d(O2w(H)···Cl1) = 3.259 Å, d(O3w(H)···O1w) = 2.789 Å, d(O2w(H)···O3w^{ii}) = 3.022 Å, ii = (–1–x, –y, –1–z).

Table 1. Data collection and handling.

Crystal:	colorless prism, size 0.2 × 0.25 × 0.3 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	2.95 cm^{-1}
Diffractometer, scan mode:	KM-4 CCD, ω
$2\theta_{max}$:	50°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	8762, 4381
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 1684
$N(param)_{refined}$:	280
Programs:	SHELXS-97 [7], SHELXL-97[8], SHELXTL-PC [9]

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Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(2B)	2*i*	0.0813	0.3420	–0.2352	0.067
H(2A)	2*i*	0.2799	0.3300	–0.1819	0.067
H(3B)	2*i*	0.4206	0.3605	–0.3148	0.071
H(3A)	2*i*	0.2503	0.2663	–0.3548	0.071
H(4)	2*i*	0.0644	0.3817	–0.4008	0.080
H(2D)	2*i*	0.2564	0.6133	–0.2086	0.086
H(2C)	2*i*	0.0694	0.5304	–0.2535	0.086
H(3D)	2*i*	0.2239	0.5540	–0.3878	0.099
H(3C)	2*i*	0.4092	0.5277	–0.3336	0.099
H(5B)	2*i*	0.4018	0.3994	–0.4867	0.073
H(5A)	2*i*	0.2059	0.4234	–0.5315	0.073
H(6B)	2*i*	0.0751	0.2375	–0.5360	0.074
H(6A)	2*i*	0.2903	0.2226	–0.5263	0.074
H(7B)	2*i*	0.3187	0.2861	–0.6716	0.101
H(7A)	2*i*	0.1000	0.2929	–0.6828	0.101
H(8B)	2*i*	0.2452	0.1032	–0.7036	0.085
H(8A)	2*i*	0.0255	0.1067	–0.7052	0.085

Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
H(12)	2*i*	0.2412	0.3713	–0.0463	0.059
H(14)	2*i*	0.2721	0.6029	0.1991	0.063
H(15)	2*i*	0.2790	0.7259	0.1022	0.067
H(16)	2*i*	0.2640	0.6744	–0.0696	0.083
H(23)	2*i*	0.5259	0.1078	–1.0010	0.096
H(24)	2*i*	0.4729	0.0954	–1.1765	0.091
H(25)	2*i*	0.1695	0.1033	–1.2554	0.101
H(26)	2*i*	–0.0940	0.1235	–1.1631	0.084
H(29)	2*i*	–0.1575	0.1419	–0.8430	0.075
H(1W1)	2*i*	–0.2831	0.2346	–0.6567	0.150
H(1W2)	2*i*	–0.4335	0.1399	–0.6948	0.150
O(2W)	2*i*	–0.287(1)	0.1507(6)	–0.3479(6)	0.156(3)
H(2W1)	2*i*	–0.1421	0.1605	–0.3571	0.233
H(2W2)	2*i*	–0.4185	0.1213	–0.3873	0.233
O(3W)	2*i*	–0.316(2)	–0.0168(8)	–0.5833(8)	0.203(4)
H(3W1)	2*i*	–0.4286	–0.0022	–0.6255	0.304
H(3W2)	2*i*	–0.4051	–0.0520	–0.5449	0.304

Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cl(1)	2*i*	0.2564(3)	0.3913(1)	0.1585(1)	0.084(1)	0.055(1)	0.0338(9)	0.0120(9)	0.0156(8)	0.0179(7)
Cl(2)	2*i*	–0.2375(2)	0.3531(2)	–0.4402(1)	0.038(1)	0.103(2)	0.082(1)	0.019(1)	0.0148(9)	0.021(1)
N(1)	2*i*	0.2647(7)	0.4758(4)	–0.1797(3)	0.061(3)	0.037(3)	0.029(3)	0.005(2)	0.007(2)	0.030(2)
C(2)	2*i*	0.2183(9)	0.3660(4)	–0.2260(4)	0.056(4)	0.037(4)	0.030(3)	–0.013(3)	0.007(3)	0.001(3)
C(3)	2*i*	0.283(1)	0.3406(4)	–0.3252(4)	0.092(5)	0.028(3)	0.036(3)	0.044(3)	0.028(3)	0.004(3)
N(4)	2*i*	0.2028(7)	0.3975(4)	–0.3936(4)	0.039(3)	0.055(4)	0.062(4)	0.007(3)	0.018(3)	0.000(3)
C(2A)	2*i*	0.208(1)	0.5408(5)	–0.2417(5)	0.082(5)	0.027(3)	0.062(4)	–0.001(3)	0.041(4)	0.000(3)
C(3A)	2*i*	0.270(1)	0.5127(6)	–0.3447(5)	0.047(4)	0.099(6)	0.057(4)	0.006(4)	0.025(3)	0.026(4)
C(5)	2*i*	0.2639(8)	0.3802(5)	–0.4939(4)	0.025(3)	0.041(4)	0.060(4)	–0.014(3)	0.016(3)	–0.019(3)
C(6)	2*i*	0.2009(9)	0.2636(5)	–0.5488(4)	0.045(4)	0.086(5)	0.027(3)	0.022(4)	0.008(3)	0.028(3)
C(7)	2*i*	0.195(1)	0.2550(5)	–0.6600(5)	0.113(6)	0.037(4)	0.064(5)	0.019(4)	0.026(4)	0.027(3)
C(8)	2*i*	0.144(1)	0.1402(5)	–0.7204(5)	0.061(4)	0.056(4)	0.060(4)	0.001(3)	0.022(3)	0.025(3)
C(11)	2*i*	0.2558(7)	0.5152(4)	–0.0789(4)	0.031(3)	0.042(3)	0.033(3)	0.009(3)	0.006(2)	0.034(3)
C(12)	2*i*	0.2522(7)	0.4454(5)	–0.0182(4)	0.034(3)	0.042(4)	0.038(3)	0.015(3)	0.006(3)	–0.003(3)
C(13)	2*i*	0.2624(8)	0.4808(5)	0.0849(5)	0.031(3)	0.059(4)	0.049(4)	0.008(3)	0.005(3)	0.028(3)
C(14)	2*i*	0.2666(7)	0.5818(5)	0.1281(4)	0.028(3)	0.073(5)	0.034(3)	0.014(3)	0.017(3)	0.023(3)
C(15)	2*i*	0.2736(8)	0.6529(5)	0.0713(4)	0.054(4)	0.041(4)	0.032(3)	0.010(3)	0.013(3)	–0.009(3)
C(16)	2*i*	0.2650(9)	0.6234(5)	–0.0304(5)	0.057(4)	0.030(4)	0.051(4)	–0.022(3)	–0.021(3)	–0.011(3)
N(20)	2*i*	0.1237(7)	0.1379(4)	–0.8310(3)	0.050(3)	0.035(3)	0.043(3)	0.005(2)	0.004(3)	–0.006(2)
O(21)	2*i*	0.4484(7)	0.1374(4)	–0.8275(3)	0.057(3)	0.102(4)	0.042(3)	0.026(3)	0.005(2)	0.014(3)
C(21)	2*i*	0.2879(9)	0.1335(5)	–0.8749(5)	0.031(4)	0.063(5)	0.066(5)	0.020(3)	–0.001(4)	–0.021(4)
C(22)	2*i*	0.252(1)	0.1254(5)	–0.9801(5)	0.064(5)	0.037(4)	0.056(4)	–0.009(3)	0.044(4)	–0.018(3)
C(23)	2*i*	0.401(1)	0.1117(5)	–1.0340(5)	0.090(6)	0.047(4)	0.045(4)	0.004(4)	0.004(4)	–0.001(3)
C(24)	2*i*	0.370(1)	0.1041(5)	–1.1379(6)	0.063(5)	0.038(4)	0.096(6)	0.025(4)	0.043(4)	0.020(4)
C(25)	2*i*	0.192(1)	0.1088(5)	–1.1849(5)	0.128(7)	0.066(5)	0.028(3)	0.041(5)	0.032(4)	0.029(3)
C(26)	2*i*	0.033(1)	0.1204(5)	–1.1316(5)	0.076(5)	0.035(4)	0.043(4)	0.006(3)	–0.017(4)	0.000(3)
C(27)	2*i*	0.0686(8)	0.1285(4)	–1.0280(5)	0.025(3)	0.023(3)	0.083(5)	0.000(2)	–0.005(3)	–0.011(3)
N(28)	2*i*	–0.0884(7)	0.1333(4)	–0.9749(5)	0.040(3)	0.067(4)	0.078(4)	0.018(3)	–0.003(3)	0.028(3)
C(29)	2*i*	–0.0521(9)	0.1376(4)	–0.8802(5)	0.040(4)	0.029(3)	0.075(5)	–0.011(3)	–0.003(4)	0.018(3)
O(1W)	2*i*	–0.3038(8)	0.1691(5)	–0.6464(4)	0.095(4)	0.102(5)	0.094(4)	0.017(4)	0.005(3)	0.014(4)

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Crystal structure of *N*-(2,2-dimethoxyethyl)-*N′*-(trifluoroacetyl)-phenylalanyl-dehydrophenylalaninamide hydrate, $C_{24}H_{26}N_3O_5F_3 \cdot H_2O$, *a precursor of intramolecular double cyclization into imidazolopyrazinone*

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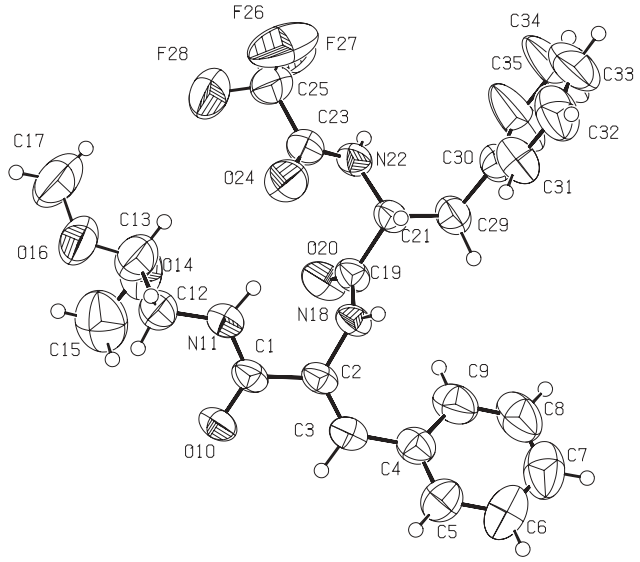

Abstract

$C_{24}H_{28}F_3N_3O_6$, monoclinic, $P12_1/c1$ (No. 14), a = 9.677(4) Å, b = 11.005(5) Å, c = 24.858(7) Å, β = 92.12°, V = 2645.5 Å^3, Z = 4, $R_{gt}(F)$ = 0.064, $wR_{ref}(F^2)$ = 0.199, T = 293 K.

Source of material

The titled compound was obtained by coupling *N′*-(trifluoroacetyl)-phenylalanyl-dehydrophenylalanine with aminoacetaldehyde dimethylacetal in the usual conditions of peptide synthesis [1]. Chromatographic purification on silica gel (elution with CH_2Cl_2/ EtOAc 75/25; yield 59%) furnished pure compound as a white solid. Analysis: calc. for $C_{24}H_{26}F_3N_3O_5$ – C, 58.41%; H, 5.31%; N, 8.25 %; found – C, 57.99%; H, 5.29%; N, 8.40%. Recrystallization from $CHCl_3$ by slow evaporation, gave the sample presently analyzed by X-ray diffraction (white crystal; mp 334.5 K – 335.5 K) .

Experimental details

The H atoms of the CH_2, CH_3 and aromatic groups were calculated. Those of the CH, NH and water molecule were located from difference Fourier maps. The H atoms were refined with a common isotropic temperature factor (U_{iso} = 0.127(2) Å^2). The CF_3 and one of the methoxy (C16–O17) groups are disordered. Two positions of these groups were localized and refined. At the end of the refinement, their site occupation factors converge to 0.66 for position A of the trifluoromethyl group and to 0.78 for the major position of the C16–O17 methoxy. Constraints were applied to the bond lengths for these two disordered groups.

Discussion

Recently, we demonstrated that imidazolopyrazinone derivatives, structurally related to coelenterazine (luciferin) [2], are endowed with excellent antioxidative properties, and protect cells [3] and animals [4] against damages induced by reactive oxygen species (ROS). For a potential development as drugs, we searched for different synthetic routes towards such molecules. One convergent approach was based on a biomimetic route [5] involving a pseudo-dehydrotripeptide as precursor [1] and its cyclization via a double intramolecular dehydration. The titled compound is a fully protected precursor of cyclization (masked aldehyde and amine functions).

The crystal structure showed the *Z* configuration of the C=C double bond, the torsion angle ∠N18–C2–C3–C4 being 4°. On the other hand, the view of the molecule showed the parallel orientation of the two chains geminally fixed on this double bond, thus favouring intramolecular interaction. Two intramolecular H-bonds involving N11, N18 and O24 help for this conformation. The intramolecular interaction is indeed favoured as after treatment of the titled compound with trimethylsilyliodide (deprotection of acetal), and then with K_2CO_3 in aqueous acetonitrile (deprotection of trifluoroacetamide), the corresponding imidazolopyrazinone was smoothly formed [1]. There are a total of six hydrogen bonds, the first two being intramolecular, the last three involving the co-crystallized water molecule.

Table 1. Data collection and handling.

Crystal:	white parallelepiped, size 0.3 × 0.3 × 0.4 mm
Wavelength:	Mo K_α radiation (0.71069 Å)
μ:	1.06 cm^{-1}
Diffractometer, scan mode:	MAR345, 100 images, $\Delta\phi$ = 3°
$2\theta_{max}$:	52.74°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	30813, 5285
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 4174
$N(param)_{refined}$:	407
Programs:	SHELXS-97 [6], SHELXL-97 [7], PLATON [8]

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Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	Occ.	*x*	*y*	*z*	U_{iso}
H(5)	4*e*		0.3519	0.1832	0.1769	0.127(2)
H(6)	4*e*		0.5500	0.074	0.1600	0.127
H(7)	4*e*		0.6386	–0.0592	0.2233	0.127
H(8)	4*e*		0.5335	–0.0817	0.3038	0.127
H(9)	4*e*		0.3326	0.0227	0.3207	0.127
H(13)	4*e*		–0.3313	0.1457	0.3786	0.127
H(15A)	4*e*		–0.1614	0.4509	0.4239	0.127
H(15B)	4*e*		–0.3151	0.4561	0.4018	0.127
H(15C)	4*e*		–0.1951	0.4356	0.3621	0.127
H(17A)	4*e*	0.785(5)	–0.6241	0.2714	0.4162	0.127
H(17B)	4*e*	0.785	–0.4822	0.2733	0.4487	0.127
H(17C)	4*e*	0.785	–0.5353	0.1526	0.4216	0.127
H(17D)	4*e*	0.215	–0.4768	0.0927	0.4510	0.127
H(17E)	4*e*	0.215	–0.5398	0.2130	0.4268	0.127
H(17F)	4*e*	0.215	–0.4037	0.2174	0.4629	0.127

Table 2. Continued.

Atom	Site	Occ.	*x*	*y*	*z*	U_{iso}
H(31)	4*e*		0.1293	–0.3686	0.3231	0.127
H(32)	4*e*		0.1169	–0.5745	0.3327	0.127
H(33)	4*e*		0.1529	–0.6611	0.4147	0.127
H(34)	4*e*		0.2253	–0.5413	0.4851	0.127
H(35)	4*e*		0.2447	–0.3331	0.4754	0.127
H(3)	4*e*		0.181(3)	0.258(3)	0.241(1)	0.127
H(11)	4*e*		–0.156(3)	0.091(3)	0.315(1)	0.127
H(12A)	4*e*		–0.279(3)	0.314(4)	0.297(1)	0.127
H(12B)	4*e*		–0.368(3)	0.195(3)	0.288(2)	0.127
H(18)	4*e*		0.060(3)	–0.044(3)	0.283(1)	0.127
H(21)	4*e*		0.017(3)	–0.181(3)	0.339(1)	0.127
H(22)	4*e*		–0.009(3)	–0.159(3)	0.451(2)	0.127
H(29A)	4*e*		0.258(3)	–0.170(3)	0.361(2)	0.127
H(29B)	4*e*		0.221(3)	–0.147(3)	0.423(1)	0.127
H(101)	4*e*		0.131(3)	0.694(3)	0.042(1)	0.127

Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	Occ.	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	4*e*		–0.0501(2)	0.2186(1)	0.28409(6)	0.081(1)	0.0460(8)	0.0419(7)	0.0027(7)	0.0021(7)	0.0038(6)
C(2)	4*e*		0.0754(2)	0.1390(1)	0.28228(6)	0.076(1)	0.0416(7)	0.0402(7)	–0.0021(6)	0.0012(7)	0.0011(5)
C(3)	4*e*		0.1866(2)	0.1766(2)	0.25664(7)	0.075(1)	0.0512(9)	0.0548(9)	–0.0047(7)	–0.0003(8)	0.0045(7)
C(4)	4*e*		0.3167(2)	0.1113(2)	0.24911(8)	0.068(1)	0.058(1)	0.074(1)	–0.0087(8)	–0.0046(8)	0.0004(8)
C(5)	4*e*		0.3860(2)	0.1278(2)	0.2024(1)	0.079(1)	0.095(2)	0.075(1)	–0.001(1)	0.005(1)	–0.006(1)
C(6)	4*e*		0.5061(3)	0.0634(3)	0.1923(1)	0.077(1)	0.140(3)	0.107(2)	0.007(2)	0.009(1)	–0.032(2)
C(7)	4*e*		0.5591(3)	–0.0152(3)	0.2301(2)	0.075(2)	0.102(2)	0.177(3)	0.007(1)	–0.012(2)	–0.026(2)
C(8)	4*e*		0.4954(3)	–0.0295(3)	0.2778(2)	0.076(2)	0.091(2)	0.181(3)	–0.002(1)	–0.032(2)	0.030(2)
C(9)	4*e*		0.3748(2)	0.0329(2)	0.2880(1)	0.072(1)	0.085(2)	0.112(2)	–0.010(1)	–0.017(1)	0.028(1)
O(10)	4*e*		–0.0468(2)	0.3236(1)	0.26655(6)	0.103(1)	0.0524(7)	0.0788(9)	0.0119(6)	0.0203(7)	0.0217(6)
N(11)	4*e*		–0.1630(2)	0.1702(2)	0.30425(6)	0.0720(9)	0.0581(8)	0.0639(9)	0.0027(7)	0.0040(7)	0.0117(7)
C(12)	4*e*		–0.2911(2)	0.2372(2)	0.31083(9)	0.073(1)	0.085(1)	0.068(1)	0.011(1)	0.0001(9)	0.012(1)
C(13)	4*e*		–0.3309(3)	0.2318(3)	0.3686(1)	0.089(2)	0.142(3)	0.086(2)	0.026(2)	0.015(1)	0.022(2)
O(14)	4*e*		–0.2384(2)	0.2896(3)	0.40471(7)	0.133(2)	0.164(2)	0.066(1)	0.062(2)	–0.005(1)	0.003(1)
C(15)	4*e*		–0.2265(5)	0.4188(4)	0.3976(2)	0.156(3)	0.162(4)	0.121(3)	0.033(3)	–0.022(2)	0.001(3)
O(16A)	4*e*	0.785(5)	–0.4630(3)	0.2704(3)	0.3703(1)	0.091(2)	0.157(3)	0.120(2)	0.048(2)	0.036(1)	0.032(2)
C(17A)	4*e*	0.785	–0.5317(6)	0.2394(7)	0.4181(3)	0.134(4)	0.246(8)	0.171(5)	0.062(5)	0.084(4)	0.060(5)
O(16B)	4*e*	0.215	–0.379(1)	0.157(1)	0.3915(5)	0.18(1)	0.118(8)	0.120(8)	0.029(7)	0.073(8)	0.046(6)
C(17B)	4*e*	0.215	–0.456(2)	0.171(2)	0.4364(7)	0.10(1)	0.16(2)	0.12(1)	0.02(1)	0.026(9)	0.02(1)
N(18)	4*e*		0.0655(2)	0.0200(1)	0.30475(5)	0.0776(9)	0.0397(6)	0.0422(6)	–0.0002(6)	0.0037(6)	–0.0001(5)
C(19)	4*e*		0.0690(2)	–0.0011(1)	0.35796(6)	0.073(1)	0.0469(8)	0.0436(7)	0.0041(7)	0.0018(7)	0.0009(6)
O(20)	4*e*		0.0844(2)	0.0797(1)	0.39137(5)	0.124(1)	0.0547(7)	0.0457(6)	–0.0023(7)	0.0005(6)	–0.0059(5)
C(21)	4*e*		0.0540(2)	–0.1347(1)	0.37356(6)	0.070(1)	0.0471(8)	0.0472(8)	0.0055(7)	0.0045(7)	0.0057(6)
N(22)	4*e*		–0.0455(2)	–0.1473(1)	0.41589(6)	0.0728(9)	0.0577(8)	0.0479(7)	0.0075(6)	0.0049(6)	0.0113(6)
C(23)	4*e*		–0.1770(2)	–0.1262(2)	0.40340(8)	0.073(1)	0.069(1)	0.061(1)	0.0067(8)	0.0035(8)	0.0133(8)
O(24)	4*e*		–0.2223(2)	–0.0924(2)	0.35928(6)	0.0782(9)	0.118(1)	0.0723(9)	0.0114(8)	–0.0055(7)	0.0248(8)
C(25)	4*e*		–0.2786(3)	–0.1493(3)	0.4481(1)	0.081(2)	0.104(2)	0.090(2)	0.006(1)	0.019(1)	0.023(2)
F(26A)	4*e*	0.66(2)	–0.350(1)	–0.2460(9)	0.4378(3)	0.152(6)	0.185(8)	0.151(4)	–0.088(6)	0.053(4)	–0.015(4)
F(27A)	4*e*	0.66	–0.2227(5)	–0.1642(9)	0.4960(2)	0.113(2)	0.193(7)	0.069(2)	–0.012(3)	0.022(2)	0.037(3)
F(28A)	4*e*	0.66	–0.365(1)	–0.0564(8)	0.4525(4)	0.156(6)	0.180(6)	0.164(6)	0.082(5)	0.089(5)	0.059(5)
F(26B)	4*e*	0.34	–0.267(2)	–0.261(1)	0.465(1)	0.18(1)	0.16(1)	0.27(2)	0.04(1)	0.12(1)	0.13(2)
F(27B)	4*e*	0.34	–0.258(2)	–0.083(2)	0.4874(7)	0.20(2)	0.23(2)	0.111(9)	–0.04(1)	0.08(1)	–0.06(1)
F(28B)	4*e*	0.34	–0.4030(7)	–0.144(2)	0.4295(5)	0.072(3)	0.22(2)	0.158(7)	0.001(5)	0.025(3)	0.028(9)
C(29)	4*e*		0.1930(2)	–0.1900(2)	0.39135(9)	0.075(1)	0.061(1)	0.070(1)	0.0104(8)	0.0000(9)	0.0063(8)
C(30)	4*e*		0.1846(2)	–0.3265(2)	0.39854(8)	0.082(1)	0.063(1)	0.064(1)	0.0225(9)	0.0120(9)	0.0112(8)
C(31)	4*e*		0.1487(3)	–0.4024(2)	0.3569(1)	0.105(2)	0.066(1)	0.100(2)	0.006(1)	–0.019(1)	0.003(1)
C(32)	4*e*		0.1398(3)	–0.5265(3)	0.3625(2)	0.120(2)	0.070(2)	0.171(3)	0.006(1)	–0.011(2)	–0.015(2)
C(33)	4*e*		0.1638(6)	–0.5779(3)	0.4101(2)	0.274(6)	0.069(2)	0.171(4)	0.047(3)	0.079(4)	0.036(2)
C(34)	4*e*		0.2043(9)	–0.5061(4)	0.4517(2)	0.55(1)	0.104(3)	0.101(2)	0.130(5)	0.056(4)	0.048(2)
C(35)	4*e*		0.2155(6)	–0.3802(3)	0.4461(1)	0.383(7)	0.094(2)	0.068(2)	0.105(3)	–0.009(3)	0.005(1)
O(100)	4*e*		0.0712(2)	0.6492(2)	0.02191(6)	0.139(2)	0.144(2)	0.0515(8)	–0.055(1)	–0.0036(9)	–0.0017(9)

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Refinement of the crystal structure of dichloro-bis(pyridine-*N*)-copper(II), $C_{10}H_{10}Cl_2CuN_2$, *at 100 K*

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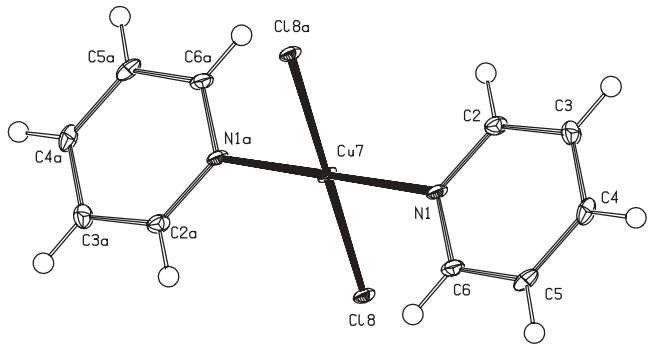

Abstract

$C_{10}H_{10}Cl_2CuN_2$, monoclinic, $P12_1/n1$ (No. 14), a = 3.7911(2) Å, b = 8.5205(3) Å, c = 16.9910(7) Å, β = 91.973(3)°, V = 548.5 Å^3, Z = 2, $R_{gt}(F)$ = 0.033, $wR_{ref}(F^2)$ = 0.086, T = 100 K.

Source of material

Crystals of the dichloro-bis(pyridine-*N*)-copper(II) complex were unexpectly formed during an experiment to synthesize lanthanide-containing copper-metallacrowns [1]. Lysine hydroxamic acid hydrochloride, L-LysHa · HCl (2 mmol) was dissolved in 50 mL of water in presence of 2 mmol of $Cu(OAc)_2 \cdot H_2O$. The deep green solution turned blue after adding 0.4 mmol of $La(NO_3)_3 \cdot 6H_2O$. The solvent was partially removed under reduced pressure and pyridine was added as a base. The solution was left to evaporate at room temperature. X-ray diffraction indicated that no crystals of a metallacrown were formed, but that the blue needle-like crystals are of dichloro-bis(pyridine-*N*)-copper(II).

Discussion

The crystal structure of this compound at room temperature was described first by Kabalkina [2] and later by Morosin [3]. The unit cell parameters at 100 K were refined on 3492 reflections and indicate a decrease of the cell volume by 1.8% as compared to room temperature [3]. The low temperature refinement resulted in a more accurate determination of the crystallographic parameters as illustrated for example by the lower $R_{gt}(F)$ value (0.033 compared to 0.052 in [3]) and the lower e.s.d. values.

The average e.s.d. on C—C and C–N bond lengths is 0.0035 Å and 0.0030 Å, respectively (compared to 0.010 Å and 0.008 Å in [3]), the e.s.d. on the Cu—Cl bond length is reduced from 0.002 Å in [3] to 0.0005 Å in this refinement.

The point group of the complex is C_{2h}, with a square planar coordination geometry for Cu and the pyridine rings in *trans* position. These ring makes an angle of 57.45(8)° with the Cu7—Cl8 bond. The packing is dominated by aromatic ring stacking interactions (distance between stacking pyridine rings is 5.903 Å).

Table 1. Data collection and handling.

Crystal:	blue needles, size 0.10 × 0.10 × 0.30 mm
Wavelength:	Cu K_α radiation (1.54178 Å)
μ:	70.01 cm^{-1}
Diffractometer, scan mode:	Bruker SMART 6000 CCD, ω/φ
$2\theta_{max}$:	141.62°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	4612, 1042
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 1010
$N(param)_{refined}$:	70
Programs:	SHELXS-97 [4], SHELXL-97 [5], PLATON [6]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(2)	4*e*	0.3644	0.0405	0.1689	0.013
H(3)	4*e*	0.3926	0.2302	0.2654	0.015
H(4)	4*e*	0.5781	0.4830	0.2336	0.015
H(5)	4*e*	0.7179	0.5378	0.1039	0.016
H(6)	4*e*	0.6691	0.3418	0.0109	0.013

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Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
N(1)	4*e*	0.5163(5)	0.1721(2)	0.0809(1)	0.014(1)	0.0042(9)	0.0083(9)	0.0010(7)	–0.0020(8)	0.0008(7)
C(2)	4*e*	0.4350(6)	0.1415(3)	0.1559(1)	0.014(1)	0.007(1)	0.010(1)	–0.0009(8)	–0.0016(9)	0.0000(8)
C(3)	4*e*	0.4526(7)	0.2546(3)	0.2142(1)	0.015(1)	0.013(1)	0.009(1)	0.0001(9)	0.0012(9)	–0.0030(9)
C(4)	4*e*	0.5614(7)	0.4053(3)	0.1952(2)	0.014(1)	0.010(1)	0.013(1)	0.0016(9)	–0.0015(9)	–0.0065(9)
C(5)	4*e*	0.6446(7)	0.4379(3)	0.1181(2)	0.016(1)	0.004(1)	0.019(1)	–0.0004(9)	–0.0003(9)	–0.0012(9)
C(6)	4*e*	0.6166(6)	0.3192(3)	0.0627(1)	0.015(1)	0.006(1)	0.012(1)	0.0004(9)	0.0001(9)	0.0024(9)
Cu(7)	2*b*	1/2	0	0	0.0166(3)	0.0022(3)	0.0061(3)	0.0020(2)	–0.0032(2)	–0.0020(2)
Cl(8)	4*e*	0.1081(1)	0.14445(6)	–0.07764(3)	0.0147(3)	0.0040(3)	0.0086(3)	0.0004(2)	–0.0023(2)	0.0005(2)

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Crystal structure of pentakispiperidyltantal(V), $Ta(NC_5H_{10})_5$

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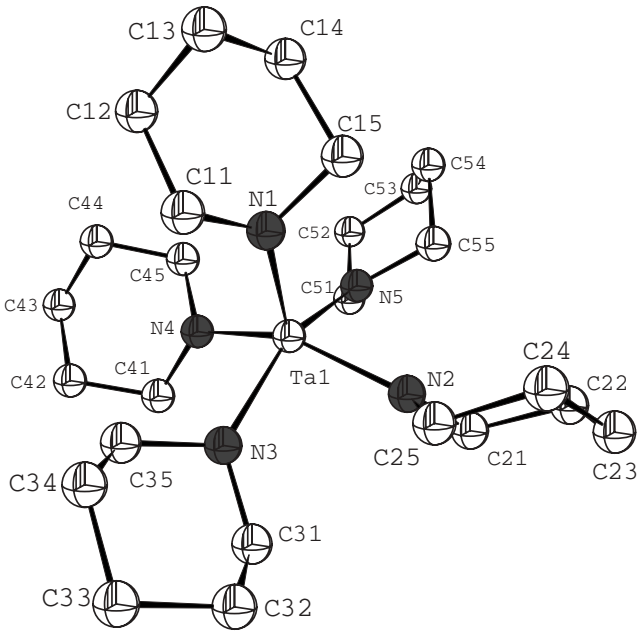

Abstract

$C_{25}H_{50}N_5Ta$, monoclinic, $P12_1/c1$ (No. 14), $a = 15.3542(9)$ Å, $b = 9.9150(6)$ Å, $c = 18.141(1)$ Å, $\beta = 108.109(1)°$, $V = 2624.9$ Å^3, $Z = 4$, $R_{gt(F)} = 0.053$, $wR_{ref(F^2)} = 0.142$, $T = 100$ K.

Source of material

Pentakispiperidyltantal(V) was obtained by reacting tantal pentachloride with lithiated piperidine in hexane [1]. Transparent red crystals were grown from hexane solution at 278 K. The compound is sensitive to air and moisture, so that it is to be handled under dry and oxygen-free argon.

Experimental details

All non-hydrogen atoms were refined anisotropically, hydrogen atoms were calculated isotropically with fixed positions.

Discussion

The coordination sphere of tantalum in $Ta(NC_5H_{10})_5$ is square pyramidal as it has been observed in $Ta[N(CH_3)_2]_5$ [2] and $Nb(NC_5H_{10})_5$ [3,4], the shortest distances are d(Ta—N1) = 197.5(4) pm, d(Ta—N2-5) in the range from 202.3(5) pm to 203.8(5) pm. The piperidine rings are in the common *armchair* conformation. Because of nitrogen-tantalum backbond interactions the nitrogen seeks for a trigonal planar coordination. Bond lengths are in good agreement with literature values [2,4].

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Table 1. Data collection and handling.

Crystal:	red transparent block, size 0.1 × 0.2 × 0.4 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	42.08 cm^{-1}
Diffractometer, scan mode:	Smart APEX (Bruker AXS), ω
$2\theta_{max}$:	70.42°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	40945, 11119
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 9332
$N(param)_{refined}$:	280
Programs:	SHELXS-97 [5], SHELXL-97 [6], DIAMOND [7]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(11A)	4*e*	0.8262	0.7485	–0.1002	0.156
H(11B)	4*e*	0.7620	0.6803	–0.0579	0.156
H(12A)	4*e*	0.9120	0.6363	0.0529	0.110
H(12B)	4*e*	0.8940	0.5392	–0.0198	0.110
H(13A)	4*e*	0.9609	0.7298	–0.0772	0.156
H(13B)	4*e*	1.0335	0.6428	–0.0130	0.156
H(14A)	4*e*	1.0487	0.8556	0.0469	0.201
H(14B)	4*e*	0.9804	0.7805	0.0825	0.201
H(15A)	4*e*	0.9152	1.0048	0.0192	0.078
H(15B)	4*e*	0.9063	0.9357	–0.0616	0.078
H(21A)	4*e*	0.6873	1.2249	0.0589	0.113
H(21B)	4*e*	0.6108	1.2444	–0.0208	0.113
H(22A)	4*e*	0.7045	1.4346	0.0023	0.127
H(22B)	4*e*	0.7923	1.3452	0.0151	0.127
H(23A)	4*e*	0.7561	1.4328	–0.1064	0.129
H(23B)	4*e*	0.6542	1.3836	–0.1262	0.129
H(24A)	4*e*	0.7302	1.2318	–0.1829	0.075
H(24B)	4*e*	0.8081	1.2111	–0.1036	0.075
H(25A)	4*e*	0.6233	1.1298	–0.1327	0.097
H(25B)	4*e*	0.7048	1.0298	–0.1243	0.097
H(31A)	4*e*	0.5346	1.0244	–0.0748	0.033
H(31B)	4*e*	0.4779	0.8979	–0.0651	0.033
H(32A)	4*e*	0.4362	0.9532	–0.1970	0.034
H(32B)	4*e*	0.5388	0.9461	–0.1957	0.034
H(33A)	4*e*	0.4704	0.7465	–0.2488	0.068
H(33B)	4*e*	0.4319	0.7230	–0.1790	0.068
H(34A)	4*e*	0.6199	0.7160	–0.1680	0.106
H(34B)	4*e*	0.5621	0.5897	–0.1594	0.106
H(35A)	4*e*	0.5437	0.6838	–0.0447	0.096
H(35B)	4*e*	0.6481	0.6627	–0.0349	0.096
H(41A)	4*e*	0.5690	0.7792	0.0732	0.078
H(41B)	4*e*	0.6125	0.7909	0.1635	0.078
H(42A)	4*e*	0.5560	0.5713	0.1364	0.096
H(42B)	4*e*	0.6086	0.5513	0.0757	0.096
H(43A)	4*e*	0.6911	0.5658	0.2383	0.142
H(43B)	4*e*	0.6905	0.4382	0.1868	0.142
H(44A)	4*e*	0.7854	0.5414	0.1292	0.144
H(44B)	4*e*	0.8311	0.5508	0.2194	0.144
H(45A)	4*e*	0.7828	0.7747	0.2191	0.164
H(45B)	4*e*	0.8402	0.7609	0.1615	0.164

Table 2. Continued.

Atom	Site	*x*	*y*	*z*	U_{iso}
H(51A)	4*e*	0.7398	0.9827	0.2066	0.072
H(51B)	4*e*	0.7594	1.1374	0.2045	0.072
H(52A)	4*e*	0.8560	1.0468	0.3190	0.074
H(52B)	4*e*	0.8940	0.9410	0.2723	0.074
H(53A)	4*e*	0.9996	1.1145	0.3086	0.204

Table 2. Continued.

Atom	Site	*x*	*y*	*z*	U_{iso}
H(53B)	4*e*	0.9232	1.2223	0.2714	0.204
H(54A)	4*e*	0.9805	1.0194	0.1838	0.298
H(54B)	4*e*	1.0045	1.1733	0.1818	0.298
H(55A)	4*e*	0.8425	1.2231	0.1294	0.236
H(55B)	4*e*	0.833	1.1310	0.0725	0.236

Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ta(1)	4*e*	0.72872(1)	0.92399(2)	0.032239(9)	0.01708(8)	0.01652(8)	0.01783(8)	0.00133(5)	0.00358(5)	–0.00361(5)
N(1)	4*e*	0.8256(3)	0.8438(5)	–0.0041(3)	0.029(2)	0.042(3)	0.029(2)	0.013(2)	0.009(2)	–0.006(2)
N(2)	4*e*	0.7016(3)	1.1046(4)	–0.0235(3)	0.020(2)	0.014(2)	0.056(3)	–0.000(1)	–0.006(2)	–0.001(2)
N(3)	4*e*	0.6105(3)	0.8576(4)	–0.0462(2)	0.037(2)	0.014(2)	0.021(2)	–0.004(1)	–0.009(2)	0.002(1)
N(4)	4*e*	0.7059(4)	0.7873(5)	0.1074(3)	0.052(3)	0.028(2)	0.025(2)	–0.018(2)	–0.016(2)	0.011(2)
N(5)	4*e*	0.7998(5)	1.0320(7)	0.1275(3)	0.090(5)	0.065(4)	0.025(2)	–0.056(4)	0.028(3)	–0.023(2)
C(11)	4*e*	0.8201(6)	0.726(1)	–0.0500(8)	0.044(5)	0.15(1)	0.20(2)	–0.030(6)	0.042(7)	–0.14(1)
C(12)	4*e*	0.9026(7)	0.6322(9)	–0.0025(8)	0.117(9)	0.038(4)	0.16(1)	0.033(5)	0.106(9)	0.029(6)
C(13)	4*e*	0.9791(8)	0.699(1)	–0.024(1)	0.107(9)	0.058(6)	0.29(2)	0.041(6)	0.15(1)	0.034(9)
C(14)	4*e*	0.9888(7)	0.814(2)	0.0349(7)	0.051(6)	0.38(3)	0.061(6)	0.10(1)	0.008(5)	0.00(1)
C(15)	4*e*	0.9083(7)	0.9196(9)	–0.0083(7)	0.059(5)	0.053(5)	0.082(7)	0.003(4)	0.021(5)	0.005(4)
C(21)	4*e*	0.6760(7)	1.2305(6)	0.0034(9)	0.070(5)	0.014(2)	0.24(2)	–0.003(3)	0.105(8)	–0.007(5)
C(22)	4*e*	0.7278(8)	1.3528(7)	–0.014(1)	0.115(8)	0.015(3)	0.25(2)	–0.017(4)	0.14(1)	–0.021(5)
C(23)	4*e*	0.7172(5)	1.3615(7)	–0.098(1)	0.032(3)	0.026(3)	0.26(2)	0.004(3)	0.042(6)	0.051(6)
C(24)	4*e*	0.7431(6)	1.2280(7)	–0.1271(5)	0.066(5)	0.035(3)	0.054(4)	–0.024(3)	–0.029(4)	0.022(3)
C(25)	4*e*	0.6878(7)	1.1148(8)	–0.1060(5)	0.090(6)	0.043(4)	0.056(4)	–0.043(4)	–0.053(4)	0.034(3)
C(31)	4*e*	0.5258(3)	0.9287(5)	–0.0857(3)	0.021(2)	0.035(2)	0.022(2)	–0.007(2)	–0.001(2)	0.002(2)
C(32)	4*e*	0.4941(4)	0.9074(5)	–0.1740(3)	0.028(2)	0.027(2)	0.021(2)	–0.005(2)	–0.004(2)	0.002(2)
C(33)	4*e*	0.4830(6)	0.7592(7)	–0.1934(4)	0.075(5)	0.030(3)	0.036(3)	–0.008(3)	–0.027(3)	–0.004(2)
C(34)	4*e*	0.5701(8)	0.6859(8)	–0.1498(5)	0.113(8)	0.032(3)	0.065(5)	0.025(4)	–0.051(5)	–0.029(3)
C(35)	4*e*	0.5938(8)	0.7135(6)	–0.0627(5)	0.116(7)	0.015(2)	0.053(4)	–0.009(3)	–0.054(5)	0.004(2)
C(41)	4*e*	0.6188(8)	0.7480(7)	0.1173(5)	0.127(8)	0.031(3)	0.068(5)	–0.025(4)	0.075(6)	–0.012(3)
C(42)	4*e*	0.6119(9)	0.5931(8)	0.1248(8)	0.126(9)	0.035(4)	0.121(9)	–0.028(5)	0.099(9)	–0.012(4)
C(43)	4*e*	0.693(1)	0.5360(9)	0.1880(6)	0.28(2)	0.032(4)	0.043(4)	–0.023(7)	0.055(8)	0.011(3)
C(44)	4*e*	0.780(1)	0.5814(8)	0.1763(7)	0.16(1)	0.036(4)	0.084(7)	–0.041(5)	–0.083(8)	0.036(4)
C(45)	4*e*	0.783(1)	0.7349(9)	0.1704(7)	0.18(1)	0.039(4)	0.092(7)	–0.044(6)	–0.108(8)	0.037(5)
C(51)	4*e*	0.7848(8)	1.0485(7)	0.2023(4)	0.129(8)	0.029(3)	0.028(3)	0.012(4)	0.033(4)	–0.004(2)
C(52)	4*e*	0.8708(7)	1.0322(9)	0.2713(4)	0.109(7)	0.057(4)	0.026(3)	–0.029(5)	0.030(4)	–0.016(3)
C(53)	4*e*	0.943(1)	1.131(2)	0.2669(5)	0.26(2)	0.20(2)	0.023(3)	–0.20(2)	0.009(7)	–0.015(6)
C(54)	4*e*	0.959(1)	1.110(3)	0.1876(5)	0.22(2)	0.48(4)	0.024(4)	–0.30(2)	0.009(7)	–0.015(9)
C(55)	4*e*	0.866(1)	1.134(2)	0.1230(5)	0.26(2)	0.28(2)	0.022(3)	–0.25(2)	0.011(7)	–0.005(7)

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Crystal structure of tetrakis(isopropylamino)silane, $Si(NHC_3H_7)_4$

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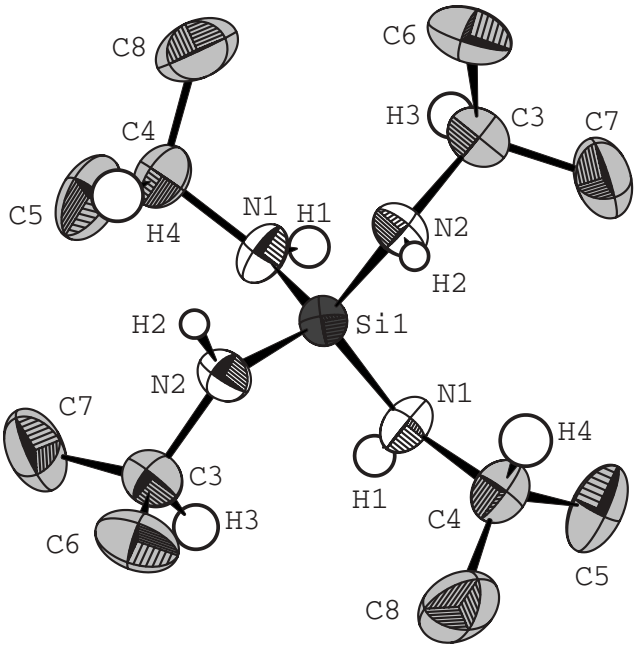

Abstract

$C_{12}H_{32}N_4Si$, monoclinic, *C*121 (No. 5), $a = 19.041(4)$ Å, $b = 5.211(1)$ Å, $c = 9.187(2)$ Å, $\beta = 111.60(2)°$, $V = 847.6$ Å^3, $Z = 2$, $R_{gt}(F) = 0.051$, $wR_{ref}(F^2) = 0.061$, $T = 293$ K.

Source of material

The silazane $Si(NHC_3H_7)_4$ was received as the major product from the reaction of $SiCl_4$ with $H_2NC_3H_7$ in hexane, analogue to the synthesis of tetrakis(methylamino)silane [1]. Transparent colourless crystals were obtained by crystallization from diethylether at 243 K. The compound was handled under dry and oxygen free argon as it is sensitive to air and moisture.

Experimental details

All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were found also from difference Fourier map, and refined isotropically. The absolute configuration in respect to the polarity of the space group was proven by changing the sign of the *hkl* indices. The $wR(F^2)$ values for the possible orientations were 0.0607 and 0.0612 respectively. The first one represents the absolute structure of the crystal studied. The corresponding Flack parameter is 0.1(2).

Discussion

The central silicon atom in $Si(NHC_3H_7)_4$ resides on a twofold crystallographic axis and is coordinated in a distorted tetrahedral way by four nitrogen atoms. The nitrogen coordination sphere is trigonal planar because of nitrogen-silicon backbond interactions, d(Si—N2) = 170.3(2) pm.

Table 1. Data collection and handling.

Crystal:	colourless plate, size 0.03 × 0.4 × 0.5 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	1.29 cm^{-1}
Diffractometer, scan mode:	Stoe Stadi4 CCD, ω
$2\theta_{max}$:	52.12°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	7154, 1676
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 1175
$N(param)_{refined}$:	142
Programs:	SHELXS-97 [2], SHELXL-97 [3], DIAMOND [4]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	*x*	*y*	*z*	U_{iso}
H(1)	4*e*	–0.025(1)	0.844(5)	0.613(3)	0.023(7)
H(2)	4*e*	0.071(1)	0.145(4)	0.602(2)	0.011(6)
H(3)	4*e*	0.076(1)	0.500(5)	0.826(2)	0.028(6)
H(4)	4*e*	–0.138(1)	0.465(5)	0.543(2)	0.037(7)
H(5A)	4*e*	–0.190(2)	0.906(6)	0.442(4)	0.06(1)
H(5B)	4*e*	–0.219(2)	0.844(6)	0.582(3)	0.09(1)
H(5C)	4*e*	–0.145(2)	1.026(8)	0.625(4)	0.11(2)
H(6A)	4*e*	0.123(2)	–0.041(7)	0.858(4)	0.10(1)
H(6B)	4*e*	0.131(2)	0.155(6)	1.028(4)	0.12(2)
H(6C)	4*e*	0.050(2)	0.093(6)	0.908(3)	0.07(1)
H(7A)	4*e*	0.187(2)	0.551(9)	0.746(5)	0.13(2)
H(7B)	4*e*	0.210(2)	0.454(7)	0.936(4)	0.12(1)
H(7C)	4*e*	0.203(2)	0.262(8)	0.786(4)	0.10(1)
H(8A)	4*e*	–0.066(2)	0.744(7)	0.842(4)	0.10(1)
H(8B)	4*e*	–0.138(2)	0.512(7)	0.793(4)	0.09(1)
H(8C)	4*e*	–0.058(3)	0.43(1)	0.808(5)	0.15(2)

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Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Si(1)	2*b*	0	0.4970(2)	1/2	0.0322(7)	0.0344(8)	0.0344(7)	0	0.0112(6)	0
N(1)	4*e*	–0.0502(1)	0.7053(4)	0.5683(3)	0.037(2)	0.033(2)	0.055(2)	–0.003(1)	0.026(1)	–0.007(1)
N(2)	4*e*	0.0551(1)	0.2895(4)	0.6382(3)	0.043(2)	0.032(2)	0.034(2)	0.006(1)	0.008(1)	–0.001(1)
C(3)	4*e*	0.1009(2)	0.3476(5)	0.8010(4)	0.053(2)	0.033(2)	0.043(2)	0.005(2)	0.012(2)	–0.003(2)
C(4)	4*e*	–0.1164(2)	0.6448(5)	0.6058(4)	0.047(2)	0.035(2)	0.062(3)	–0.004(2)	0.026(2)	–0.001(2)
C(5)	4*e*	–0.1722(2)	0.8637(8)	0.5573(7)	0.054(3)	0.061(3)	0.120(5)	0.018(2)	0.047(3)	0.015(3)
C(6)	4*e*	0.1001(3)	0.1231(7)	0.9053(5)	0.101(4)	0.063(3)	0.044(3)	0.002(2)	0.021(3)	0.009(2)
C(7)	4*e*	0.1813(2)	0.418(1)	0.8226(6)	0.053(3)	0.101(4)	0.072(4)	–0.015(2)	0.000(2)	0.000(3)
C(8)	4*e*	–0.0957(3)	0.581(1)	0.7773(6)	0.091(4)	0.106(5)	0.084(4)	0.005(3)	0.056(3)	0.022(3)

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Crystal structure of 2′*H*,7′*H*-dispiro[fluorene-9,2′-dibenzo[*c*,*e*]-oxepine-7′,9″-fluorene], $C_{38}H_{24}O$

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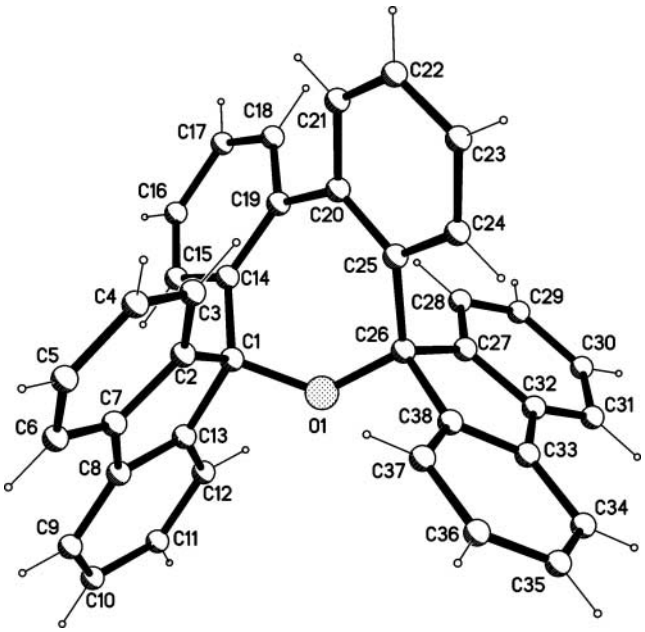

Abstract

$C_{38}H_{24}O$, monoclinic, $P12_1/n1$ (No. 14), a = 10.737(2) Å, b = 16.963(3) Å, c = 15.246(3) Å, β = 109.30(3)°, V = 2620.8 Å^3, Z = 4, $R_{gt}(F)$ = 0.088, $wR_{ref}(F^2)$ = 0.252, T = 293 K.

Source of material

Crystallization of 2,2′-bis(9-hydroxy-9-fluorenyl)biphenyl (BHFB) from solution in acetone at 330 K yielded together with single crystals of interest a relatively small amount of crystals of the title compound.

Experimental details

The single crystal chosen for data collection was the largest among other several crystals of the title compound, but its quality was poor. This explains the low quality of the experimental data (low ratio $N(hkl)_{obs}/N(param)_{refined} \approx 4$) and the relatively high R-values.

Discussion

In the parent compound 2,2′-bis(9-hydroxy-9-fluorenyl)biphenyl, the two hydroxyls are involved in intramolecular H-bonding that facilitated etherification reaction between these groups with closing of the seven membered ring. The fluorenyl fragments of the title compound are planar while the central heterocycle is in boat conformation.

Table 1. Data collection and handling.

Crystal:	colourless prism, size 0.05 × 0.20 × 0.20 mm
Wavelength:	Cu K_α radiation (1.54178 Å)
μ:	5.70 cm^{-1}
Diffractometer, scan mode:	Enraf-Nonius CAD-4, $\omega/2\theta$
$2\theta_{max}$:	129.92°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	4683, 4441
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 1399
$N(param)_{refined}$:	352
Programs:	SHELXS-97 [1], SHELXL-97 [2]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(15A)	4*e*	–0.1718	0.5898	0.5352	0.08
H(18A)	4*e*	–0.2269	0.6327	0.2234	0.08
H(24A)	4*e*	0.1971	0.8433	0.3453	0.08
H(12A)	4*e*	0.0810	0.5710	0.6196	0.08
H(21A)	4*e*	–0.2411	0.7633	0.2156	0.08
H(37A)	4*e*	0.1976	0.8804	0.5329	0.08
H(28A)	4*e*	0.0756	0.5817	0.3551	0.08
H(3A)	4*e*	–0.1021	0.8543	0.4102	0.08
H(16A)	4*e*	–0.3144	0.5100	0.4212	0.08
H(17A)	4*e*	–0.3341	0.5262	0.2663	0.08
H(29A)	4*e*	0.2143	0.4847	0.3273	0.08
H(35A)	4*e*	0.5910	0.8865	0.6019	0.08
H(22A)	4*e*	–0.1615	0.8624	0.1446	0.08
H(9A)	4*e*	–0.0495	0.7549	0.8037	0.08
H(4A)	4*e*	–0.1812	0.9704	0.4548	0.08
H(11A)	4*e*	0.0991	0.5400	0.7741	0.08
H(23A)	4*e*	0.0601	0.9048	0.2099	0.08
H(5A)	4*e*	–0.1621	0.9920	0.6084	0.08
H(36A)	4*e*	0.4002	0.9432	0.6042	0.08
H(30A)	4*e*	0.4379	0.5035	0.3766	0.08
H(6A)	4*e*	–0.1109	0.8857	0.7129	0.08
H(34A)	4*e*	0.5942	0.7546	0.5461	0.08
H(10A)	4*e*	0.0444	0.6339	0.8682	0.08
H(31A)	4*e*	0.5470	0.6173	0.4403	0.05

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Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(1)	4*e*	0.1094(4)	0.7067(3)	0.5207(3)	0.038(3)	0.074(4)	0.034(3)	0.009(3)	0.010(2)	0.011(3)
C(2)	4*e*	–0.0697(6)	0.7969(4)	0.5339(5)	0.032(4)	0.040(5)	0.043(4)	0.005(4)	0.005(4)	–0.007(4)
C(20)	4*e*	–0.0691(7)	0.7401(4)	0.3199(5)	0.054(5)	0.047(5)	0.034(4)	0.006(4)	0.012(4)	0.001(4)
C(27)	4*e*	0.2246(7)	0.6586(4)	0.4212(4)	0.049(5)	0.032(4)	0.036(4)	0.018(4)	0.014(4)	0.011(3)
C(13)	4*e*	–0.0025(6)	0.6795(4)	0.6211(4)	0.030(4)	0.061(5)	0.033(4)	–0.003(4)	0.010(3)	0.000(4)
C(38)	4*e*	0.2765(7)	0.7824(4)	0.4947(5)	0.050(5)	0.041(5)	0.046(5)	0.001(4)	0.017(4)	–0.004(4)
C(14)	4*e*	–0.1169(6)	0.6616(4)	0.4472(4)	0.034(4)	0.047(5)	0.032(4)	0.006(4)	0.006(3)	–0.005(4)
C(25)	4*e*	0.0602(7)	0.7676(4)	0.3616(5)	0.050(5)	0.036(5)	0.041(4)	–0.003(4)	0.011(4)	0.001(4)
C(15)	4*e*	–0.1856(7)	0.6007(4)	0.4709(5)	0.047(5)	0.055(5)	0.064(6)	–0.003(4)	0.021(5)	0.003(5)
C(19)	4*e*	–0.1312(7)	0.6757(4)	0.3540(5)	0.046(5)	0.045(5)	0.046(5)	0.006(4)	0.012(4)	–0.007(4)
C(1)	4*e*	–0.0229(7)	0.7117(4)	0.5241(5)	0.044(4)	0.039(4)	0.037(4)	–0.001(4)	0.017(3)	–0.009(4)
C(18)	4*e*	–0.2147(7)	0.6236(5)	0.2878(5)	0.053(5)	0.062(6)	0.048(5)	0.002(5)	0.005(4)	–0.009(4)
C(24)	4*e*	0.1067(8)	0.8272(4)	0.3190(5)	0.065(6)	0.057(6)	0.053(5)	–0.005(5)	0.002(4)	0.012(4)
C(12)	4*e*	0.0498(7)	0.6068(5)	0.6564(5)	0.069(6)	0.061(6)	0.044(5)	0.012(5)	0.021(4)	0.003(4)
C(21)	4*e*	–0.1499(8)	0.7786(5)	0.2388(5)	0.061(5)	0.063(6)	0.046(5)	0.001(5)	0.000(4)	0.005(4)
C(26)	4*e*	0.1582(7)	0.7301(4)	0.4472(5)	0.049(5)	0.052(5)	0.032(4)	0.005(4)	0.017(4)	0.002(4)
C(8)	4*e*	–0.0332(7)	0.7357(5)	0.6766(5)	0.051(5)	0.073(6)	0.036(4)	–0.003(5)	0.015(4)	–0.013(4)
C(37)	4*e*	0.2780(8)	0.8550(5)	0.5341(5)	0.065(6)	0.059(6)	0.059(5)	–0.001(5)	0.016(5)	–0.014(5)
C(33)	4*e*	0.3922(7)	0.7467(5)	0.4965(5)	0.039(5)	0.066(6)	0.044(5)	0.001(5)	0.011(4)	0.002(4)
C(7)	4*e*	–0.0756(7)	0.8084(5)	0.6234(5)	0.057(5)	0.062(6)	0.044(5)	0.005(5)	0.009(4)	–0.011(4)
C(28)	4*e*	0.1691(8)	0.5905(4)	0.3740(5)	0.073(6)	0.049(5)	0.046(5)	0.000(5)	0.021(5)	–0.001(4)
C(3)	4*e*	–0.1085(8)	0.8587(5)	0.4713(5)	0.069(6)	0.053(6)	0.055(5)	0.011(5)	0.008(5)	–0.004(5)
C(31)	4*e*	0.4429(8)	0.6119(6)	0.4378(6)	0.051(6)	0.081(7)	0.075(6)	0.024(5)	0.029(5)	0.002(5)
C(32)	4*e*	0.3605(7)	0.6692(5)	0.4508(5)	0.046(5)	0.058(5)	0.047(5)	0.012(5)	0.026(4)	0.010(4)
C(16)	4*e*	–0.2648(7)	0.5509(5)	0.4043(6)	0.046(5)	0.058(6)	0.072(6)	–0.004(4)	0.016(5)	–0.011(5)
C(17)	4*e*	–0.2812(7)	0.5626(5)	0.3117(6)	0.052(6)	0.067(6)	0.063(6)	–0.014(5)	–0.004(5)	–0.025(5)
C(29)	4*e*	0.250(1)	0.5325(5)	0.3594(5)	0.087(7)	0.048(6)	0.066(6)	0.001(5)	0.033(5)	–0.009(5)
C(35)	4*e*	0.511(1)	0.8564(6)	0.5774(6)	0.051(7)	0.113(9)	0.101(8)	–0.033(7)	0.021(6)	–0.031(7)
C(22)	4*e*	–0.104(1)	0.8381(5)	0.2001(6)	0.109(9)	0.061(6)	0.050(5)	–0.004(6)	0.001(6)	0.007(5)
C(9)	4*e*	–0.0158(9)	0.7178(6)	0.7695(6)	0.104(8)	0.095(8)	0.053(6)	0.021(7)	0.043(6)	–0.003(5)
C(4)	4*e*	–0.1411(8)	0.9304(5)	0.4999(6)	0.088(7)	0.047(6)	0.069(6)	0.023(5)	0.001(5)	–0.011(5)
C(11)	4*e*	0.0671(9)	0.5909(5)	0.7492(6)	0.105(8)	0.077(7)	0.053(6)	0.001(6)	0.028(6)	0.012(5)
C(23)	4*e*	0.024(1)	0.8636(5)	0.2374(6)	0.118(9)	0.053(6)	0.061(6)	–0.007(6)	0.019(6)	0.021(5)
C(5)	4*e*	–0.1451(9)	0.9407(5)	0.5883(7)	0.101(8)	0.052(6)	0.092(8)	0.013(6)	0.015(7)	–0.029(6)
C(36)	4*e*	0.397(1)	0.8919(6)	0.5769(6)	0.080(8)	0.097(8)	0.089(8)	–0.037(7)	0.023(6)	–0.032(6)
C(30)	4*e*	0.385(1)	0.5439(5)	0.3906(6)	0.097(8)	0.056(6)	0.086(7)	0.021(6)	0.049(6)	–0.010(5)
C(6)	4*e*	–0.1121(9)	0.8793(5)	0.6500(6)	0.106(8)	0.068(6)	0.060(6)	0.009(6)	0.020(6)	–0.028(5)
C(34)	4*e*	0.5143(8)	0.7833(6)	0.5387(6)	0.041(5)	0.098(8)	0.067(6)	–0.001(6)	0.003(5)	–0.004(6)
C(10)	4*e*	0.034(1)	0.6456(6)	0.8045(6)	0.125(9)	0.105(9)	0.045(6)	0.005(7)	0.037(6)	0.012(6)

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Crystal structure of bis(dipentyldithiocarbamato)nickel(II), $Ni(C_{11}H_{22}NS_2)_2$

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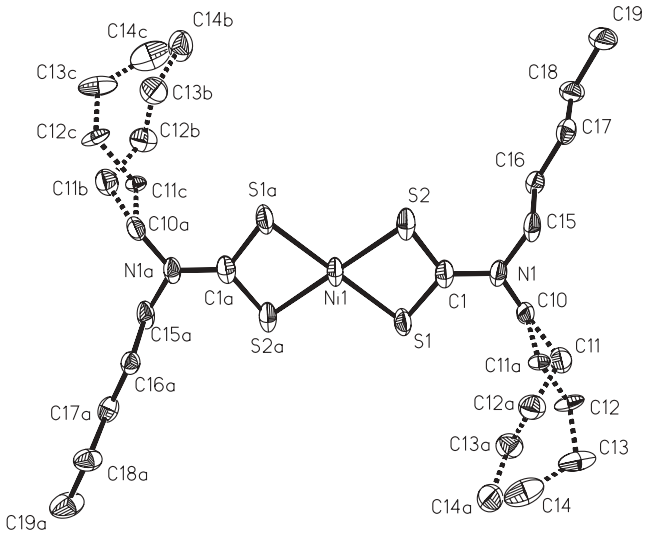

Abstract

$C_{22}H_{44}N_2NiS_4$, monoclinic, $P12_1/n1$ (No. 14), a = 10.402(2) Å, b = 13.261(3) Å, c = 10.701(2) Å, β = 114.79(3)°, V = 1340.1 Å^3, Z = 2, $R_{gt(F)}$ = 0.049, $wR_{ref(F^2)}$ = 0.118, T = 120 K.

Source of material

The title compound, a known species [1], was isolated as a green blocks by the slow evaporation of an *n*-hexane solution.

Discussion

From the figure, it is apparent that the central atom is four-coordinated. The NiS_4 chromophore is essentially planar and deviation of carbon atom from dithiocarbamate group plane is about 0.07 Å [2]. The Ni—S distances are 2.190(1) Å and 2.179(1) Å; the bond lengths of S1—C1 and S2—C1 are 1.700(4) Å and 1.705(4) Å, respectively. The N1—C1 distance is very short (1.315 Å) which is well known for the dithiocarbamate complexes [3]. The best convergence was reached for two positions for C11 to C14 atoms with occupating factors 0.5.

Table 1. Data collection and handling.

Crystal:	dark green prism, size 0.35 × 0.35 × 0.25 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	10.47 cm^{-1}
Diffractometer, scan mode:	KUMA KM-4, ω
$2\theta_{max}$:	57.02°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	10565, 3120
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2199
$N(param)_{refined}$:	169
Programs:	PARST 95 [2], SHELXS-97 [4], SHELXL-97 [5]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	Occ.	*x*	*y*	*z*	U_{iso}
H(10B)	4*e*		0.6094	0.1738	0.4050	0.050
H(10A)	4*e*		0.7829	0.2365	0.4811	0.050
H(11C)	4*e*	0.50	0.6703	0.3770	0.3287	0.050
H(11B)	4*e*	0.50	0.7167	0.3650	0.3861	0.050
H(11A)	4*e*	0.50	0.5175	0.3065	0.2384	0.050
H(11D)	4*e*	0.50	0.6242	0.3668	0.2799	0.050
H(12D)	4*e*	0.50	0.6478	0.3632	0.5155	0.050
H(12A)	4*e*	0.50	0.5665	0.3223	0.4991	0.050
H(12C)	4*e*	0.50	0.5141	0.4403	0.2858	0.050
H(12B)	4*e*	0.50	0.4719	0.2861	0.3113	0.050
H(13D)	4*e*	0.50	0.2979	0.3851	0.3261	0.050
H(13C)	4*e*	0.50	0.3741	0.2443	0.3331	0.050
H(13A)	4*e*	0.50	0.4960	0.4937	0.3491	0.050
H(13B)	4*e*	0.50	0.4422	0.3343	0.4513	0.050
H(14A)	4*e*	0.50	0.4170	0.4094	0.3281	0.050
H(14B)	4*e*	0.50	0.2623	0.4124	0.1988	0.050
H(14E)	4*e*	0.50	0.1987	0.3593	0.1328	0.050
H(14C)	4*e*	0.50	0.2559	0.4710	0.2732	0.050
H(14D)	4*e*	0.50	0.3393	0.3666	0.2359	0.050
H(14F)	4*e*	0.50	0.1449	0.3475	0.2825	0.050
H(15B)	4*e*		0.9060	0.2762	0.3570	0.046
H(15A)	4*e*		0.8764	0.2098	0.2257	0.044
H(16B)	4*e*		0.9874	0.1374	0.5052	0.040
H(16A)	4*e*		0.9492	0.0684	0.3614	0.049
H(17B)	4*e*		1.1616	0.2272	0.4583	0.047
H(17A)	4*e*		1.1241	0.1512	0.3230	0.060
H(18B)	4*e*		1.2428	0.0926	0.6104	0.046
H(18A)	4*e*		1.1964	0.0032	0.4640	0.090
H(19C)	4*e*		1.4249	0.1640	0.5707	0.080
H(19B)	4*e*		1.3832	0.0966	0.4182	0.090
H(19A)	4*e*		1.4595	0.0454	0.5808	0.130

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Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	Occ.	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ni(1)	2*b*		1/2	0	0	0.0531(4)	0.0207(3)	0.0302(3)	–0.0019(2)	–0.0101(2)	–0.0002(2)
S(1)	4*e*		0.48692(9)	0.09220(6)	0.16405(9)	0.0483(5)	0.0439(5)	0.0435(5)	0.0003(4)	–0.0115(4)	–0.0137(4)
S(2)	4*e*		0.7045(1)	0.07592(6)	0.07825(8)	0.0608(5)	0.0303(4)	0.0334(4)	–0.0071(3)	–0.0032(4)	–0.0021(3)
N(1)	4*e*		0.7343(3)	0.1876(2)	0.2979(3)	0.048(2)	0.024(1)	0.039(1)	0.006(1)	–0.009(1)	–0.006(1)
C(1)	4*e*		0.6544(3)	0.1286(2)	0.1962(3)	0.051(2)	0.021(1)	0.038(2)	0.003(1)	–0.009(1)	0.002(1)
C(10)	4*e*		0.6883(3)	0.2242(3)	0.4006(4)	0.034(2)	0.048(2)	0.064(2)	0.010(2)	–0.013(2)	–0.028(2)
C(11)	4*e*	0.50	0.6396(8)	0.3263(5)	0.4172(9)	0.045(4)	0.044(4)	0.045(4)	–0.004(3)	0.010(4)	–0.001(4)
C(11A)	4*e*	0.50	0.6066(6)	0.3240(4)	0.3317(7)	0.028(3)	0.028(3)	0.026(3)	0.008(2)	0.017(3)	0.008(2)
C(12)	4*e*	0.50	0.5597(7)	0.3669(5)	0.4406(6)	0.055(4)	0.045(3)	0.039(3)	0.027(3)	0.035(3)	0.010(3)
C(12A)	4*e*	0.50	0.5016(7)	0.3562(6)	0.3078(7)	0.047(4)	0.049(4)	0.062(5)	0.001(3)	0.025(4)	0.005(3)
C(13)	4*e*	0.50	0.3772(8)	0.3265(6)	0.3434(7)	0.054(4)	0.053(4)	0.049(4)	0.007(3)	0.016(3)	0.007(3)
C(13A)	4*e*	0.50	0.4517(9)	0.4486(6)	0.3915(9)	0.069(5)	0.047(4)	0.103(7)	0.028(4)	0.062(5)	0.030(4)
C(14)	4*e*	0.50	0.245(1)	0.3735(7)	0.248(1)	0.064(6)	0.061(6)	0.049(5)	0.013(4)	0.005(4)	–0.006(4)
C(14A)	4*e*	0.50	0.310(1)	0.4165(8)	0.289(1)	0.11(1)	0.053(6)	0.095(9)	0.027(6)	0.061(8)	0.022(6)
C(15)	4*e*		0.8785(3)	0.2106(2)	0.3182(3)	0.054(2)	0.022(1)	0.039(2)	–0.005(1)	–0.003(1)	–0.003(1)
C(16)	4*e*		0.9830(3)	0.1346(2)	0.4104(3)	0.041(2)	0.027(1)	0.030(1)	0.000(1)	0.009(1)	–0.001(1)
C(17)	4*e*		1.1298(3)	0.1534(2)	0.4214(3)	0.053(2)	0.030(2)	0.042(2)	–0.010(1)	0.024(2)	–0.006(1)
C(18)	4*e*		1.2381(3)	0.0829(2)	0.5199(4)	0.041(2)	0.042(2)	0.071(2)	–0.001(1)	0.031(2)	–0.001(2)
C(19)	4*e*		1.3848(4)	0.1014(3)	0.5291(5)	0.056(2)	0.062(2)	0.127(4)	–0.010(2)	0.060(3)	–0.020(3)

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Crystal structure of pyridynium pentachloro(pyridine)rhenate(IV), $(C_5H_6N)(C_5H_5N)ReCl_5$

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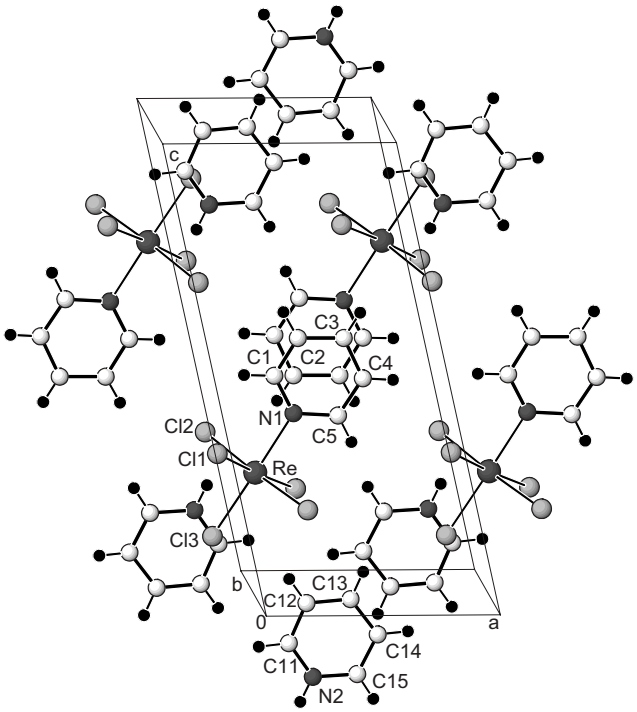

Abstract

$C_{10}H_{11}Cl_5N_2Re$, monoclinic, $P12_1/m1$ (No. 11), $a = 7.193(1)$ Å $b = 6.991(1)$ Å, $c = 15.142(3)$ Å, $\beta = 103.14(3)°$, $V = 741.5$ Å^3, $Z = 2$, $R_{gt}(F) = 0.041$, $wR_{ref}(F^2) = 0.092$, $T = 100$ K.

Source of material

The title compound has been obtained by heating $(pyH)_2ReCl_6$ with water free pyridine in the glass tubes. The $(pyH)_2ReCl_6$ was obtained in a reaction of $(NH)_2ReCl_6$ [1] with pyridine hydrochloride in HCl solution. The mixture was sealed in 15 cm^3 glass tubes. The filling of the solution was about 30% of the glass tubes. The glass tubes were subsequently heated at 453 K for 14 hours. After the completion of the reaction the container was left overnight for slow crystallization. The crystals were washed with methanol and ethyl ether and dried at the temperature 373 K. All starting materials were used without further purification. The crystals were plate-shaped and yellow in color.

Discussion

Transition metal complexes with aromatic amines ligands have been discussed in recent reviews [2-4]. Rhenium(IV) complexes with aromatic amine in the coordination sphere indicate antiferromagentic interactions [5].

The title compound has slightly distorted octahedral environment around the Re atom. The bonds lengths are d(Re—N) = 2.17(1) Å, d(Re—Cl1) = 2.352(3) Å, d(Re—Cl2) = 2.355(3) Å and d(Re—Cl3) = 2.357(4) Å. The plane of pyridine ring intersects the plane formed by the Re and four chlorine atoms. In the 010 direction the orientation of the molecules shows a pseudo layered structure. The $ReCl_5^{1-}$ moieties alternate with pyridine situated in the layers.

Table 1. Data collection and handling.

Crystal:	yellow plate, size 0.05 × 0.1 × 0.1 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	9.077 cm^{-1}
Diffractometer, scan mode:	Kuma KM4CCD, ω
$2\theta_{max}$:	52°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	7706, 1586
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 1564
$N(param)_{refined}$:	104
Program:	SHELX-97 [6]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(1)	2*e*	0.1473	1/4	0.4861	0.029
H(2)	2*e*	0.3748	1/4	0.6187	0.024
H(3)	2*e*	0.7021	1/4	0.6165	0.023
H(4)	2*e*	0.7791	1/4	0.4740	0.028
H(5)	2*e*	0.5433	1/4	0.3432	0.026
H(2A)	2*e*	0.0811	1/4	0.7944	0.050
H(13)	2*e*	0.4718	1/4	1.0685	0.083
H(11)	2*e*	–0.0447	1/4	0.9115	0.041
H(12)	2*e*	0.1489	1/4	1.0542	0.033
H(14)	2*e*	0.6067	1/4	0.9421	0.103
H(15)	2*e*	0.3957	1/4	0.7998	0.051

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Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Re	2*e*	0.1038(1)	1/4	0.27954(4)	0.0188(3)	0.0235(2)	0.0115(2)	0	–0.0001(2)	0
Cl(1)	4*f*	–0.0564(4)	0.0116(4)	0.3430(2)	0.018(1)	0.026(1)	0.017(1)	–0.0048(9)	0.0034(9)	–0.0002(9)
Cl(2)	4*f*	0.2773(4)	0.0127(4)	0.2225(2)	0.023(1)	0.026(1)	0.016(1)	0.003(1)	0.0019(9)	–0.0021(9)
Cl(3)	2*e*	–0.1387(5)	1/4	0.1455(2)	0.017(2)	0.034(2)	0.019(2)	0	–0.004(1)	0
N(1)	2*e*	0.323(2)	1/4	0.4047(8)	0.006(5)	0.020(6)	0.017(5)	0	–0.002(5)	0
C(1)	2*e*	0.276(3)	1/4	0.4842(9)	0.036(8)	0.023(6)	0.018(6)	0	0.016(7)	0
C(2)	2*e*	0.412(2)	1/4	0.564(1)	0.022(9)	0.027(7)	0.017(6)	0	0.015(6)	0
C(3)	2*e*	0.608(3)	1/4	0.563(1)	0.020(7)	0.025(7)	0.011(6)	0	0.000(6)	0
C(4)	2*e*	0.652(2)	1/4	0.4777(9)	0.024(8)	0.034(8)	0.014(6)	0	0.010(6)	0
C(5)	2*e*	0.511(2)	1/4	0.399(1)	0.022(8)	0.018(7)	0.031(8)	0	0.019(7)	0
N(2)	2*e*	0.158(3)	1/4	0.847(1)	0.06(1)	0.045(9)	0.015(6)	0	–0.001(7)	0
C(13)	2*e*	0.392(3)	1/4	1.011(1)	0.04(1)	0.13(2)	0.02(1)	0	–0.015(9)	0
C(11)	2*e*	0.087(3)	1/4	0.919(1)	0.04(1)	0.035(9)	0.021(8)	0	0.001(8)	0
C(12)	2*e*	0.200(3)	1/4	1.003(1)	0.04(1)	0.039(9)	0.007(6)	0	0.005(7)	0
C(14)	2*e*	0.475(4)	1/4	0.936(1)	0.05(2)	0.19(3)	0.030(9)	0	0.02(1)	0
C(15)	2*e*	0.350(2)	1/4	0.852(1)	0.02(1)	0.09(1)	0.031(9)	0	0.018(7)	0

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Crystal structure of 3′-benzyloxy-2′-naphthyl-1-bromo-2-naphthoate, $C_{28}H_{19}BrO_3$

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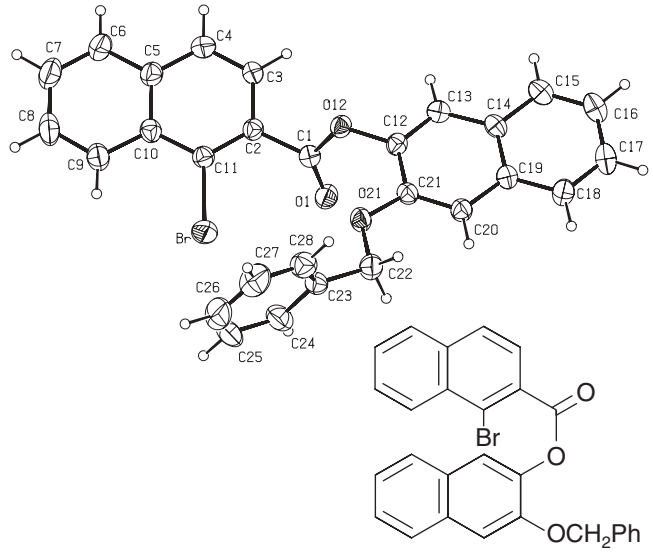

Abstract

$C_{28}H_{19}BrO_3$, monoclinic, $P12_1/c1$ (No. 14), a = 13.769(1) Å, b = 19.058(2) Å, c = 8.716(1) Å, β = 107.964(6)°, V = 2175.7 Å^3, Z = 4, $R_{gt}(F)$ = 0.059, $wR_{ref}(F^2)$ = 0.164, T = 293 K.

Source of material

The title compound was prepared according to [1] by esterification of the commercially available σ-1-bromonaphthoic acid [2] with the likewise known [3] 3-benzyloxy-2-naphthol. It is a useful intermediate in the synthesis of a twofold lactone bridged teraryl [1].

Discussion

Although the title compound is a useful synthetic precursor for the intramolecular biaryl coupling to link the bromine-bearing C-atom (C11) with C13 to give a six-membered lactone ring [1], it adopts a quite different conformation in the crystal, with C13 far away from the bromine (6.26 Å). The bromine is, in turn, quite close to the aromatic ring of the benzyl group, with ca. 4.50 Å distance as an average. Likewise remarkable is the non-coplanar array of the carboxyl unit (O1–C1–O12) with the naphthalene nucleus, with a significant dihedral angle between these two planes (58.1°), apparently due to the bulky bromine substituent at C11.

Table 1. Data collection and handling.

Crystal:	pale yellow plate, size 0.1 × 0.95 × 1.05 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	19.18 cm^{-1}
Diffractometer, scan mode:	Bruker AXS P4, ω
$2\theta_{max}$:	55°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	4866, 4593
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 3037
$N(param)_{refined}$:	289
Program:	SHELXTL [4]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(3)	4*e*	0.4967	1.0220	0.3019	0.08
H(4)	4*e*	0.4214	1.0839	0.4565	0.08
H(6)	4*e*	0.2694	1.1172	0.5317	0.08
H(7)	4*e*	0.1008	1.1034	0.5058	0.08
H(8)	4*e*	0.0009	1.0273	0.3124	0.08
H(9)	4*e*	0.0718	0.9618	0.1547	0.08
H(13)	4*e*	0.6814	0.9326	0.1624	0.08
H(15)	4*e*	0.8556	0.9187	0.1273	0.08
H(16)	4*e*	0.9619	0.8617	0.0120	0.08
H(17)	4*e*	0.8995	0.7697	–0.1664	0.08
H(18)	4*e*	0.7372	0.7307	–0.2145	0.08
H(20)	4*e*	0.5691	0.7373	–0.1633	0.08
H(22A)	4*e*	0.4562	0.6817	–0.0682	0.08
H(22B)	4*e*	0.3905	0.7234	–0.2208	0.08
H(24)	4*e*	0.2105	0.7534	–0.2425	0.08
H(25)	4*e*	0.0637	0.7160	–0.1860	0.08
H(26)	4*e*	0.0779	0.6322	0.0130	0.08
H(27)	4*e*	0.2329	0.5887	0.1558	0.08
H(28)	4*e*	0.3764	0.6279	0.1057	0.08

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Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Br	4*e*	0.18957(3)	0.89885(3)	–0.00974(5)	0.0636(3)	0.0927(4)	0.0755(3)	–0.0263(2)	0.0248(2)	–0.0305(2)
O(1)	4*e*	0.4020(2)	0.9405(1)	–0.0791(3)	0.059(2)	0.065(2)	0.049(1)	0.014(1)	0.019(1)	0.004(1)
C(1)	4*e*	0.4228(3)	0.9347(2)	0.0636(4)	0.045(2)	0.044(2)	0.048(2)	0.000(1)	0.015(1)	0.001(1)
C(2)	4*e*	0.3684(3)	0.9702(2)	0.1673(4)	0.045(2)	0.045(2)	0.045(2)	0.005(1)	0.015(1)	0.001(1)
C(3)	4*e*	0.4272(3)	1.0167(2)	0.2868(4)	0.041(2)	0.068(2)	0.059(2)	0.001(2)	0.014(2)	–0.014(2)
C(4)	4*e*	0.3820(3)	1.0534(2)	0.3787(4)	0.057(2)	0.072(2)	0.060(2)	–0.003(2)	0.013(2)	–0.019(2)
C(5)	4*e*	0.2778(3)	1.0471(2)	0.3610(4)	0.055(2)	0.062(2)	0.054(2)	0.010(2)	0.018(2)	–0.001(2)
C(6)	4*e*	0.2306(4)	1.0856(2)	0.4560(5)	0.071(3)	0.080(3)	0.069(2)	0.013(2)	0.029(2)	–0.013(2)
C(7)	4*e*	0.1299(4)	1.0780(3)	0.4401(6)	0.084(4)	0.101(3)	0.082(3)	0.023(3)	0.044(3)	–0.009(3)
C(8)	4*e*	0.0701(4)	1.0317(3)	0.3246(6)	0.058(3)	0.109(4)	0.092(3)	0.019(3)	0.041(2)	0.011(3)
C(9)	4*e*	0.1124(3)	0.9929(2)	0.2296(5)	0.053(2)	0.077(3)	0.073(2)	0.002(2)	0.026(2)	0.001(2)
C(10)	4*e*	0.2170(3)	0.9994(2)	0.2438(4)	0.046(2)	0.054(2)	0.049(2)	0.006(2)	0.016(2)	0.008(1)
C(11)	4*e*	0.2667(3)	0.9622(2)	0.1478(4)	0.047(2)	0.047(2)	0.047(2)	–0.003(2)	0.015(1)	–0.000(1)
O(12)	4*e*	0.5033(2)	0.8974(1)	0.1560(3)	0.050(1)	0.047(1)	0.047(1)	0.008(1)	0.016(1)	–0.0009(9)
C(12)	4*e*	0.5666(3)	0.8661(2)	0.0759(4)	0.048(2)	0.043(2)	0.044(2)	0.008(1)	0.015(1)	0.003(1)
C(13)	4*e*	0.6611(3)	0.8925(2)	0.1000(4)	0.050(2)	0.043(2)	0.049(2)	0.000(2)	0.012(1)	0.001(1)
C(14)	4*e*	0.7296(3)	0.8591(2)	0.0303(4)	0.041(2)	0.046(2)	0.053(2)	0.001(2)	0.011(1)	0.010(1)
C(15)	4*e*	0.8311(3)	0.8808(2)	0.0593(5)	0.051(2)	0.058(2)	0.069(2)	–0.004(2)	0.014(2)	0.005(2)
C(16)	4*e*	0.8944(3)	0.8473(2)	–0.0105(6)	0.046(2)	0.071(3)	0.093(3)	–0.002(2)	0.023(2)	0.007(2)
C(17)	4*e*	0.8572(3)	0.7914(2)	–0.1158(5)	0.054(2)	0.074(3)	0.092(3)	0.011(2)	0.036(2)	0.008(2)
C(18)	4*e*	0.7602(3)	0.7684(2)	–0.1450(5)	0.061(2)	0.060(2)	0.069(2)	0.001(2)	0.032(2)	–0.004(2)
C(19)	4*e*	0.6939(3)	0.8005(2)	–0.0722(4)	0.046(2)	0.046(2)	0.054(2)	0.002(2)	0.018(1)	0.004(1)
C(20)	4*e*	0.5931(3)	0.7752(2)	–0.0950(4)	0.047(2)	0.049(2)	0.059(2)	–0.002(2)	0.019(2)	–0.008(1)
C(21)	4*e*	0.5316(3)	0.8055(2)	–0.0187(4)	0.041(2)	0.048(2)	0.051(2)	–0.004(1)	0.015(1)	–0.002(1)
O(21)	4*e*	0.4366(2)	0.7825(1)	–0.0224(3)	0.045(1)	0.052(1)	0.070(1)	–0.007(1)	0.024(1)	–0.010(1)
C(22)	4*e*	0.4036(3)	0.7171(2)	–0.1058(5)	0.060(2)	0.055(2)	0.078(2)	–0.009(2)	0.030(2)	–0.016(2)
C(23)	4*e*	0.3081(3)	0.6944(2)	–0.0723(4)	0.048(2)	0.050(2)	0.057(2)	–0.006(2)	0.016(2)	–0.007(2)
C(24)	4*e*	0.2150(3)	0.7207(2)	–0.1613(5)	0.053(2)	0.081(3)	0.078(3)	0.004(2)	0.007(2)	–0.001(2)
C(25)	4*e*	0.1273(4)	0.6980(4)	–0.1286(8)	0.043(3)	0.138(5)	0.130(5)	–0.002(3)	0.007(3)	–0.050(4)
C(26)	4*e*	0.1363(5)	0.6480(4)	–0.0087(9)	0.093(5)	0.141(6)	0.141(6)	–0.066(4)	0.076(4)	–0.062(5)
C(27)	4*e*	0.2280(5)	0.6223(3)	0.0763(8)	0.125(6)	0.096(4)	0.105(4)	–0.043(4)	0.068(4)	–0.014(3)
C(28)	4*e*	0.3131(3)	0.6455(2)	0.0456(5)	0.071(3)	0.073(3)	0.064(2)	–0.004(2)	0.021(2)	0.000(2)

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Crystal structure of di(2,2′-bipyridine)di[μ-(2-furancarboxylato-*O*,*O*′)-μ-(2-furancarboxylato-*O*,*O*′:*O*′)]di(nitrato)disamarium(III), $Sm_2(NO_3)_2(C_5H_3O_3)_4(C_{10}H_8N_2)_2$

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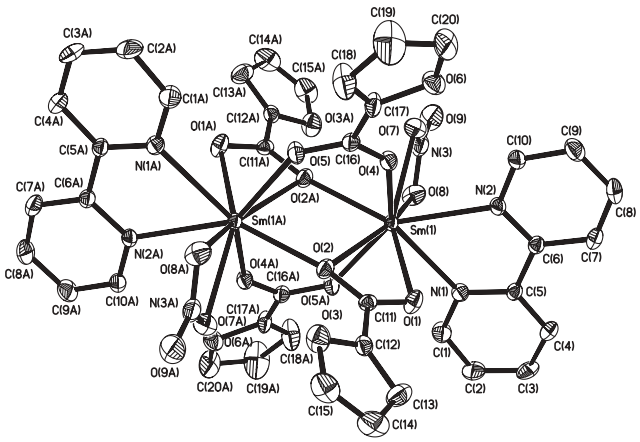

Abstract

$C_{20}H_{14}N_3O_9Sm$, triclinic, $P\bar{1}$ (No. 2), a = 9.981(4) Å, b = 10.266(5) Å, c = 11.082(5) Å, α = 85.556(8)°, β = 75.913(8)°, γ = 70.087(7)°, V = 1035.5 Å^3, Z = 2, $R_{gt}(F)$ = 0.029, $wR_{ref}(F^2)$ = 0.070, T = 293 K.

Source of material

1.5 mmol 2-Furancarboxylic acid and 0.5 mmol 2,2′-bipyridine were dissolved in 25 ml 95% C_2H_5OH. The pH of the solution was adjusted to range 6 – 7 with 2M NaOH solution. The 0.5 mmol $Sm(NO_3)_3 \cdot 6H_2O$ dissolved in 5 ml H_2O was added to the solution. The mixture was heated under reflux with stirring for 4 h. A precipitate was formed. Single crystal were obtained from the mother liquor after one week at room temperature.

Discussion

Crystal structure and luminescence of ternary lanthanide complex with organic acids and 2,2′-bipyridine or 1,10-phenanthroline have been extensively studied. But only few quaternary mixed anion complexes of lanthanide have been reported. We obtained a new quaternary samarium complex with 2-furancarboxylic acid and 2,2′-bipyridine, whose structure is reported here.

In the title compound, the two Sm^{3+} ions are coordinated by four carboxylate groups of furancarboxylic acid through their carboxyl oxygen atoms, forming a dimeric unit. The carboxylate groups are coordinated to Sm^{3+} ion in bridging and bridging-chelating modes. Carboxylate group O4–C16–O5 coordinates to two different Sm^{3+} ions; O1–C11–O2 groups are in a chelating-bridging coordination mode in which two O atoms chelate one Sm^{3+} ion, with O2 also linked to another Sm^{3+} ion. The Sm—Sm distance is 4.00(2) Å. Sm—$O_{carboxyl}$ distances range from 2.370(3) Å to 2.689(3) Å, with a mean value of 2.453(3) Å. In comparison to an average La—$O_{carboxyl}$ distance of 2.573(4) Å in the complex $La(C_5H_3O_3)_3 \cdot 2H_2O$ [1], the average Sm—O distance for the title complex is shorter. This may be attributed to the larger radius of the La^{3+} ion and close packing for the mixed ligands in the title complex. The Sm1—O2 distance of 2.689(3) Å and the Sm1—O1 distance of 2.441(3) Å are larger. This may be attributed O2–C11–O1 group is in a chelating mode in which two O atoms linked to the same Sm^{3+} ion, forming an unstable four-membered ring. The O–Sm–O angles vary from 72.8(1)° to 148.4(1)°. The O–Sm–O–C four-member ring, with the angle O–Sm–O much smaller than 90°, is distorted seriously. The 2,2′-bipyring ligand chelates to the Sm^{3+} ion. The average bond length of Sm—N is 2.601(3) Å. Two oxygen atoms from the nitrate coordinate to the Sm^{3+} ion in bidentate chelating model. E.g., in $Nd_2(NO_3)_2(C_9H_9O_4)_4(C_{12}H_8N_2)_2$ [2], the NO_3^- anion is coordinated to the metal. In the title complex, the average distance between Sm and O from the nitrates is 2.522(8) Å.

Table 1. Data collection and handling.

Crystal:	white square prism, size 0.16 × 0.20 × 0.24 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	28.95 cm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD, φ/ω
$2\theta_{max}$:	53.16°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	6133, 4207
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 3645
$N(param)_{refined}$:	328
Programs:	SHELXS-97 [3], SHELXL-97 [4]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	Occ.	x	y	z	U_{iso}
H(1A)	2*i*		0.4941	–0.1244	0.8828	0.054
H(2A)	2*i*		0.7251	–0.1094	0.8291	0.063
H(3A)	2*i*		0.7815	0.0321	0.6651	0.060
H(4A)	2*i*		0.6015	0.1552	0.5623	0.050
H(7A)	2*i*		0.4341	0.2640	0.4725	0.053
H(8A)	2*i*		0.2437	0.3727	0.3762	0.063
H(9A)	2*i*		0.0245	0.3292	0.4440	0.057

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Table 2. Continued.

Atom	Site	Occ.	*x*	*y*	*z*	U_{iso}
H(10A)	2*i*		0.0018	0.1794	0.6057	0.044
H(13A)	2*i*		0.2201	0.4129	1.0388	0.063
H(14A)	2*i*		0.0736	0.5925	1.2109	0.074
H(15A)	2*i*		–0.1459	0.5443	1.3019	0.072
H(18A)	2*i*	0.69(2)	–0.5180	0.3654	0.9996	0.086
H(19A)	2*i*	0.69	–0.6252	0.5320	0.8455	0.125
H(20A)	2*i*	0.69	–0.4387	0.4927	0.6450	0.087
H(18B)	2*i*	0.31	–0.5167	0.2515	0.9653	0.040
H(19B)	2*i*	0.31	–0.6666	0.4148	0.8433	0.094
H(20B)	2*i*	0.31	–0.5077	0.4962	0.6787	0.091

Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	Occ.	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Sm(1)	2*i*		0.14520(2)	–0.00615(2)	0.83853(2)	0.0203(1)	0.0290(1)	0.0211(1)	–0.00807(7)	–0.00251(7)	0.00342(7)
N(1)	2*i*		0.4115(3)	0.0001(4)	0.7572(3)	0.023(2)	0.038(2)	0.030(2)	–0.007(1)	–0.004(1)	0.001(2)
N(2)	2*i*		0.1962(3)	0.1357(4)	0.6393(3)	0.025(2)	0.040(2)	0.023(2)	–0.011(2)	–0.003(1)	0.002(1)
O(1)	2*i*		0.1785(3)	0.1914(3)	0.9213(3)	0.036(2)	0.040(2)	0.044(2)	–0.018(1)	0.008(1)	–0.005(1)
O(2)	2*i*		0.0054(3)	0.1334(3)	1.0537(3)	0.039(2)	0.033(2)	0.036(2)	–0.020(1)	–0.005(1)	0.003(1)
O(3)	2*i*		–0.0746(4)	0.3785(3)	1.1849(3)	0.054(2)	0.047(2)	0.045(2)	–0.015(2)	0.003(2)	–0.009(2)
O(4)	2*i*		–0.0951(3)	0.1461(3)	0.8315(3)	0.022(1)	0.045(2)	0.029(2)	–0.007(1)	–0.004(1)	0.007(1)
O(5)	2*i*		–0.2609(3)	0.1379(3)	1.0073(3)	0.026(1)	0.047(2)	0.030(2)	–0.007(1)	–0.004(1)	0.012(1)
C(1)	2*i*		0.5162(5)	–0.0679(5)	0.8166(5)	0.033(2)	0.051(3)	0.047(3)	–0.010(2)	–0.013(2)	0.012(2)
C(2)	2*i*		0.6553(5)	–0.0594(6)	0.7855(5)	0.033(2)	0.066(3)	0.064(3)	–0.017(2)	–0.025(2)	0.010(3)
C(3)	2*i*		0.6885(5)	0.0244(6)	0.6888(5)	0.027(2)	0.069(3)	0.064(3)	–0.025(2)	–0.012(2)	0.001(3)
C(4)	2*i*		0.5815(5)	0.0970(5)	0.6277(4)	0.034(2)	0.051(3)	0.044(3)	–0.024(2)	–0.005(2)	0.005(2)
C(5)	2*i*		0.4438(4)	0.0835(4)	0.6633(4)	0.028(2)	0.032(2)	0.026(2)	–0.013(2)	–0.000(2)	–0.003(2)
C(6)	2*i*		0.3249(4)	0.1595(4)	0.5990(4)	0.029(2)	0.031(2)	0.027(2)	–0.012(2)	–0.002(2)	–0.001(2)
C(7)	2*i*		0.3452(5)	0.2483(5)	0.4996(4)	0.042(3)	0.055(3)	0.043(3)	–0.030(2)	–0.007(2)	0.014(2)
C(8)	2*i*		0.2320(6)	0.3124(6)	0.4419(5)	0.064(3)	0.058(3)	0.040(3)	–0.030(3)	–0.014(2)	0.025(2)
C(9)	2*i*		0.1020(5)	0.2871(5)	0.4819(4)	0.048(3)	0.052(3)	0.040(3)	–0.013(2)	–0.018(2)	0.015(2)
C(10)	2*i*		0.0894(5)	0.1978(5)	0.5795(4)	0.031(2)	0.051(3)	0.029(2)	–0.016(2)	–0.007(2)	0.007(2)
C(11)	2*i*		0.0798(4)	0.2135(4)	1.0194(4)	0.027(2)	0.026(2)	0.033(2)	–0.010(2)	–0.012(2)	0.003(2)
C(12)	2*i*		0.0520(4)	0.3345(4)	1.0951(4)	0.033(2)	0.032(2)	0.028(2)	–0.011(2)	–0.008(2)	0.006(2)
C(13)	2*i*		0.1304(6)	0.4191(5)	1.0922(5)	0.053(3)	0.049(3)	0.068(4)	–0.030(3)	–0.018(3)	0.005(3)
C(14)	2*i*		0.0473(7)	0.5208(5)	1.1885(5)	0.097(5)	0.032(3)	0.067(4)	–0.023(3)	–0.033(3)	–0.006(2)
C(15)	2*i*		–0.0717(7)	0.4928(5)	1.2380(5)	0.087(4)	0.038(3)	0.050(3)	–0.014(3)	–0.014(3)	–0.008(2)
C(16)	2*i*		–0.2221(4)	0.1849(4)	0.9019(4)	0.022(2)	0.033(2)	0.033(2)	–0.008(2)	–0.008(2)	0.006(2)
O(6)	2*i*	0.69(2)	–0.3027(8)	0.338(1)	0.7353(7)	0.043(4)	0.050(4)	0.042(3)	–0.009(3)	–0.015(3)	0.009(3)
C(17)	2*i*	0.69	–0.3301(8)	0.2934(8)	0.8581(8)	0.027(4)	0.048(5)	0.036(5)	–0.011(4)	0.001(4)	0.014(4)
C(18)	2*i*	0.69	–0.4717(8)	0.373(1)	0.9171(9)	0.032(4)	0.084(8)	0.061(5)	0.011(5)	0.004(4)	0.030(6)
C(19)	2*i*	0.69	–0.5317(9)	0.466(1)	0.8307(8)	0.053(6)	0.09(1)	0.120(8)	0.021(6)	–0.011(6)	0.049(8)
C(20)	2*i*	0.69	–0.427(1)	0.4444(9)	0.7184(8)	0.064(7)	0.068(6)	0.085(6)	–0.020(5)	–0.037(5)	0.057(5)
O(6′)	2*i*	0.31	–0.343(2)	0.371(3)	0.751(2)	0.057(9)	0.07(1)	0.07(1)	–0.020(9)	0.006(8)	0.024(9)
C(17′)	2*i*	0.31	–0.346(2)	0.288(2)	0.847(2)	0.024(6)	0.05(1)	0.04(1)	0.002(8)	–0.021(7)	0.015(8)
C(18′)	2*i*	0.31	–0.483(2)	0.299(2)	0.896(1)	0.019(5)	0.05(1)	0.018(6)	0.000(6)	–0.003(4)	0.004(6)
C(19′)	2*i*	0.31	–0.565(2)	0.388(3)	0.829(2)	0.033(7)	0.10(2)	0.07(1)	0.013(9)	–0.017(7)	0.02(1)
C(20′)	2*i*	0.31	–0.478(3)	0.432(2)	0.739(2)	0.07(1)	0.08(1)	0.07(1)	–0.01(1)	–0.041(9)	0.051(9)
N(3)	2*i*		0.1999(5)	–0.2051(4)	0.6396(4)	0.052(3)	0.056(3)	0.034(2)	–0.034(2)	0.004(2)	–0.004(2)
O(7)	2*i*		0.0792(4)	–0.1066(4)	0.6661(3)	0.050(2)	0.056(2)	0.044(2)	–0.019(2)	–0.016(2)	0.001(2)
O(8)	2*i*		0.2934(3)	–0.2108(3)	0.7013(3)	0.036(2)	0.051(2)	0.056(2)	–0.011(2)	–0.002(2)	–0.017(2)
O(9)	2*i*		0.2269(5)	–0.2907(5)	0.5580(3)	0.092(3)	0.090(3)	0.045(2)	–0.052(3)	0.015(2)	–0.033(2)

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Crystal structure of di(2,2′-bipyridine)di[μ-(2,3-dimethoxylbenzoato-*O*,*O*′)]-di[μ-2,3-dimethoxylbenzoato-*O*,*O*′:*O*′]di(2,3-dimethoxybenzoato)]-dineodymium(III), $Nd_2(C_9H_9O_4)_6(C_{10}H_8N_2)_2$

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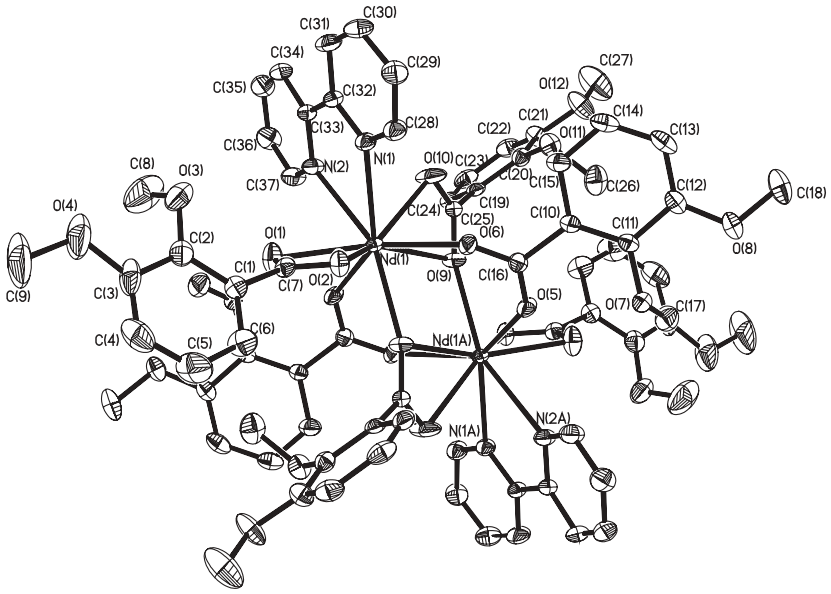

Abstract

$C_{37}H_{35}N_2NdO_{12}$, triclinic, $P\bar{1}$ (No. 2), a = 10.9793(5) Å, b = 12.0965(5) Å, c = 15.3714(9) Å, α = 67.072(1)°, β = 83.799(2)°, γ = 72.887(2)°, V = 1796.9 Å^3, Z = 2, $R_{gt}(F)$ = 0.037, $wR_{ref}(F^2)$ = 0.058, T = 293 K.

Source of material

1.5 mmol of 2,3-dimethoxybenzoic acid and 1 mmol of 2,2′-bipyridine were dissolved in 25 ml 95% ethanol. The pH of the mixed solution was controlled to be in a range of 6 – 7 with 1 mol dm^{-3} NaOH solution. Finally, the $Nd(NO_3)_3$ solution obtained by 0.5 mmol $Nd(NO_3)_3 \cdot 6H_2O$ dissolved in 6 ml H_2O was dropped into the mixed solution. The mixture was heated under reflux with stirring for 3 h. A pricipitate was formed. Single crystals were obtained from the mother liquor after 1 week at room temperature.

Discussion

The title complex $Nd_2(C_9H_9O_4)_6(C_{10}H_8N_2)_2$ (**I**) is a dimeric molecule. The two Nd^{3+} ions are held together by four carboxylate groups of 2,3-dimethoxybenzoic acid. Each neodymium ion is coordinated to seven O atoms from 2,3-dimethoxybenzoato groups and to two N atoms from 2,2′-bipyridine molecule. The coordination number of the central ion is nine. There are three coordinated modes for carboxylate groups, chelating, bidentate bridging and bridging-chelating. The title complex **I** is unlike the complexes $[Nd_2(C_9H_9O_4)_4(NO_3)_2(C_{12}H_8N_2)_2]$ (**II**) [1] and $Nd_2(m\text{-}CH_3C_6H_4COO)_3$ (**III**) [2] in coordinated modes for carboxylate groups. In the complex **II**, the carboxylate groups of 2,3-dimethoxybenzoic acid coordinates to Nd^{3+} ions in two coordination modes, bidentate bridging and bridging-chelating. In the complex **III**, the coordinated modes for carboxylate groups of *m*-methylbenzoic acid are bridging-chelating, only one style. These facts indicate that there are many different coordination modes of carboxylate groups and many different types of crystal structure of lanthanide complexes with organic acid. The Nd—O distances in the title complex range from 2.404(2) Å to 2.712(2) Å. The largest bond distance is *d*(Nd1—O9). The O9 atom is linked to two different neodymium ions to form an oxygen bridge. O9–Nd1–O10–C25 is an unstable four-membered ring. This also indicate that the bond between Nd1 and O9 is a weaker one. Average bond length of Nd—O in the title complex is 2.494(2) Å, which is larger than average Nd—O distance of 2.489(2) Å in the complex **II**. This is because the volume of NO_3^- is smaller than 2,3-dimethoxybenzoato. It also leads to the distance *d*(Nd—Nd) of 4.034(4) Å in **I**, which is larger than *d*(Nd—Nd) of 3.961(7) Å in complex **II**. The 2,2′-bipyridine ligand with two N atoms chelates to the Nd^{3+} ion in the title complex, and the Nd—N distances are *d*(Nd—N1) = 2.601(2) Å and *d*(Nd—N2) = 2.647(2) Å, respectively. Free bipyridine is in the *trans*-form while bipyridine coordinated with lanthanide elements is in the *cis*-form, and the average bond length of Nd—N is 2.624(2) Å.

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Table 1. Data collection and handling.

Crystal:	white, square prism, size 0.10 × 0.18 × 0.68 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	15.11 cm^{-1}
Diffractometer, scan mode:	Rigaku R-AXIS RAPID, ω
$2\theta_{max}$:	54.92°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	13145, 8117
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 5631
$N(param)_{refined}$:	470
Programs:	SHELXS-97 [3], SHELXL-97 [4]

Table 2. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	*x*	*y*	*z*	U_{iso}
H(4A)	2*i*	–0.1924	1.4087	0.0964	0.097
H(5A)	2*i*	–0.1231	1.2091	0.2002	0.102
H(6A)	2*i*	0.0329	1.1562	0.3071	0.073
H(8A)	2*i*	0.1762	1.6459	0.1587	0.186
H(8B)	2*i*	0.1091	1.6220	0.0853	0.186
H(8C)	2*i*	0.2242	1.5176	0.1459	0.186
H(9A)	2*i*	–0.2281	1.7345	–0.0186	0.252
H(9B)	2*i*	–0.2845	1.6224	0.0403	0.252
H(9C)	2*i*	–0.1721	1.6056	–0.0297	0.252

Table 2. Continued.

Atom	Site	*x*	*y*	*z*	U_{iso}
H(13A)	2*i*	0.3144	0.9792	1.0086	0.072
H(14A)	2*i*	0.2903	1.1589	0.8752	0.074
H(15A)	2*i*	0.3167	1.1500	0.7281	0.058
H(17A)	2*i*	0.5048	0.5782	0.8672	0.090
H(17B)	2*i*	0.5176	0.6390	0.9379	0.090
H(17C)	2*i*	0.5641	0.6912	0.8335	0.090
H(18A)	2*i*	0.3955	0.6627	1.1516	0.122
H(18B)	2*i*	0.3250	0.8052	1.1227	0.122
H(18C)	2*i*	0.4703	0.7628	1.1007	0.122
H(22A)	2*i*	1.0564	1.0900	0.6888	0.060
H(23A)	2*i*	1.0334	1.1056	0.5371	0.059
H(24A)	2*i*	0.8460	1.1030	0.4872	0.052
H(26A)	2*i*	0.5880	0.9500	0.8586	0.100
H(26B)	2*i*	0.7374	0.9107	0.8565	0.100
H(26C)	2*i*	0.6597	0.9035	0.7800	0.100
H(27A)	2*i*	0.9812	1.0685	0.9198	0.175
H(27B)	2*i*	1.0094	1.1539	0.8174	0.175
H(27C)	2*i*	1.0617	1.0084	0.8507	0.175
H(28A)	2*i*	0.1538	1.2792	0.5805	0.053
H(29A)	2*i*	0.0419	1.4341	0.6335	0.062
H(30A)	2*i*	0.0832	1.6271	0.5665	0.073
H(31A)	2*i*	0.2473	1.6523	0.4612	0.063
H(34A)	2*i*	0.4149	1.6594	0.3835	0.060
H(35A)	2*i*	0.5974	1.6598	0.2951	0.070
H(36A)	2*i*	0.6985	1.4887	0.2562	0.067
H(37A)	2*i*	0.6140	1.3224	0.3077	0.060

Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Nd(1)	2*i*	0.39398(2)	1.17961(2)	0.45067(1)	0.0329(1)	0.02016(9)	0.0311(1)	–0.00334(7)	–0.00093(8)	–0.01320(8)
O(1)	2*i*	0.2763(2)	1.3042(2)	0.2992(2)	0.034(2)	0.074(2)	0.041(2)	–0.017(1)	–0.004(1)	–0.003(1)
O(2)	2*i*	0.1620(2)	1.2203(2)	0.4181(2)	0.037(2)	0.049(1)	0.033(1)	–0.015(1)	–0.002(1)	–0.006(1)
O(3)	2*i*	0.0651(3)	1.5365(2)	0.2165(2)	0.079(2)	0.043(2)	0.071(2)	–0.013(2)	0.014(2)	–0.012(2)
O(4)	2*i*	–0.1181(4)	1.6069(3)	0.0883(2)	0.118(3)	0.098(3)	0.069(2)	0.032(2)	–0.026(2)	–0.001(2)
O(5)	2*i*	0.4452(2)	0.8675(2)	0.6606(2)	0.052(2)	0.023(1)	0.038(1)	–0.001(1)	0.014(1)	–0.012(1)
O(6)	2*i*	0.3255(2)	1.0650(2)	0.6055(2)	0.051(2)	0.027(1)	0.032(1)	–0.001(1)	0.001(1)	–0.009(1)
O(7)	2*i*	0.3765(2)	0.7404(2)	0.8458(2)	0.050(2)	0.034(1)	0.037(1)	–0.013(1)	–0.004(1)	–0.010(1)
O(8)	2*i*	0.3584(3)	0.7502(2)	1.0161(2)	0.095(2)	0.070(2)	0.031(2)	–0.024(2)	0.002(2)	–0.018(2)
O(9)	2*i*	0.6063(2)	1.0185(2)	0.5504(2)	0.045(2)	0.035(1)	0.057(2)	–0.013(1)	–0.000(1)	–0.028(1)
O(10)	2*i*	0.5357(3)	1.2010(2)	0.5581(2)	0.075(2)	0.035(1)	0.114(3)	0.016(1)	–0.056(2)	–0.044(2)
O(11)	2*i*	0.6596(2)	1.0736(2)	0.7597(2)	0.039(2)	0.057(2)	0.045(2)	–0.014(1)	0.006(1)	–0.020(1)
O(12)	2*i*	0.8787(3)	1.0710(3)	0.8218(2)	0.047(2)	0.124(2)	0.058(2)	–0.021(2)	–0.014(2)	–0.050(2)
C(1)	2*i*	0.0636(3)	1.3247(3)	0.2663(2)	0.030(2)	0.042(2)	0.042(2)	–0.005(2)	0.001(2)	–0.017(2)
C(2)	2*i*	0.0199(4)	1.4484(3)	0.2061(3)	0.048(3)	0.050(2)	0.044(2)	–0.003(2)	0.004(2)	–0.019(2)
C(3)	2*i*	–0.0802(4)	1.4814(4)	0.1405(3)	0.055(3)	0.069(3)	0.044(3)	0.021(3)	–0.004(2)	–0.007(3)
C(4)	2*i*	–0.1292(5)	1.3885(6)	0.1400(4)	0.053(3)	0.120(4)	0.083(4)	–0.011(3)	–0.019(3)	–0.057(4)
C(5)	2*i*	–0.0876(5)	1.2696(5)	0.2011(4)	0.060(4)	0.090(4)	0.119(5)	–0.011(3)	–0.032(4)	–0.051(4)
C(6)	2*i*	0.0064(4)	1.2382(4)	0.2642(3)	0.041(3)	0.055(2)	0.085(3)	–0.006(2)	–0.018(3)	–0.026(3)
C(7)	2*i*	0.1724(4)	1.2829(3)	0.3317(3)	0.027(2)	0.030(2)	0.042(2)	–0.003(2)	–0.004(2)	–0.014(2)
C(8)	2*i*	0.1505(5)	1.5844(4)	0.1459(4)	0.143(6)	0.083(4)	0.132(5)	–0.056(4)	0.059(5)	–0.022(4)
C(9)	2*i*	–0.2081(7)	1.6455(5)	0.0139(4)	0.180(8)	0.156(6)	0.074(4)	0.069(5)	–0.059(5)	–0.014(4)
C(10)	2*i*	0.3502(3)	0.9613(3)	0.7711(2)	0.035(2)	0.034(2)	0.035(2)	–0.008(2)	0.001(2)	–0.019(2)
C(11)	2*i*	0.3602(3)	0.8545(3)	0.8514(2)	0.030(2)	0.039(2)	0.035(2)	–0.012(2)	0.003(2)	–0.020(2)
C(12)	2*i*	0.3476(4)	0.8610(3)	0.9411(3)	0.049(3)	0.058(2)	0.034(2)	–0.017(2)	0.002(2)	–0.021(2)
C(13)	2*i*	0.3226(4)	0.9746(4)	0.9492(3)	0.072(3)	0.079(3)	0.046(3)	–0.021(3)	0.008(2)	–0.043(3)
C(14)	2*i*	0.3094(4)	1.0821(4)	0.8692(3)	0.080(4)	0.056(2)	0.065(3)	–0.014(2)	0.004(3)	–0.044(3)
C(15)	2*i*	0.3240(4)	1.0770(3)	0.7814(3)	0.063(3)	0.041(2)	0.049(2)	–0.016(2)	0.006(2)	–0.026(2)
C(16)	2*i*	0.3740(3)	0.9633(3)	0.6718(2)	0.037(2)	0.037(2)	0.031(2)	–0.017(2)	0.007(2)	–0.014(2)
C(17)	2*i*	0.5011(4)	0.6551(3)	0.8734(3)	0.067(3)	0.046(2)	0.055(3)	–0.001(2)	–0.005(2)	–0.015(2)
C(18)	2*i*	0.3898(5)	0.7448(4)	1.1049(3)	0.089(4)	0.107(4)	0.037(3)	–0.021(3)	–0.015(3)	–0.017(3)
C(19)	2*i*	0.7485(3)	1.0908(3)	0.6080(2)	0.040(2)	0.019(2)	0.042(2)	–0.005(2)	–0.003(2)	–0.015(2)
C(20)	2*i*	0.7630(4)	1.0806(3)	0.6997(3)	0.035(2)	0.031(2)	0.038(2)	–0.006(2)	0.004(2)	–0.012(2)
C(21)	2*i*	0.8769(4)	1.0817(3)	0.7298(3)	0.032(2)	0.055(2)	0.048(3)	–0.011(2)	–0.004(2)	–0.024(2)
C(22)	2*i*	0.9793(4)	1.0902(3)	0.6689(3)	0.040(3)	0.043(2)	0.074(3)	–0.015(2)	–0.001(2)	–0.027(2)
C(23)	2*i*	0.9652(4)	1.0990(3)	0.5785(3)	0.042(3)	0.034(2)	0.071(3)	–0.015(2)	0.020(2)	–0.021(2)

Table 3. Continued.

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(24)	2*i*	0.8527(4)	1.0984(3)	0.5483(3)	0.061(3)	0.028(2)	0.040(2)	–0.012(2)	0.009(2)	–0.015(2)
C(25)	2*i*	0.6220(4)	1.1037(3)	0.5725(2)	0.050(3)	0.026(2)	0.030(2)	–0.011(2)	–0.003(2)	–0.011(2)
C(26)	2*i*	0.6613(4)	0.9495(4)	0.8184(3)	0.056(3)	0.082(3)	0.057(3)	–0.032(2)	0.007(2)	–0.013(3)
C(27)	2*i*	0.9919(5)	1.0759(5)	0.8551(4)	0.074(4)	0.194(6)	0.107(5)	–0.029(4)	–0.031(4)	–0.080(5)
C(28)	2*i*	0.1746(4)	1.3547(3)	0.5576(3)	0.045(3)	0.036(2)	0.049(2)	–0.004(2)	0.003(2)	–0.018(2)
C(29)	2*i*	0.1049(4)	1.4478(3)	0.5881(3)	0.046(3)	0.051(2)	0.054(3)	0.001(2)	0.007(2)	–0.027(2)
C(30)	2*i*	0.1311(4)	1.5610(3)	0.5498(3)	0.068(3)	0.041(2)	0.074(3)	0.004(2)	0.006(3)	–0.038(2)
C(31)	2*i*	0.2281(4)	1.5760(3)	0.4869(3)	0.066(3)	0.031(2)	0.064(3)	–0.006(2)	0.005(2)	–0.027(2)
C(32)	2*i*	0.2980(3)	1.4783(3)	0.4611(2)	0.043(2)	0.025(2)	0.039(2)	–0.006(2)	–0.004(2)	–0.014(2)
C(33)	2*i*	0.4094(3)	1.4873(3)	0.3987(2)	0.046(2)	0.029(2)	0.036(2)	–0.012(2)	–0.003(2)	–0.015(2)
C(34)	2*i*	0.4568(4)	1.5907(3)	0.3681(3)	0.075(3)	0.033(2)	0.053(3)	–0.023(2)	–0.003(2)	–0.020(2)
C(35)	2*i*	0.5648(4)	1.5912(4)	0.3153(3)	0.082(4)	0.054(2)	0.054(3)	–0.046(2)	0.006(3)	–0.018(2)
C(36)	2*i*	0.6248(4)	1.4902(4)	0.2922(3)	0.059(3)	0.069(3)	0.056(3)	–0.038(2)	0.015(2)	–0.029(2)
C(37)	2*i*	0.5732(4)	1.3910(3)	0.3237(3)	0.059(3)	0.049(2)	0.055(3)	–0.024(2)	0.014(2)	–0.031(2)
N(1)	2*i*	0.2707(3)	1.3681(2)	0.4967(2)	0.036(2)	0.029(1)	0.039(2)	–0.003(1)	0.003(2)	–0.017(1)
N(2)	2*i*	0.4679(3)	1.3867(2)	0.3760(2)	0.045(2)	0.034(2)	0.045(2)	–0.015(1)	0.009(2)	–0.023(2)

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Crystal structure of 1-[[(*Z*)-1-chloroethylidene]-amino]-ethaneiminium chloride, $[CH_3ClNCNH_2CH_3]Cl$

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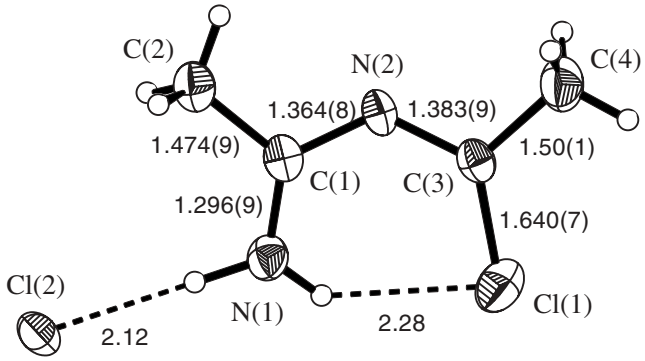

Abstract

$C_4H_8Cl_2N_2$, orthorhombic, $P2_12_12_1$ (No. 19), $a = 4.828(2)$ Å, $b = 10.497(3)$ Å, $c = 14.830(4)$ Å, $V = 751.6$ Å^3, $Z = 4$, $R_{gt}(F) = 0.052$, $wR_{ref}(F^2) = 0.132$, $T = 193$ K.

Source of material

The title compound was obtained inadvertedly in a reaction of $P(C_6H_5)_4Cl$ and Na_2S_4 in acetonitrile in the presence of TaS_3 (36 h reflux). After filtration and cooling red $(P(C_6H_5)_4)_2S_7$ crystallized. From the filtrate of this, a small amount of the title compound crystallized in the presence of $TaCl_5$.

Discussion

The compound is known to form from acetonitrile and HCl [1]. Probably it was formed this way in a side reaction, the other above-mentioned components being of no importance. In the title molecule, the atoms C1 and C3 are coplanar with the atoms bonded to them, but the two planes are mutually tilted by 11°.

Table 1. Data collection and handling.

Crystal:	colourless plate, size 0.008 × 0.025 × 0.030 mm
Wavelength:	Mo K_α radiation (0.71070 Å)
μ:	7.69 cm^{-1}
Diffractometer, scan mode:	Enraf-Nonius CAD4, ω
$2\theta_{max}$:	45.96°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	941, 889
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 699
$N(param)_{refined}$:	81
Program:	SHELX-97 [2]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	*x*	*y*	*z*	U_{iso}
H(2A)	4*a*	0.6570	0.5478	0.2681	0.06
H(2B)	4*a*	0.3700	0.5937	0.3057	0.06
H(2C)	4*a*	0.6030	0.6933	0.2844	0.06
H(1A)	4*a*	0.17(2)	0.769(8)	0.203(6)	0.06(3)
H(1B)	4*a*	0.17(2)	0.715(6)	0.100(5)	0.01(2)
H(4A)	4*a*	0.5010	0.3911	–0.0745	0.07
H(4B)	4*a*	0.5140	0.3313	0.0222	0.07
H(4C)	4*a*	0.7620	0.4128	–0.0138	0.07

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Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cl(1)	4*a*	0.2166(5)	0.6079(2)	–0.0339(1)	0.055(2)	0.052(1)	0.0332(9)	–0.002(1)	–0.008(1)	0.004(1)
Cl(2)	4*a*	–0.0066(5)	0.3715(2)	0.1857(1)	0.029(1)	0.0304(8)	0.0421(9)	–0.004(1)	0.002(1)	0.0096(8)
C(1)	4*a*	0.415(1)	0.6268(6)	0.1730(4)	0.025(4)	0.022(3)	0.028(4)	–0.011(4)	0.008(3)	0.000(3)
C(2)	4*a*	0.521(2)	0.6143(7)	0.2659(4)	0.039(5)	0.037(4)	0.035(4)	–0.002(7)	0.002(4)	–0.007(4)
N(1)	4*a*	0.231(2)	0.7122(6)	0.1539(5)	0.041(5)	0.030(4)	0.025(4)	0.000(4)	0.002(4)	0.003(3)
N(2)	4*a*	0.522(2)	0.6431(4)	0.1118(4)	0.029(4)	0.025(3)	0.026(3)	–0.004(3)	0.007(4)	–0.005(2)
C(3)	4*a*	0.435(2)	0.5210(6)	0.0244(5)	0.023(5)	0.028(3)	0.029(4)	–0.004(3)	0.007(4)	–0.004(3)
C(4)	4*a*	0.564(2)	0.4035(7)	–0.0138(5)	0.048(6)	0.050(4)	0.041(5)	0.000(4)	–0.003(4)	–0.015(4)

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Crystal structure of *trans*,*cis*-(±)-3′-(4-fluorophenyl)-2-phenylspiro[2*H*-1-benzothiopyran-3(4*H*),2′-oxiran]-4-one 1-oxide, $C_{22}H_{15}FO_3S$

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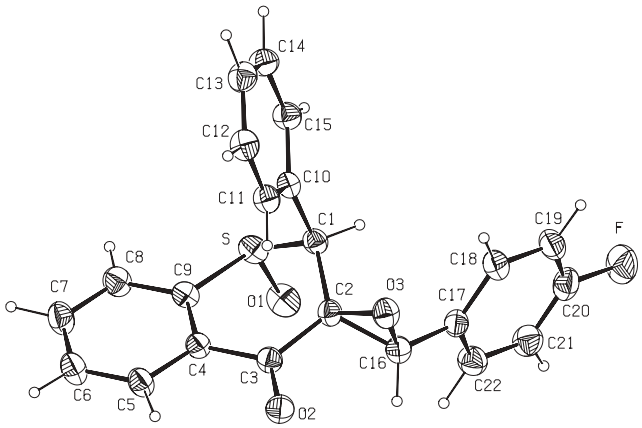

Abstract

$C_{22}H_{15}FO_3S$, monoclinic, $P12_1/c1$ (No. 14), a = 8.739(1) Å, b = 15.948(3) Å, c = 12.993(1) Å, β = 94.99(1)°, V = 1804.0 Å^3, Z = 4, $R_{gt}(F)$ = 0.045, $wR_{ref}(F^2)$ = 0.119, T = 298 K.

Source of material

The title compound was synthesized by oxidation of the *trans*,*cis*-epoxide of (*Z*)-3-(4′-fluorarylidene)-1-thioflavan-4-one with dimethyldioxirane [1]. Crystals were obtained from 1,2-dichloroethane after silica gel chromatography.

Discussion

This study confirms the axial arrangement of the sulfoxide group (*trans* to the phenyl ring on the adjacent carbon atom), which was previously suggested from ^{17}O-NMR spectra and ab-initio quantum-chemical calculations [2]. Selected torsion angles are as follows: ∠C10–C1–S–O1 = 174.9(2)° and ∠C10–C1–C2–O3 = –63.9(3)°. The molecule contains the chiral atoms C1, C2 and C16. Because of the centrosymmetric space group, there are the *R*/*S*/*S* as well as the *S*/*S*/*R* enantiomers in the packing.

Table 1. Data collection and handling.

Crystal:	white plate, size 0.10 × 0.20 × 0.30 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	2.09 cm^{-1}
Diffractometer, scan mode:	Stoe IPDS 2, 140 frames, $\Delta\omega$ = 1°
$2\theta_{max}$:	49.28°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	8369, 3018
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 1823
$N(param)_{refined}$:	305
Programs:	SHELXS-97 [3], SHELXL-97 [4]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(1)	4*e*	1.159(4)	0.995(2)	1.141(2)	0.067(8)
H(5)	4*e*	0.751(4)	0.980(2)	1.462(3)	0.09(1)
H(6)	4*e*	0.516(5)	1.063(2)	1.425(3)	0.10(1)
H(7)	4*e*	0.462(5)	1.129(2)	1.268(3)	0.11(1)
H(8)	4*e*	0.637(4)	1.107(2)	1.140(3)	0.10(1)
H(11)	4*e*	1.131(4)	1.089(2)	1.380(3)	0.08(1)
H(12)	4*e*	1.201(4)	1.224(2)	1.422(3)	0.09(1)
H(13)	4*e*	1.257(4)	1.326(2)	1.294(3)	0.10(1)
H(14)	4*e*	1.228(4)	1.283(2)	1.118(3)	0.10(1)
H(15)	4*e*	1.157(4)	1.142(2)	1.083(2)	0.072(9)
H(16)	4*e*	1.132(4)	0.821(2)	1.309(2)	0.066(8)
H(18)	4*e*	1.429(5)	0.927(3)	1.196(3)	0.11(1)
H(19)	4*e*	1.554(4)	0.871(2)	1.053(2)	0.08(1)
H(21)	4*e*	1.230(5)	0.693(3)	0.996(3)	0.12(2)
H(22)	4*e*	1.094(5)	0.746(2)	1.140(3)	0.11(1)

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Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	4*e*	1.0895(3)	1.0147(2)	1.1927(2)	0.059(2)	0.063(2)	0.048(1)	0.001(1)	0.010(1)	–0.000(1)
C(2)	4*e*	1.0902(3)	0.9494(2)	1.2774(2)	0.052(2)	0.064(2)	0.053(1)	0.005(1)	0.004(1)	–0.001(1)
C(3)	4*e*	0.9654(3)	0.9496(2)	1.3504(2)	0.062(2)	0.063(2)	0.049(2)	0.003(1)	0.007(1)	0.000(1)
C(4)	4*e*	0.8224(3)	0.9975(2)	1.3229(2)	0.054(2)	0.062(2)	0.055(1)	0.001(1)	0.006(1)	0.000(1)
C(5)	4*e*	0.7180(4)	1.0079(2)	1.3970(2)	0.060(2)	0.089(2)	0.062(2)	0.005(2)	0.014(1)	0.004(2)
C(6)	4*e*	0.5871(4)	1.0545(3)	1.3758(3)	0.063(2)	0.107(3)	0.079(2)	0.008(2)	0.020(2)	–0.001(2)
C(7)	4*e*	0.5559(4)	1.0920(3)	1.2811(3)	0.057(2)	0.105(3)	0.090(2)	0.011(2)	0.008(2)	0.003(2)
C(8)	4*e*	0.6570(4)	1.0816(2)	1.2060(3)	0.060(2)	0.093(3)	0.071(2)	0.002(2)	–0.003(2)	0.011(2)
C(9)	4*e*	0.7898(3)	1.0348(2)	1.2257(2)	0.055(2)	0.070(2)	0.051(1)	–0.006(1)	0.000(1)	0.002(1)
C(10)	4*e*	1.1348(3)	1.1023(2)	1.2254(2)	0.048(2)	0.062(2)	0.053(2)	0.002(1)	0.007(1)	–0.003(1)
C(11)	4*e*	1.1516(4)	1.1277(2)	1.3290(2)	0.066(2)	0.073(2)	0.052(2)	0.002(2)	0.007(1)	–0.006(2)
C(12)	4*e*	1.1969(4)	1.2079(2)	1.3542(3)	0.077(2)	0.080(3)	0.063(2)	–0.001(2)	0.004(2)	–0.014(2)
C(13)	4*e*	1.2240(4)	1.2651(2)	1.2790(3)	0.076(2)	0.069(2)	0.086(2)	–0.001(2)	0.002(2)	–0.011(2)
C(14)	4*e*	1.2075(4)	1.2414(2)	1.1770(3)	0.086(2)	0.065(2)	0.072(2)	–0.004(2)	0.011(2)	0.001(2)
C(15)	4*e*	1.1643(4)	1.1606(2)	1.1508(2)	0.076(2)	0.072(2)	0.053(2)	–0.001(2)	0.009(1)	–0.002(2)
C(16)	4*e*	1.1707(3)	0.8673(2)	1.2680(2)	0.060(2)	0.066(2)	0.061(2)	0.005(2)	0.006(1)	–0.000(2)
C(17)	4*e*	1.2497(4)	0.8399(2)	1.1766(2)	0.060(2)	0.065(2)	0.065(2)	0.012(2)	0.010(1)	0.004(2)
C(18)	4*e*	1.3840(4)	0.8768(2)	1.1510(3)	0.059(2)	0.086(2)	0.076(2)	0.004(2)	0.011(2)	–0.001(2)
C(19)	4*e*	1.4584(4)	0.8459(3)	1.0682(3)	0.059(2)	0.103(3)	0.084(2)	0.009(2)	0.017(2)	0.013(2)
C(20)	4*e*	1.3942(5)	0.7788(3)	1.0146(2)	0.096(3)	0.087(3)	0.065(2)	0.033(2)	0.017(2)	0.004(2)
C(21)	4*e*	1.2620(5)	0.7417(3)	1.0367(3)	0.099(3)	0.077(3)	0.079(2)	0.005(2)	0.015(2)	–0.008(2)
C(22)	4*e*	1.1897(5)	0.7725(2)	1.1193(3)	0.081(2)	0.077(2)	0.079(2)	–0.004(2)	0.016(2)	–0.007(2)
O(1)	4*e*	0.8650(3)	0.9337(2)	1.0797(2)	0.093(2)	0.096(2)	0.076(1)	–0.020(1)	0.010(1)	–0.028(1)
O(2)	4*e*	0.9835(3)	0.9109(1)	1.4312(2)	0.085(2)	0.085(2)	0.058(1)	0.015(1)	0.015(1)	0.017(1)
O(3)	4*e*	1.2400(2)	0.9329(1)	1.3302(1)	0.061(1)	0.084(2)	0.061(1)	0.006(1)	–0.0022(9)	–0.002(1)
S	4*e*	0.90099(9)	1.01893(5)	1.11916(5)	0.0670(5)	0.0850(6)	0.0471(4)	–0.0060(4)	0.0018(3)	0.0006(4)
F	4*e*	1.4694(3)	0.7481(2)	0.9350(2)	0.146(2)	0.131(2)	0.092(1)	0.039(2)	0.051(1)	–0.004(1)

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4. Sheldrick, G. M.: SHELXL-97 Program for the refinement of crystal structures. University of Göttingen, Germany 1997.

Crystal structure of (1*E*,3*E*)-4-methylthio-2-nitro-3-phenylsulfonyl-1-pyrrolidino-1,3-butadiene, $C_{15}H_{18}N_2O_4S_2$

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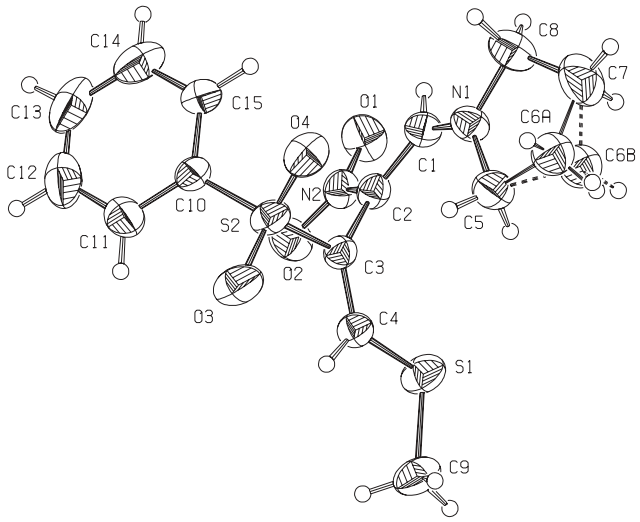

Abstract

$C_{15}H_{18}N_2O_4S_2$, monoclinic, $P12_1/c1$ (No. 14), a = 8.754(3) Å, b = 12.499(2) Å, c = 15.599(3) Å, β = 95.09(2)°, V = 1700.1 Å^3, Z = 4, $R_{gt}(F)$ = 0.049, $wR_{ref}(F^2)$ = 0.128, T = 294 K.

Source of material

The title compound was synthesized in 87% yield from 3-nitro-4-(phenylsulfonyl)thiophene [1] with a proper modification of our ring-opening procedure of thiophene derivatives [2] and crystallized from ethanol. Mp 463.7-464.3°.

Experimental details

In the refinement, the atoms C6A and C6B were considered as isotropic and the sum of their site occupancy factors was tied to unity [final values: 0.613(7) and 0.387(7) respectively, with U(C6A) = U(C6B) = 0.070(1) Å^2]. No further constraints were imposed on heavy atoms. The high displacement parameters of C7 indicated its trend to disordered behaviour, but the resolution of the data was not sufficient to consider the atom split over two distinct positions. Several H atoms were located by difference syntheses and refined without constraints; those bonded to C12 and C9 were subjected to a riding and to a rigid group refinement respectively. The positions of H atoms bonded to C6A and C6B were calculated but not allowed to be refined.

Discussion

The crystal structure of the title compound proves an (*E*,*E*)-configuration which is of relevance for the study of the reactivity of derivatives obtained therefrom in cyclization processes [3]. The structure is affected by disorder, one atom of the pyrrolidine ring being split over two different positions (C6A, C6B). For both of them the pyrrolidine moiety is in an envelope conformation, the ring asymmetry parameters [4,5] evidencing a pseudo-mirror plane through atom C7 in the "C6A-ring" [ΔC_s = 0.002(2); atoms N1, C5, C6A, C8 coplanar within 0.002(6) Å], and another pseudo-mirror plane through atom C5 in the "C6B-ring" [ΔC_s 0.017(3); atoms N1, C6B, C7, C8 coplanar within 0.022(9) Å]. The out-of-plane atoms (C7 and C5, respectively) lie at distances of 0.500(5) Å and 0.468(3) Å from the relevant mean planes above. The internal strain imposed by the bulky pyrrolidine moiety reflects on a short 1,5-intramolecular contact [C3···C5 3.093(4) Å] and, even more evidently, on a deviation of the C1=C2 sp^2 system from planarity, the torsion angle N1–C1–C2–C3 being as large as 22.6(4)°. Correspondingly a rather long C1=C2 bond distance [1.370(3) Å] is found.

In order to ascertain the effect of packing forces on the molecular conformation, the geometry of the title compound was optimized with quantum mechanical calculations [6] at the HF/3-21G* level (263 basis functions). Starting data were the experimental coordinates, considering in separate calculations both the "C6A" and the "C6B" forms; they converged to the same molecular model. The resulting molecular conformation shows a remarkable increase of the C1–C2–C3–C4 torsion angle [from –114.6(3)° in the crystal to –93.0° in the isolated molecule], accompanied by a general relief of the steric hindrance, the N1–C1–C2–C3 torsion angle decreasing from 22.6(4)° to a mere 0.2° in the isolated molecule. Other changes in geometry are less dramatic: the C1=C2 bond distance decreases to 1.359°A and the short C3···C5 intramolecular contact increases to 3.152 Å. These values indicate however a residual strain due to the molecular overcrowding. On the other side, in the crystal the intermolecular distances are in the normal range, the shortest contact (with respect to the sum of the involved van der Waals radii) being d(C5···O3) = 3.162(3) Å (O3 in –x, 1–y, 1–z). Therefore, we consider that crystal forces are effective in amplifying the internal strain, as observed in the experimental conformation.

Table 1. Data collection and handling.

Crystal:	pale yellow prism, size 0.22 × 0.24 × 0.48 mm
Wavelength:	Mo K_α radiation (0.71070 Å)
μ:	3.33 cm^{-1}
Diffractometer, scan mode:	Enraf-Nonius CAD4, ω
$2\theta_{max}$:	54.94°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	3886, 3886
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2596
$N(param)_{refined}$:	244
Programs:	NRCVAX [7], SHELXL-97 [8], PLATON [9]

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Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	Occ.	*x*	*y*	*z*	U_{iso}
H(1)	4*e*		0.131(3)	0.806(2)	0.723(2)	0.056
H(4)	4*e*		0.246(3)	0.524(2)	0.496(2)	0.056
H(5A)	4*e*		0.010(3)	0.551(3)	0.688(2)	0.078
H(5B)	4*e*		–0.077(3)	0.592(2)	0.607(2)	0.078
C(6A)	4*e*	0.613(7)	–0.2263(6)	0.5786(4)	0.6980(4)	0.070(1)
C(6B)	4*e*	0.387	–0.176(1)	0.5593(7)	0.7374(6)	0.070
H(6A)	4*e*	0.613	–0.2357	0.5061	0.7192	0.084(1)
H(6B)	4*e*	0.613	–0.3058	0.5917	0.6519	0.084
H(6C)	4*e*	0.387	–0.1170	0.5208	0.7832	0.084
H(6D)	4*e*	0.387	–0.2576	0.5141	0.7122	0.084
H(7A)	4*e*		–0.168(5)	0.627(3)	0.816(2)	0.116

Table 2. Comtinued.

Atom	Site	Occ.	*x*	*y*	*z*	U_{iso}
H(7B)	4*e*		–0.332(5)	0.666(3)	0.787(2)	0.116
H(8A)	4*e*		–0.218(3)	0.800(2)	0.701(2)	0.082
H(8B)	4*e*		–0.101(4)	0.794(2)	0.789(2)	0.082
H(9A)	4*e*		0.3047	0.3281	0.5604	0.086
H(9B)	4*e*		0.4639	0.3191	0.6145	0.086
H(9C)	4*e*		0.4506	0.3802	0.5264	0.086
H(11)	4*e*		0.311(3)	0.766(2)	0.356(2)	0.080
H(12)	4*e*		0.4322	0.9286	0.3255	0.108
H(13)	4*e*		0.393(4)	1.075(3)	0.400(2)	0.113
H(14)	4*e*		0.230(4)	1.073(3)	0.506(2)	0.101
H(15)	4*e*		0.095(3)	0.920(2)	0.542(2)	0.075

Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	4*e*	0.1072(3)	0.7505(2)	0.6908(2)	0.053(1)	0.043(1)	0.044(1)	–0.006(1)	0.000(1)	–0.0087(9)
C(2)	4*e*	0.2198(2)	0.7198(2)	0.6403(1)	0.046(1)	0.040(1)	0.044(1)	–0.0061(9)	0.0010(9)	0.0000(9)
C(3)	4*e*	0.2021(2)	0.6534(2)	0.5621(1)	0.047(1)	0.038(1)	0.043(1)	–0.0018(9)	0.0034(9)	–0.0004(9)
C(4)	4*e*	0.2603(3)	0.5566(2)	0.5514(2)	0.048(1)	0.045(1)	0.046(1)	–0.001(1)	0.001(1)	–0.002(1)
C(5)	4*e*	–0.0697(3)	0.5966(2)	0.6676(2)	0.068(2)	0.052(2)	0.079(2)	–0.016(1)	0.022(2)	–0.013(1)
C(7)	4*e*	–0.2365(5)	0.6582(3)	0.7694(3)	0.082(2)	0.108(3)	0.106(3)	–0.017(2)	0.044(2)	–0.003(2)
C(8)	4*e*	–0.1476(3)	0.7520(3)	0.7447(2)	0.054(2)	0.081(2)	0.070(2)	–0.004(1)	0.009(1)	–0.025(2)
C(9)	4*e*	0.3996(3)	0.3642(2)	0.5769(2)	0.062(2)	0.052(2)	0.100(2)	0.013(1)	0.002(2)	0.009(2)
C(10)	4*e*	0.1941(3)	0.8307(2)	0.4506(1)	0.053(1)	0.045(1)	0.050(1)	0.010(1)	0.002(1)	0.007(1)
C(11)	4*e*	0.2925(3)	0.8310(3)	0.3861(2)	0.063(2)	0.083(2)	0.055(2)	0.025(2)	0.007(1)	0.010(1)
C(12)	4*e*	0.3659(4)	0.9265(4)	0.3689(2)	0.064(2)	0.121(3)	0.086(2)	0.011(2)	0.021(2)	0.044(2)
C(13)	4*e*	0.3422(4)	1.0158(3)	0.4142(3)	0.070(2)	0.081(3)	0.129(3)	–0.007(2)	0.004(2)	0.051(2)
C(14)	4*e*	0.2453(4)	1.0147(2)	0.4782(3)	0.087(2)	0.046(2)	0.118(3)	–0.000(2)	0.002(2)	0.004(2)
C(15)	4*e*	0.1692(3)	0.9218(2)	0.4972(2)	0.071(2)	0.045(1)	0.071(2)	0.008(1)	0.013(1)	0.001(1)
N(1)	4*e*	–0.0255(2)	0.7047(2)	0.6980(1)	0.051(1)	0.051(1)	0.052(1)	–0.0044(9)	0.0071(8)	–0.0113(9)
N(2)	4*e*	0.3644(2)	0.7711(2)	0.6572(1)	0.051(1)	0.048(1)	0.051(1)	–0.0103(9)	0.0028(9)	–0.0008(9)
O(1)	4*e*	0.3874(2)	0.8309(2)	0.7200(1)	0.071(1)	0.074(1)	0.064(1)	–0.027(1)	0.0002(9)	–0.0203(9)
O(2)	4*e*	0.4641(2)	0.7536(2)	0.6080(1)	0.054(1)	0.073(1)	0.078(1)	–0.0142(9)	0.0168(9)	–0.011(1)
O(3)	4*e*	0.1021(3)	0.6414(2)	0.4002(1)	0.124(2)	0.054(1)	0.053(1)	0.013(1)	–0.026(1)	–0.0117(8)
O(4)	4*e*	–0.0507(2)	0.7433(2)	0.4977(1)	0.049(1)	0.066(1)	0.085(1)	–0.0009(9)	–0.0067(9)	0.010(1)
S(1)	4*e*	0.36130(9)	0.48596(6)	0.63147(4)	0.0748(5)	0.0546(4)	0.0631(4)	0.0107(3)	–0.0128(3)	0.0031(3)
S(2)	4*e*	0.09621(7)	0.71212(5)	0.47258(4)	0.0610(4)	0.0418(3)	0.0490(3)	0.0037(3)	–0.0094(3)	–0.0031(2)

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Crystal structure of diazelaatobis(tetraaquacobalt(II)) tetrahydrate, $[Co(H_2O)_4]_2(C_9H_{14}O_4)_2 \cdot 4H_2O$

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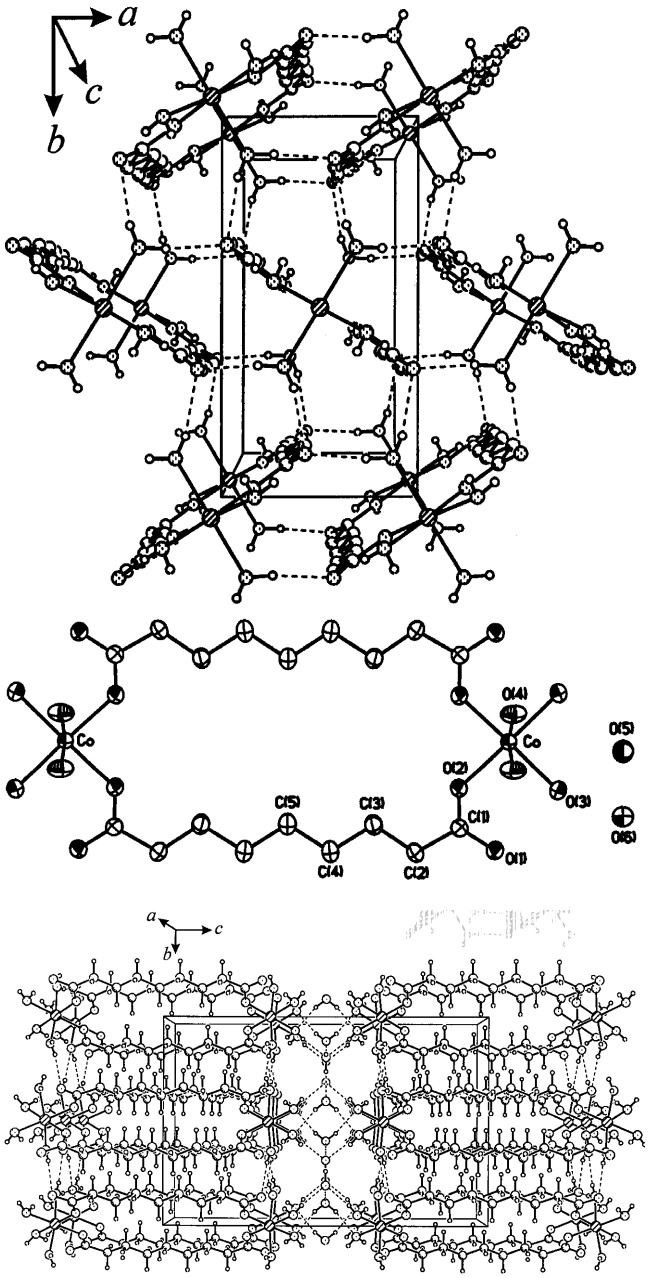

Abstract

$C_{18}H_{52}Co_2O_{20}$, orthorhombic, *Pbam* (No. 55), $a = 6.573(1)$ Å, $b = 12.533(3)$ Å, $c = 19.934(4)$ Å, $V = 1642.2$ Å^3, $Z = 2$, $R_{gt}(F) = 0.037$, $wR_{ref}(F^2) = 0.116$, $T = 293$ K.

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Source of material

Addition of 4.0 ml (1 M) NaOH to a stirred aqueous solution of $CoCl_2 \cdot 6H_2O$ (0.477 g, 2.00 mmol) in 6.0 ml H_2O produced a pale red precipitate. On standing, the initial pale red precipitate rapidly turned blue and finally dark green. After centrifugation, the dark green precipitate was added to a stirred aqueous solution of azelaic acid (0.37 g, 2.00 mmol) in 10 ml H_2O and adjusted to pH = 5.0 by dropwise addition of NaOH (1 M). The resulting mixture was then loaded into a 23 ml teflon-lined stainless steel autoclave, which was heated at 438 K for 4 days. After cooling and filtration, the filtrate was allowed to stand at room temperature and rose-colored plate-like crystals grew in two weeks (yield: ca. 24% based on the initial $CoCl_2 \cdot 6H_2O$ input). Analysis: calc. for $C_{18}H_{52}Co_2O_{20}$ (%) – C, 30.60; H, 7.42; found – C, 30.52; H, 7.59. IR data as well as TG/DTA results are included in the deposited CIF file.

Discussion

The crystal structure of the title compound consists of crystal water molecules and dinuclear cyclic $[Co(H_2O)_4]_2L_2$ complex molecules with H_2L = HOOC-$(CH_2)_7$-COOH. The complex molecules centered at the cystallographic 2*a* position are crystallographically imposed by a 2/*m* symmetry with two-fold axis through two Co atoms (figure, top). The complex molecules are generated from two $[Co(H_2O)_4]^{2+}$ moieties bridged by two azelaate anions, $(C_9H_{14}O_4)^{2-}$, forming 24-membered ring (figure, middle). The Co atoms are in octahedral sites defined by six oxygen atoms of four aqua ligands and two azelaato groups. The Co—O bond distances to the carboxylato O(2) atoms are 2.071(2) Å, practically identical with those of 2.070(2) Å to the axial aqua O(4) atoms, but significantly smaller than those of 2.143(2) Å to the equatorial aqua O(3) atoms. The cisoid O–Co–O bond angles fall in the region 85.1° – 93.1° while the transoid ones of 172.4° and 177° (2×), respectively, exhibit substantial deviation of the principal axes of the octahedral coordination from linearity. The equatorial aqua ligands are involved in strong intramolecular hydrogen bonds to the uncoordinating carboxylato O(1) atoms with d(O···O) = 2.629 Å and ∠O–H···O = 167°. The dinuclear molecules are pseudo hexagonally arranged so that each axial aqua ligand forms intermolecular hydrogen bonds to the uncoordinating carboxylato O(1) atoms of different neighbors while the uncoordinating carboxylato O(1) atoms, in turn, are each involved in intermolecular hydrogen bonds to two axial aqua ligands belonging to different neighbors, which results in formation of the hydrogen bonded thick layers parallel to the (010) plane (see figure, bottom) . On the other hand, two crystallographically distinct lattice water molecules are hydrogen bonded to one another to form zigzag chains along the [100] direction. Through hydrogen bonds, the formed chains function as connector between the hydrogen bonded thick layers.

Table 1. Data collection and handling.

Crystal:	rose-colored plate, size 0.267 × 0.311 × 0.444 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	10.85 cm^{-1}
Diffractometer, scan mode:	Bruker P4, $\theta/2\theta$
$2\theta_{max}$:	54.96°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	2593, 1947
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 1494
$N(param)_{refined}$:	98
Programs:	SHELXS-97 [1], SHELXL-97 [2]

Table 2. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{iso}
H(2A)	8*i*	0.4309	–0.2321	0.1901	0.045
H(2B)	8*i*	0.5701	–0.1310	0.1871	0.045
H(3A)	8*i*	0.1769	–0.1400	0.1304	0.045
H(3B)	8*i*	0.3186	–0.0395	0.1267	0.045
H(4A)	8*i*	0.4026	–0.2364	0.0639	0.045
H(4B)	8*i*	0.5541	–0.1401	0.0628	0.045
H(5A)	4*g*	0.3170	–0.0406	0	0.045
H(5B)	4*g*	0.1693	–0.1387	0	0.045
H(6A)	8*i*	0.1663	–0.1022	0.4277	0.054
H(6B)	8*i*	0.2932	–0.0893	0.3777	0.067
H(7A)	8*i*	0.2860	0.1382	0.3231	0.057
H(7B)	8*i*	0.1199	0.1924	0.3253	0.050
H(8)	8*i*	0.3160	0.0587	0.5329	0.061
H(9A)	4*h*	–0.0725	–0.1828	1/2	0.050
H(9B)	4*h*	0.0630	–0.2623	1/2	0.050

Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Co	4*e*	0	0	0.32924(2)	0.0269(3)	0.0291(3)	0.0245(3)	0.0048(2)	0	0
O(1)	8*i*	0.4320(2)	–0.1472(1)	0.30916(8)	0.0313(8)	0.0394(9)	0.0288(8)	0.0057(7)	–0.0002(7)	0.0018(7)
O(2)	8*i*	0.1891(3)	–0.0594(1)	0.25498(8)	0.045(1)	0.058(1)	0.0270(8)	0.0250(9)	0.0021(8)	0.0000(8)
C(1)	8*i*	0.3424(3)	–0.1166(2)	0.2559(1)	0.028(1)	0.029(1)	0.029(1)	–0.0010(9)	0.0011(9)	–0.0006(9)
C(2)	8*i*	0.4299(4)	–0.1547(2)	0.1900(1)	0.040(1)	0.047(1)	0.028(1)	0.011(1)	0.007(1)	–0.002(1)
C(3)	8*i*	0.3176(4)	–0.1169(2)	0.1278(1)	0.039(1)	0.045(1)	0.030(1)	0.002(1)	0.003(1)	–0.002(1)
C(4)	8*i*	0.4111(4)	–0.1592(2)	0.0636(1)	0.050(2)	0.051(1)	0.028(1)	0.005(1)	0.003(1)	–0.001(1)
C(5)	4*g*	0.3115(6)	–0.1179(3)	0	0.047(2)	0.048(2)	0.029(2)	0.002(2)	0	0
O(3)	8*i*	0.2082(2)	–0.0587(1)	0.40326(7)	0.0367(8)	0.0356(8)	0.0276(8)	0.0041(7)	0.0001(7)	0.0031(7)
O(4)	8*i*	0.1640(3)	0.1405(1)	0.33611(9)	0.0327(9)	0.0321(8)	0.069(1)	0.0022(7)	0.0103(9)	0.0103(8)
O(5)	4*h*	0.3287(4)	0.0979(2)	1/2	0.056(2)	0.036(1)	0.042(1)	–0.002(1)	0	0
O(6)	4*h*	0.0517(4)	–0.1932(2)	1/2	0.042(1)	0.039(1)	0.045(1)	0.002(1)	0	0

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Crystal structure of monoaqua(1,10-phenanthroline-*N*,*N*′)-succinatocobalt(II), $Co(H_2O)(C_{12}H_8N_2)(C_4H_4O_4)$

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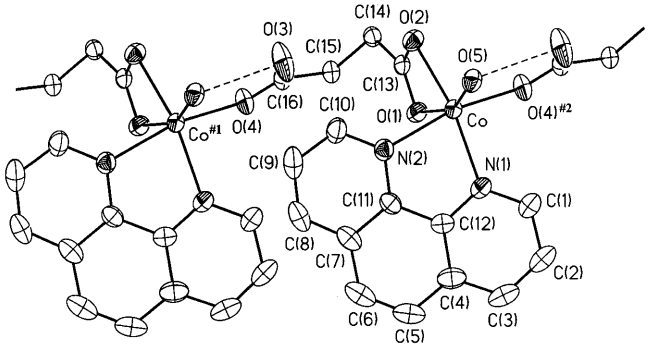

Abstract

$C_{16}H_{14}CoN_2O_5$, triclinic, $P\bar{1}$ (No. 2), a = 7.499(1) Å, b = 10.270(1) Å, c = 10.490(1) Å, α = 97.65(1)°, β = 106.80(1)°, γ = 100.57(1)°, V = 745.3 Å^3, Z = 2, $R_{gt}(F)$ = 0.058, $wR_{ref}(F^2)$ = 0.151, T = 293 K.

Source of material

Addition of 3.0 ml (1 M) Na_2CO_3 to a stirred aqueous solution of $Co(NO_3)_2 \cdot 6H_2O$ (0.734 g, 2.50 mmol) yielded red precipitate, which turned rapidly violet on standing. After centrifugation, the violet precipitate was added to a stirred mathanolic aqueous solution of phenanthroline monohydrate (0.50 g, 2.50 mmol) and succinic acid (0.30 g, 2.50 mmol) in 40 ml CH_3OH-H_2O (1:1 v/v). The resulting orange solution (pH = 6.29) was maintained at room temperature and slow evaporation affored rose-colored crystals (yield: over 85% based on the initial $Co(NO_3)_2 \cdot 6H_2O$ input).

Discussion

The crystal structure of the title compound consists of polymeric chains formulated as $^1_\infty$[$Co(H_2O)(phen)(C_4H_4O_4)_{2/2}$] resulting from $[Co(H_2O)(phen)]^{2+}$ moieties bridged by succinate anions. Within the chains, the Co atoms are in the severely distorted octahedral sites defined by two N atoms of one phenanthroline ligand and three O atoms of one aqua ligand and two succinate anions. The Co—O bond distances vary from 2.037 Å to 2.190 Å and two Co—N bond lengths are equal to 2.125 Å and 2.147 Å, respectively. The cisoid bond angles around the Co atom fall in the region 60.6° – 105.0° and the transoid ones in the region 159.1° – 165.8°. Both terminal carboxylate groups of the gauche succinate anion function in different coordination modes, one monodentately bonded to one Co atom and the other chelating one Co atom. The succinato ligands are twisted with the torsion angle of 77.2(3)° due to weak intra-chain π-π stacking interactions between phenanthroline ligands (mean interplanar distance: 3.53 Å). The aqua ligand forms an intrachain hydrogen bond to the uncoordinationg carboxylate O atoms with d(O5···O3$^{\#2}$) = 2.628 Å and ∠O5–H···O3$^{\#2}$ = 158° (#2 = x+1, y, z) and a nearly linear interchain hydrogen bond to one chelating carboxylate O atom with d(O5···O2$^{\#3}$) = 2.695 Å and ∠O5–H···O2$^{\#3}$) = 176° (#3 = $-x$+1, $-y$+1, $-z$+1). The interchain hydrogen bonds and interchain π-π stacking interactions between phenanthroline ligands (mean interplanar distances of 3.30 Å and 3.40 Å) are found to be responsible for supramolecular assembly of the polymeric chains, which extend along the [100] direction.

Table 1. Data collection and handling.

Crystal:	rose-colored block, size 0.29 × 0.38 × 0.56 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	11.82 cm^{-1}
Diffractometer, scan mode:	Bruker P4, $\theta/2\theta$
$2\theta_{max}$:	54.98°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	4197, 3418
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 3234
$N(param)_{refined}$:	228
Programs:	SHELXS-97 [1], SHELXL-97 [2]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(1)	2*i*	1.1424	0.8652	0.8609	0.059
H(2)	2*i*	1.2968	1.0891	0.9517	0.059
H(3)	2*i*	1.1237	1.2524	0.9303	0.059
H(5)	2*i*	0.8048	1.3126	0.8268	0.059
H(6)	2*i*	0.4909	1.2440	0.7029	0.059
H(8)	2*i*	0.1994	1.0503	0.5688	0.059
H(9)	2*i*	0.0797	0.8222	0.4891	0.059
H(10)	2*i*	0.2790	0.6755	0.5366	0.059
H(14A)	2*i*	0.3975	0.4116	0.8982	0.037
H(14B)	2*i*	0.2467	0.3881	0.7532	0.037
H(15A)	2*i*	0.1494	0.4785	0.9431	0.037
H(15B)	2*i*	0.2887	0.6157	0.9518	0.037
HA	2*i*	0.696(7)	0.610(5)	0.465(5)	0.06(1)
HB	2*i*	0.856(7)	0.622(5)	0.550(5)	0.07(2)

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Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Co	2*i*	0.71530(4)	0.69178(3)	0.71243(3)	0.0225(2)	0.0266(3)	0.0301(3)	0.0054(2)	0.0061(2)	0.0054(1)
N(1)	2*i*	0.8862(3)	0.8925(2)	0.7818(2)	0.030(1)	0.032(1)	0.030(1)	0.0013(8)	0.0054(8)	0.0056(8)
N(2)	2*i*	0.5133(3)	0.8100(2)	0.6388(2)	0.029(1)	0.033(1)	0.035(1)	0.0074(9)	0.0080(9)	0.0105(9)
C(1)	2*i*	1.0718(4)	0.9309(3)	0.8498(3)	0.033(1)	0.043(2)	0.040(1)	0.000(1)	0.008(1)	0.008(1)
C(2)	2*i*	1.1658(5)	1.0657(4)	0.9053(3)	0.040(2)	0.050(2)	0.041(2)	–0.012(1)	0.005(1)	0.007(1)
C(3)	2*i*	1.0637(5)	1.1624(3)	0.8908(3)	0.060(2)	0.036(1)	0.037(1)	–0.012(1)	0.012(1)	0.001(1)
C(4)	2*i*	0.8674(5)	1.1262(3)	0.8161(3)	0.061(2)	0.032(1)	0.033(1)	0.004(1)	0.019(1)	0.005(1)
C(5)	2*i*	0.7509(6)	1.2211(3)	0.7917(4)	0.080(3)	0.029(1)	0.053(2)	0.012(2)	0.027(2)	0.003(1)
C(6)	2*i*	0.5636(6)	1.1799(3)	0.7183(4)	0.082(3)	0.042(2)	0.061(2)	0.033(2)	0.036(2)	0.016(2)
C(7)	2*i*	0.4734(5)	1.0401(3)	0.6636(3)	0.055(2)	0.043(2)	0.043(1)	0.026(1)	0.023(1)	0.017(1)
C(8)	2*i*	0.2791(5)	0.9909(4)	0.5871(4)	0.049(2)	0.064(2)	0.061(2)	0.035(2)	0.024(2)	0.027(2)
C(9)	2*i*	0.2083(5)	0.8559(4)	0.5400(4)	0.033(2)	0.073(2)	0.063(2)	0.021(2)	0.015(1)	0.030(2)
C(10)	2*i*	0.3299(4)	0.7678(3)	0.5685(3)	0.031(1)	0.045(2)	0.048(2)	0.007(1)	0.006(1)	0.016(1)
C(11)	2*i*	0.5854(4)	0.9440(3)	0.6868(3)	0.039(1)	0.032(1)	0.032(1)	0.014(1)	0.015(1)	0.0113(9)
C(12)	2*i*	0.7853(4)	0.9883(3)	0.7627(2)	0.041(1)	0.029(1)	0.027(1)	0.005(1)	0.013(1)	0.0062(9)
O(1)	2*i*	0.5653(3)	0.6604(2)	0.8607(2)	0.0297(9)	0.0306(9)	0.0330(9)	0.0031(7)	0.0081(7)	0.0015(7)
O(2)	2*i*	0.5034(3)	0.5087(2)	0.6771(2)	0.0302(9)	0.0345(9)	0.0317(9)	0.0020(7)	0.0118(7)	0.0022(7)
C(13)	2*i*	0.4726(3)	0.5483(2)	0.7869(2)	0.021(1)	0.028(1)	0.029(1)	0.0076(8)	0.0037(8)	0.0067(9)
C(14)	2*i*	0.3295(3)	0.4569(2)	0.8309(3)	0.025(1)	0.029(1)	0.032(1)	0.0086(9)	0.0086(9)	0.0086(9)
C(15)	2*i*	0.2071(3)	0.5334(3)	0.8905(2)	0.024(1)	0.034(1)	0.029(1)	0.0096(9)	0.0081(9)	0.0084(9)
C(16)	2*i*	0.0501(4)	0.5692(3)	0.7828(3)	0.025(1)	0.036(1)	0.035(1)	0.0093(9)	0.0078(9)	0.012(1)
O(3)	2*i*	0.0517(4)	0.5530(4)	0.6642(2)	0.057(2)	0.121(2)	0.037(1)	0.059(2)	0.019(1)	0.027(1)
O(4)	2*i*	–0.0708(3)	0.6167(2)	0.8241(2)	0.032(1)	0.049(1)	0.037(1)	0.0211(9)	0.0109(8)	0.0131(8)
O(5)	2*i*	0.7792(3)	0.6602(2)	0.5319(2)	0.0290(9)	0.040(1)	0.0293(9)	0.0065(8)	0.0056(7)	0.0049(8)

Acknowledgments. The project was supported by the National Natural Science Foundation of China (20072022), the Excellent young Teachers Program of Moe, P. R. China (C982302), the Zhejiang Provincial Natural Science Foundation (C99034), the Ningbo Municipal Key Doctor's Funds (2003A61014), and the Ningbo Municipal Natural Science Foundation (01J201301-1). The author also thank Mr. Jian-Li Lin for X-ray data collection.

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Crystal structure of dipimelato-bis(1,10-phenanthroline-*N*,*N*′)dilead(II) monohydrate, $Pb_2(C_{12}H_8N_2)_2(C_7H_{10}O_4)_2 \cdot H_2O$

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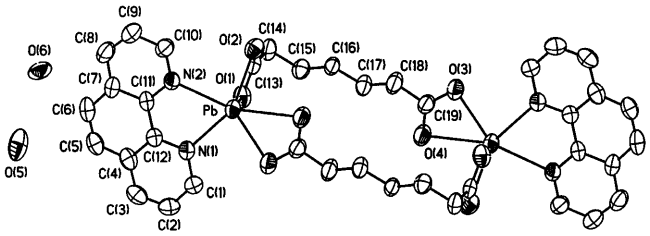

Abstract

$C_{19}H_{20}N_2O_5Pb$, triclinic, $P\bar{1}$ (No. 2), a = 7.488(2) Å, b = 11.543(2) Å, c = 11.742(2) Å, α = 83.50(3)°, β = 82.54(3)°, γ = 81.94(3)°, V = 991.7 Å^3, Z = 2, $R_{gt}(F)$ = 0.046, $wR_{ref}(F^2)$ = 0.128, T = 293 K.

Source of material

Addition of 2.0 ml (1 M) Na_2CO_3 to a stirred aqueous solution of $Pb(NO_3)_2$ (0.168 g, 0.51 mmol) in 5.0 ml H_2O produced white precipitate, which was separated out by centrifugation and then added to a stirred methanolic aqueous solution of phenanthroline monohydrate (0.102 g, 0.51 mmol) and pimelic acid (0.083 g, 0.52 mmol) in 20 ml CH_3OH–H_2O (1:1 v/v). The mixture was stirred for 30 min and the formed suspension was filtered off. The filtrate (pH = 5.90) was allowed to stand at room temperature and slow evaporation afforded a few colorless needle-like crystals.

Discussion

The title compound consists of hydrogen bonded H_2O molecules and dinuclear $[Pb_2(phen)_2(C_7H_{10}O_4)_2]$ complex molecules centered at the crystallographic 1*f* position. Within the complex molecules, the Pb atoms are coordinated by two N atoms of one phen ligand and four O atoms of two chelating carboxylate groups of different bis-chelating pimelato ligands with d(Pb—N) = 2.603 Å, 2.628 Å and d(Pb—O) = 2.304 Å – 2.662 Å. Due to the lone pair effect of the Pb atom, the coordination polyhedra can be roughly viewed as mono-capped square pyramids. In the (001) plane, the dinuclear complex molecules are so arranged that the phen ligands are each sandwiched by two symmetry-related phen neighbors. The mean interplanar distance of 3.44 Å suggests that the intermolecular π-π stacking interactions are responsible for supramolecular assembly of the dinuclear complex molecules into layers. The formed layers are further assembled by intermolecular C–H···O hydrogen bonds to generate 3D framework with the hydrogen bonded H_2O molecules located in 1D tunnels extending along the [100] direction. The bis-chelating pimelato ligands are twisted with the torsion angle of –65° for C13–C14–C15–C16 chain.

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Table 1. Data collection and handling.

Crystal:	colorless needle, size 0.133 × 0.222 × 0.333 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	85.37 cm^{-1}
Diffractometer, scan mode:	Bruker P4, $\theta/2\theta$
$2\theta_{max}$:	55°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	5584, 4540
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 3787
$N(param)_{refined}$:	256
Programs:	SHELXS-97 [1], SHELXL-97 [2]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	Occ.	x	y	z	U_{iso}
H(1)	2*i*		0.5106	0.5400	0.2750	0.08
H(2)	2*i*		0.6342	0.3454	0.2779	0.08
H(3)	2*i*		0.7967	0.2741	0.1183	0.08
H(5)	2*i*		0.9417	0.3152	–0.0871	0.08
H(6)	2*i*		0.9762	0.4393	–0.2482	0.08
H(8)	2*i*		0.9169	0.6450	–0.3502	0.08
H(9)	2*i*		0.7834	0.8338	–0.3395	0.08
H(10)	2*i*		0.6301	0.8948	–0.1680	0.08
H(14A)	2*i*		0.9531	1.0447	0.1171	0.10
H(14B)	2*i*		1.0486	0.9151	0.1337	0.10
H(15A)	2*i*		0.9103	0.8993	0.3272	0.10
H(15B)	2*i*		1.0424	0.9953	0.3050	0.10
H(16A)	2*i*		0.7934	1.1425	0.2917	0.10
H(16B)	2*i*		0.6613	1.0463	0.3143	0.10
H(17A)	2*i*		0.7478	0.9976	0.4992	0.10
H(17B)	2*i*		0.8780	1.0947	0.4765	0.10
H(18A)	2*i*		0.5019	1.1437	0.4843	0.10
H(18B)	2*i*		0.6353	1.2385	0.4691	0.10
H(19A)	2*i*	0.50	0.2935	0.3341	–0.3973	0.05
H(19B)	2*i*	0.50	0.1925	0.4330	–0.4580	0.05
H(20A)	2*i*	0.50	0.2531	0.6374	–0.5799	0.05
H(20B)	2*i*	0.50	0.0660	0.6062	–0.5500	0.05

Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	Occ.	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pb	2*i*		0.47110(4)	0.80879(2)	0.11382(2)	0.0481(2)	0.0527(2)	0.0446(2)	0.0020(1)	–0.0034(1)	–0.0110(1)
N(1)	2*i*		0.6092(9)	0.5888(6)	0.1155(6)	0.057(4)	0.051(3)	0.048(3)	–0.006(3)	–0.005(3)	–0.010(3)
N(2)	2*i*		0.661(1)	0.7417(6)	–0.0773(5)	0.064(4)	0.049(3)	0.043(3)	–0.003(3)	–0.006(3)	–0.008(3)
C(1)	2*i*		0.581(1)	0.5132(8)	0.2095(8)	0.077(6)	0.056(5)	0.051(4)	–0.009(4)	–0.004(4)	–0.001(4)
C(2)	2*i*		0.653(2)	0.3956(9)	0.2110(9)	0.095(7)	0.060(5)	0.060(5)	–0.011(5)	–0.010(5)	0.011(4)
C(3)	2*i*		0.751(2)	0.3534(8)	0.1170(9)	0.076(6)	0.044(4)	0.085(7)	0.002(4)	–0.016(5)	0.000(4)
C(4)	2*i*		0.785(1)	0.4296(7)	0.0164(8)	0.056(5)	0.051(4)	0.070(5)	–0.001(4)	–0.020(4)	–0.016(4)
C(5)	2*i*		0.888(1)	0.3928(8)	–0.0862(9)	0.061(5)	0.050(4)	0.081(6)	0.007(4)	–0.009(4)	–0.021(4)
C(6)	2*i*		0.910(1)	0.4670(9)	–0.1820(9)	0.063(5)	0.070(6)	0.075(6)	0.005(4)	–0.005(5)	–0.037(5)
C(7)	2*i*		0.835(1)	0.5858(8)	–0.1841(7)	0.055(5)	0.065(5)	0.049(4)	–0.002(4)	0.000(3)	–0.021(4)
C(8)	2*i*		0.852(1)	0.668(1)	–0.2815(8)	0.067(6)	0.088(7)	0.052(5)	–0.012(5)	0.012(4)	–0.015(4)
C(9)	2*i*		0.774(1)	0.780(1)	–0.2745(7)	0.076(6)	0.081(6)	0.044(4)	–0.012(5)	–0.006(4)	0.000(4)
C(10)	2*i*		0.680(1)	0.8166(8)	–0.1710(7)	0.072(6)	0.061(5)	0.049(4)	–0.002(4)	–0.001(4)	–0.002(4)
C(11)	2*i*		0.733(1)	0.6277(6)	–0.0813(6)	0.046(4)	0.046(4)	0.049(4)	–0.001(3)	–0.009(3)	–0.017(3)
C(12)	2*i*		0.706(1)	0.5479(6)	0.0193(6)	0.044(4)	0.046(4)	0.048(4)	–0.001(3)	–0.010(3)	–0.008(3)
O(1)	2*i*		0.7561(8)	0.8162(6)	0.1645(5)	0.054(3)	0.064(4)	0.066(4)	0.005(3)	–0.013(3)	–0.018(3)
O(2)	2*i*		0.6679(9)	0.9846(6)	0.0653(5)	0.061(4)	0.075(4)	0.053(3)	0.001(3)	–0.010(3)	–0.004(3)
C(13)	2*i*		0.777(1)	0.9235(7)	0.1231(6)	0.053(4)	0.058(4)	0.037(3)	0.002(4)	–0.001(3)	–0.018(3)
C(14)	2*i*		0.941(1)	0.9676(9)	0.1574(7)	0.052(5)	0.072(5)	0.056(5)	–0.006(4)	0.004(4)	–0.027(4)
C(15)	2*i*		0.928(1)	0.9757(8)	0.2871(7)	0.059(5)	0.066(5)	0.046(4)	–0.001(4)	–0.014(4)	–0.007(4)
C(16)	2*i*		0.776(1)	1.0661(7)	0.3320(6)	0.065(5)	0.053(4)	0.037(3)	0.000(4)	–0.004(3)	–0.008(3)
C(17)	2*i*		0.764(1)	1.0745(8)	0.4593(7)	0.065(5)	0.064(5)	0.044(4)	0.003(4)	–0.009(4)	–0.015(3)
C(18)	2*i*		0.615(2)	1.1611(9)	0.5060(7)	0.093(7)	0.071(6)	0.044(4)	0.014(5)	0.000(4)	–0.012(4)
C(19)	2*i*		0.593(1)	1.1664(8)	0.6358(7)	0.064(5)	0.061(5)	0.046(4)	0.000(4)	0.004(4)	–0.007(4)
O(3)	2*i*		0.565(1)	1.2651(6)	0.6723(6)	0.111(6)	0.060(4)	0.054(3)	0.006(4)	0.010(4)	–0.013(3)
O(4)	2*i*		0.603(1)	1.0732(6)	0.7000(5)	0.077(4)	0.066(4)	0.049(3)	0.008(3)	0.000(3)	–0.010(3)
O(5)	2*i*	0.50	0.185(2)	0.352(2)	–0.420(1)	0.072(9)	0.13(1)	0.076(9)	0.042(9)	–0.023(8)	–0.039(9)
O(6)	2*i*	0.50	0.177(2)	0.597(2)	–0.539(1)	0.09(1)	0.11(1)	0.063(8)	–0.060(9)	0.013(7)	–0.001(7)

Acknowledgments. The project was supported by the National Natural Science Foundation of China (20072022), the Excellent young Teachers Program of Moe, P. R. China (C982302), the Zhejiang Provincial Natural Science Foundation (C99034), the Ningbo Municipal Key Doctor's Funds (2003A61014), and the Ningbo Municipal Natural Science Foundation (01J201301-1). The author also thank Mr. Jian-Li Lin for X-ray data collection.

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2. Sheldrick, G. M.: SHELXL-97. Program for the refinement of crystal structures. University of Göttingen, Germany 1997.

Crystal structure of diaqua(2,2′-bipyridine-*N*,*N*′)sulfatomanganese(II) monohydrate, $Mn(H_2O)_2(C_{10}H_8N_2)(SO_4) \cdot H_2O$

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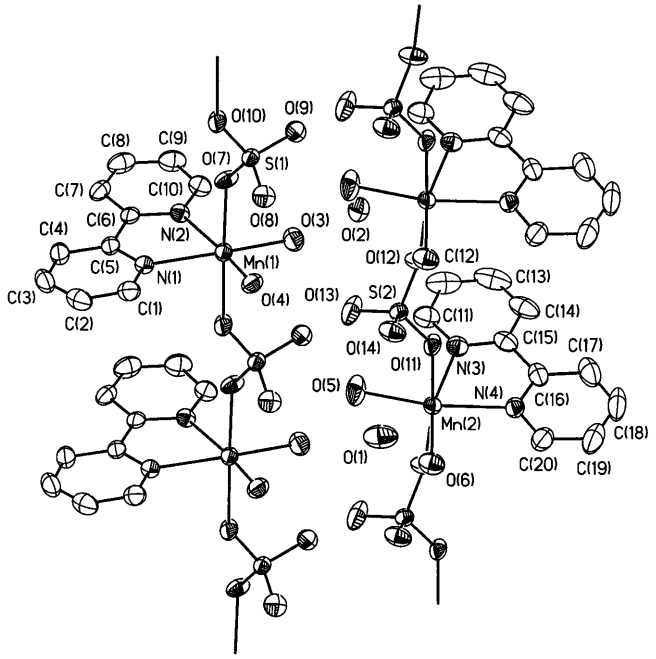

Abstract

$C_{10}H_{14}MnN_2O_7S$, monoclinic, $P12_1/c1$ (No. 14), $a = 20.924(3)$ Å, $b = 6.667(2)$ Å, $c = 20.107(2)$ Å, $\beta = 95.21(1)°$, $V = 2793.4$ Å^3, $Z = 8$, $R_{gt}(F) = 0.047$, $wR_{ref}(F^2) = 0.107$, $T = 293$ K.

Source of material

After 0.10 g 2,2′-bipyridine and 0.09 g glutaric acid were dissolved in a mixture consisting of 10 ml CH_3OH and 10 ml H_2O, 0.12 g $MnSO_4 \cdot 2H_2O$ was added and the mixture was stirred for ca. 30 min. Subsequently, 1.0 ml (1 M) Na_2CO_3 was dropped to the resulting suspension (pH = 4.1), yielding an orange solution (pH = 6.6). The resulting solution was then maintained at 328 K and turned turbid rapidly. After filtration, the filtrate was allowed to stand at room temperature and slow evaporation for several months afforded a few yellow plate-like crystals.

Discussion

The title compound is composed of lattice H_2O molecules and polymeric chains formulated as $^1_\infty[Mn(H_2O)_2(bpy)(SO_4)_{2/2}]$ resulting from the $[Mn(H_2O)_2(bpy)]^{2+}$ moieties bridged by bidentate sulfato groups. Within the crystal structure, two crystallographically distinct polymeric chains extend along the [010] direction. The Mn atoms are octahedrally coordinated by two N atoms of one 2,2′-bipyridine ligand and four O atoms of two aqua ligands and two sulfato groups with d(Mn—N) = 2.220 Å – 2.267 Å and d(Mn—O) = 2.124 Å – 2.225 Å. The cisoid and transoid bond angles around the Mn atoms fall in the regions 72.5° – 97.9° and 163.3° – 175.0°, respectively. The polymeric chains possess relatively strong intrachain hydrogen bonds between aqua ligands and uncoordinating sulfato O atoms with d(O···O) = 2.674 Å – 2.769 Å and ∠O–H···O = 153° – 166°. Two crystallographically equivalent polymeric chains are paired with the chelating bpy ligands interdigitating to generate bi-chains, which are found to be stabilized by significant interchain π-π stacking interactions between bpy ligands (mean interplanar distance: 3.30 Å). Through the interchain hydrogen bonds, the crystallographically independent bi-chains are interlinked to form 3D framework with the lattice H_2O molecules located in the tunnels parallel to [010]. Due to site and coordination effects, the bidentate sulfato groups exhibit slight deviation from T_d symmetry (d(S—O) = 1.464 Å – 1.475 Å, ∠O–S–O = 108.6° – 111.0°).

Table 1. Data collection and handling.

Crystal:	yellow plate, size 0.133 × 0.356 × 0.400 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	11.29 cm^{-1}
Diffractometer, scan mode:	Bruker P4, $\theta/2\theta$
$2\theta_{max}$:	55°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	8091, 6402
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 4367
$N(param)_{refined}$:	492
Programs:	SHELXS-97 [1], SHELXL-97 [2]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(1)	4*e*	0.013(2)	1.158(5)	–0.036(2)	0.019(8)
H(2)	4*e*	–0.095(2)	1.165(7)	–0.055(2)	0.05(1)
H(3)	4*e*	–0.151(2)	1.141(6)	–0.158(2)	0.05(1)
H(4)	4*e*	–0.090(2)	1.123(7)	–0.247(2)	0.06(1)
H(7)	4*e*	–0.030(2)	1.156(6)	–0.328(2)	0.03(1)
H(8)	4*e*	0.043(2)	1.151(6)	–0.413(2)	0.04(1)
H(9)	4*e*	0.152(2)	1.148(8)	–0.379(3)	0.08(2)
H(10)	4*e*	0.188(2)	1.121(6)	–0.260(2)	0.04(1)
H(11)	4*e*	0.347(2)	0.796(6)	–0.042(2)	0.04(1)
H(12)	4*e*	0.403(2)	0.814(7)	–0.124(2)	0.05(1)
H(13)	4*e*	0.520(3)	0.815(8)	–0.110(3)	0.08(2)
H(14)	4*e*	0.563(3)	0.751(9)	0.000(3)	0.09(2)
H(17)	4*e*	0.593(2)	0.721(8)	0.099(2)	0.07(2)
H(18)	4*e*	0.633(2)	0.644(7)	0.208(2)	0.06(1)
H(19)	4*e*	0.557(2)	0.570(8)	0.283(3)	0.08(2)
H(20)	4*e*	0.447(2)	0.575(7)	0.248(2)	0.06(1)
HA(O1)	4*e*	0.245(2)	0.913(8)	0.293(3)	0.06(2)
HB(O1)	4*e*	0.257(3)	1.00(1)	0.240(3)	0.09(3)

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Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
HA(O2)	4*e*	0.292(3)	1.456(9)	–0.060(3)	0.08(2)
HB(O2)	4*e*	0.305(2)	1.331(8)	–0.015(3)	0.06(2)
HA(O3)	4*e*	0.257(2)	1.157(8)	–0.102(2)	0.06(2)
HB(O3)	4*e*	0.245(2)	0.966(7)	–0.131(2)	0.04(1)
HA(O4)	4*e*	0.149(2)	1.335(9)	–0.010(2)	0.07(2)

Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
HB(O4)	4*e*	0.174(2)	1.148(8)	0.006(2)	0.06(2)
HA(O5)	4*e*	0.256(2)	0.848(8)	0.060(2)	0.05(2)
HB(O5)	4*e*	0.238(2)	0.694(7)	0.044(2)	0.04(1)
HA(O6)	4*e*	0.302(3)	0.706(9)	0.227(3)	0.08(2)
HB(O6)	4*e*	0.309(3)	0.516(9)	0.211(3)	0.08(2)

Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mn(1)	4*e*	0.13251(2)	1.13569(8)	–0.12255(3)	0.0263(3)	0.0217(3)	0.0305(3)	–0.0002(2)	–0.0016(2)	–0.0009(2)
Mn(2)	4*e*	0.35502(2)	0.68197(8)	0.11501(3)	0.0265(3)	0.0245(3)	0.0338(3)	–0.0005(2)	0.0020(2)	0.0001(2)
S(1)	4*e*	0.16578(4)	1.6362(1)	–0.09110(4)	0.0298(4)	0.0193(4)	0.0310(4)	0.0005(3)	–0.0041(3)	–0.0019(4)
S(2)	4*e*	0.31072(4)	1.1861(1)	0.12092(4)	0.0296(4)	0.0211(4)	0.0363(5)	0.0014(3)	0.0012(3)	0.0006(4)
N(1)	4*e*	0.0254(1)	1.1471(4)	–0.1316(1)	0.030(1)	0.026(2)	0.031(2)	–0.001(1)	0.002(1)	0.001(1)
N(2)	4*e*	0.1010(1)	1.1293(4)	–0.2310(1)	0.032(2)	0.028(2)	0.027(1)	–0.004(1)	0.003(1)	–0.002(1)
N(3)	4*e*	0.4134(1)	0.7403(5)	0.0273(2)	0.040(2)	0.029(2)	0.034(2)	–0.004(1)	0.004(1)	–0.003(1)
N(4)	4*e*	0.4588(1)	0.6590(5)	0.1524(2)	0.031(2)	0.028(2)	0.045(2)	0.001(1)	–0.001(1)	–0.001(1)
C(1)	4*e*	–0.0098(2)	1.1545(6)	–0.0792(2)	0.042(2)	0.037(2)	0.040(2)	0.002(2)	0.008(2)	0.006(2)
C(2)	4*e*	–0.0761(2)	1.1537(7)	–0.0864(3)	0.044(2)	0.034(2)	0.068(3)	0.004(2)	0.027(2)	0.001(2)
C(3)	4*e*	–0.1067(2)	1.1417(7)	–0.1494(3)	0.027(2)	0.037(2)	0.087(3)	–0.001(2)	0.006(2)	0.005(2)
C(4)	4*e*	–0.0715(2)	1.1341(6)	–0.2041(2)	0.032(2)	0.035(2)	0.052(2)	–0.001(2)	–0.004(2)	0.002(2)
C(5)	4*e*	–0.0047(2)	1.1383(5)	–0.1935(2)	0.029(2)	0.019(2)	0.044(2)	0.002(1)	–0.001(2)	0.002(2)
C(6)	4*e*	0.0372(2)	1.1356(5)	–0.2491(2)	0.033(2)	0.017(2)	0.037(2)	–0.000(1)	–0.003(1)	0.003(2)
C(7)	4*e*	0.0140(2)	1.1397(6)	–0.3166(2)	0.045(2)	0.029(2)	0.034(2)	0.001(2)	–0.012(2)	0.002(2)
C(8)	4*e*	0.0563(2)	1.1420(7)	–0.3647(2)	0.075(3)	0.039(2)	0.029(2)	–0.002(2)	–0.005(2)	0.001(2)
C(9)	4*e*	0.1213(2)	1.1366(7)	–0.3457(2)	0.066(3)	0.047(3)	0.030(2)	–0.005(2)	0.010(2)	0.001(2)
C(10)	4*e*	0.1419(2)	1.1300(6)	–0.2794(2)	0.041(2)	0.035(2)	0.037(2)	–0.002(2)	0.009(2)	–0.002(2)
C(11)	4*e*	0.3877(2)	0.7776(7)	–0.0347(2)	0.061(3)	0.040(2)	0.041(2)	–0.009(2)	0.006(2)	–0.000(2)
C(12)	4*e*	0.4257(3)	0.8044(8)	–0.0875(3)	0.112(5)	0.041(3)	0.041(3)	–0.011(3)	0.012(3)	–0.002(2)
C(13)	4*e*	0.4905(3)	0.7916(7)	–0.0757(3)	0.105(5)	0.035(3)	0.062(3)	–0.013(3)	0.048(3)	–0.011(2)
C(14)	4*e*	0.5168(3)	0.7569(7)	–0.0128(3)	0.062(3)	0.030(2)	0.082(4)	–0.005(2)	0.040(3)	–0.006(2)
C(15)	4*e*	0.4774(2)	0.7314(5)	0.0387(2)	0.043(2)	0.022(2)	0.050(2)	–0.002(2)	0.017(2)	–0.007(2)
C(16)	4*e*	0.5028(2)	0.6938(6)	0.1090(2)	0.029(2)	0.022(2)	0.068(3)	0.002(2)	0.005(2)	–0.007(2)
C(17)	4*e*	0.5679(2)	0.6917(8)	0.1296(3)	0.034(2)	0.048(3)	0.100(4)	0.000(2)	0.010(3)	–0.008(3)
C(18)	4*e*	0.5878(2)	0.6500(8)	0.1949(3)	0.037(3)	0.058(3)	0.117(5)	0.008(2)	–0.027(3)	–0.012(3)
C(19)	4*e*	0.5435(3)	0.6082(8)	0.2381(3)	0.058(3)	0.057(3)	0.073(3)	0.011(3)	–0.028(3)	–0.005(3)
C(20)	4*e*	0.4792(2)	0.6158(7)	0.2162(2)	0.049(2)	0.044(3)	0.050(3)	0.002(2)	–0.008(2)	0.004(2)
O(1)	4*e*	0.2476(2)	0.9042(7)	0.2542(2)	0.093(3)	0.056(2)	0.056(2)	0.006(2)	0.036(2)	0.007(2)
O(2)	4*e*	0.3035(1)	1.3343(5)	–0.0546(2)	0.039(2)	0.050(2)	0.044(2)	0.005(1)	0.003(1)	–0.001(2)
O(3)	4*e*	0.2330(1)	1.0828(5)	–0.1363(2)	0.034(1)	0.032(2)	0.063(2)	0.002(1)	0.003(1)	–0.003(2)
O(4)	4*e*	0.1437(1)	1.1937(5)	–0.0146(1)	0.044(2)	0.035(2)	0.035(1)	0.001(1)	–0.005(1)	0.006(1)
O(5)	4*e*	0.2626(2)	0.7333(6)	0.0650(2)	0.046(2)	0.039(2)	0.085(3)	0.001(2)	–0.029(2)	–0.021(2)
O(6)	4*e*	0.3267(2)	0.6241(6)	0.2144(2)	0.054(2)	0.036(2)	0.048(2)	–0.003(2)	0.015(1)	–0.002(2)
O(7)	4*e*	0.1415(1)	1.4642(4)	–0.1315(1)	0.058(2)	0.019(1)	0.029(1)	–0.002(1)	–0.011(1)	–0.001(1)
O(8)	4*e*	0.1645(1)	1.5889(4)	–0.0199(1)	0.047(2)	0.037(2)	0.033(1)	–0.005(1)	0.002(1)	–0.007(1)
O(9)	4*e*	0.2325(1)	1.6783(4)	–0.1051(1)	0.033(1)	0.034(2)	0.054(2)	0.002(1)	0.005(1)	0.006(1)
O(10)	4*e*	0.1256(1)	1.8122(4)	–0.1087(2)	0.031(1)	0.020(1)	0.075(2)	0.003(1)	–0.011(1)	0.002(1)
O(11)	4*e*	0.3533(1)	1.0119(4)	0.1313(1)	0.029(1)	0.023(1)	0.048(2)	0.004(1)	–0.007(1)	–0.004(1)
O(12)	4*e*	0.3471(1)	1.3568(4)	0.0965(1)	0.064(2)	0.024(1)	0.053(2)	–0.003(1)	0.025(1)	0.002(1)
O(13)	4*e*	0.2586(1)	1.1356(5)	0.0701(2)	0.053(2)	0.040(2)	0.073(2)	0.011(2)	–0.033(2)	–0.009(2)
O(14)	4*e*	0.2854(1)	1.2420(4)	0.1842(1)	0.053(2)	0.035(2)	0.049(2)	–0.003(1)	0.024(1)	–0.002(1)

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Crystal structure of tetraaqua(μ-4,4′-bipyridine-*N*,*N*′)zinc(II) succinate tetrahydrate, $Zn(H_2O)_4(C_{10}H_8N_2)(C_4H_4O_4)\cdot 4H_2O$

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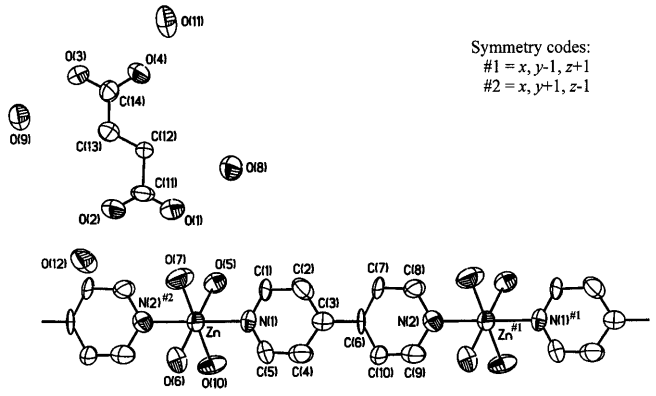

Abstract

$C_{14}H_{28}N_2O_{12}Zn$, triclinic, *P*1 (No. 1), $a = 7.189(1)$ Å, $b = 7.764(2)$ Å, $c = 9.843(2)$ Å, $\alpha = 79.16(3)°$, $\beta = 87.80(3)°$, $\gamma = 71.29(3)°$, $V = 510.9$ Å^3, $Z = 1$, $R_{gt}(F) = 0.032$, $wR_{ref}(F^2) = 0.095$, $T = 293$ K.

Source of material

Addition of 1.0 ml (1 M) Na_2CO_3 to a stirred aqueous solution of $Zn(NO_3)_2\cdot 6H_2O$ (0.194 g, 0.652 mmol) yielded white precipitate, which was centrifugated and then added to a stirred methanolic aqueous solution of 4,4′-bipyridine (0.124 g, 0.645 mmol) and succinic acid (0.078 g, 0.661 mmol) in 20 ml CH_3OH–H_2O (1:1 v/v). The resulting suspension was filtered off and the filtrate (pH = 5.24) was allowed to stand at room temperature. Slow evaporation for 10 days afforded a few yellowish needle-like crystals.

Discussion

The crystal structure of the title compound is made up from lattice H_2O molecules, succinate anions and cationic chains formulated as $^1_\infty[Zn(H_2O)_4(4,4'\text{-bpy})_{2/2})]^{2+}$ generated from $[Zn(H_2O)_4]^{2+}$ moieties linked by 4,4′-bipyridine ligands. The cationic chains propagate along the [01$\bar{1}$] direction and are arranged in layers parallel to (100). The Zn atoms are coordinated by four aqua oxygen atoms and two nitrogen atoms of different 4,4′-bipyridine ligands to form trivially distorted ZnN_2O_4 octahedra with d(Zn—N) = 2.132 Å and d(Zn—O) = 2.061 Å – 2.185 Å. The cisoid bond angles around Zn atoms vary from 88.6° to 92.5° and the transoid ones fall in the region 178.1° – 179.7°. Around the connecting C—C bond, the two component rings of the bismonodentate 4,4′-bipyridine are twisted by 1.6(3)° with respect to each other. The succinate anions adopt *anti* conformation with all non-hydrogen atoms coplanar. The lattice H_2O molecules are hydrogen bonded to the succinate anions to form ribbon-like anionic chains with d(O···O) = 2.667 Å – 2.974 Å and ∠O–H···O = 162° – 179°. The resulting hydrogen bonded anionic chains extend along the [010] direction and arranged in layers parallel to (100). The cationic and anionic layers are alternatively disposed and interlinked by extensive hydrogen bonds between them with d(O···O) = 2.622 Å – 2.857 Å and ∠O–H···O = 167° – 179°.

Table 1. Data collection and handling.

Crystal:	yellow prism, size 0.178 × 0.400 × 0.511 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	12.66 cm^{-1}
Diffractometer, scan mode:	Bruker P4, $\theta/2\theta$
$2\theta_{max}$:	60°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	3606, 3606
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 3319
$N(param)_{refined}$:	266
Programs:	SHELXS-97 [1], SHELXL-97 [2]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	*x*	*y*	*z*	U_{iso}
H(1)	1*a*	0.2189	0.5082	0.9158	0.041
H(2)	1*a*	0.1769	0.3040	1.1078	0.041
H(4)	1*a*	0.0097	0.7289	1.3072	0.041
H(5)	1*a*	0.0143	0.9172	1.1038	0.041
H(7)	1*a*	0.1843	0.1220	1.2881	0.041
H(8)	1*a*	0.1610	–0.0764	1.4896	0.041
H(9)	1*a*	–0.0255	0.3458	1.6856	0.041
H(10)	1*a*	–0.0363	0.5490	1.4868	0.041
H(12A)	1*a*	0.6810	0.3070	0.4272	0.031
H(12B)	1*a*	0.4651	0.3320	0.3843	0.031
H(13A)	1*a*	0.4947	0.5279	0.1795	0.031
H(13B)	1*a*	0.7106	0.5020	0.2223	0.031
H(14A)	1*a*	–0.1570	0.7429	0.7748	0.050
H(14B)	1*a*	–0.1545	0.8380	0.6369	0.050
H(15A)	1*a*	0.3296	1.0082	0.9692	0.050
H(15B)	1*a*	0.3263	1.0988	0.8321	0.050
H(16A)	1*a*	0.3963	0.6828	0.6865	0.050
H(16B)	1*a*	0.4433	0.7358	0.8049	0.050
H(17A)	1*a*	0.5233	0.0985	0.6233	0.050
H(17B)	1*a*	0.4705	0.2895	0.6423	0.050
H(18A)	1*a*	0.6540	0.7363	–0.0153	0.050
H(18B)	1*a*	0.7172	0.5629	–0.0401	0.050
H(19A)	1*a*	–0.2188	1.1577	0.9180	0.050
H(19B)	1*a*	–0.2743	1.1122	0.8036	0.050
H(20A)	1*a*	0.5118	–0.1456	0.2000	0.050
H(20B)	1*a*	0.5843	–0.0371	0.1378	0.050
H(21A)	1*a*	0.6752	0.9982	0.4001	0.050
H(21B)	1*a*	0.5925	0.8858	0.4665	0.050

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Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Zn	1*a*	0.0890(3)	0.9202(2)	0.8027(1)	0.0302(2)	0.0201(1)	0.0189(1)	–0.0065(1)	0.0024(1)	–0.00110(9)
C(1)	1*a*	0.169(1)	0.553(1)	0.9954(7)	0.042(4)	0.022(2)	0.011(2)	–0.013(3)	0.003(2)	0.005(2)
C(2)	1*a*	0.152(2)	0.427(1)	1.1146(9)	0.042(4)	0.020(3)	0.031(3)	–0.010(3)	–0.004(3)	–0.002(2)
C(3)	1*a*	0.098(1)	0.480(1)	1.2441(8)	0.025(3)	0.023(3)	0.027(3)	–0.005(2)	0.001(2)	–0.008(2)
C(4)	1*a*	0.048(2)	0.676(1)	1.2292(8)	0.043(4)	0.029(3)	0.030(3)	–0.009(3)	0.002(3)	–0.012(3)
C(5)	1*a*	0.055(2)	0.790(1)	1.1062(9)	0.048(5)	0.022(3)	0.027(3)	–0.016(3)	0.007(3)	0.002(2)
C(6)	1*a*	0.085(1)	0.352(1)	1.3718(7)	0.023(3)	0.023(2)	0.012(2)	–0.011(2)	–0.002(2)	0.012(2)
C(7)	1*a*	0.140(2)	0.167(1)	1.3687(7)	0.046(4)	0.022(3)	0.013(2)	–0.010(3)	0.011(2)	0.005(2)
C(8)	1*a*	0.127(2)	0.050(1)	1.4902(8)	0.044(4)	0.022(3)	0.020(3)	–0.003(3)	0.002(3)	–0.004(2)
C(9)	1*a*	0.013(2)	0.300(1)	1.6046(9)	0.040(4)	0.025(3)	0.035(4)	–0.005(3)	0.005(3)	–0.011(3)
C(10)	1*a*	0.012(1)	0.422(1)	1.4886(8)	0.037(4)	0.019(3)	0.020(3)	–0.006(2)	0.008(2)	0.000(2)
N(1)	1*a*	0.116(1)	0.7301(9)	0.9935(6)	0.032(4)	0.025(3)	0.016(3)	–0.011(3)	0.003(3)	0.002(2)
N(2)	1*a*	0.067(1)	0.1100(9)	1.6122(7)	0.030(4)	0.022(3)	0.026(3)	–0.007(3)	0.000(3)	–0.002(3)
O(1)	1*a*	0.444(2)	0.527(1)	0.5748(7)	0.100(6)	0.038(3)	0.034(3)	–0.031(4)	0.023(4)	–0.020(3)
O(2)	1*a*	0.487(1)	0.715(1)	0.3891(7)	0.084(7)	0.028(3)	0.034(3)	–0.023(4)	0.014(4)	–0.015(2)
C(11)	1*a*	0.488(2)	0.564(1)	0.4510(9)	0.033(4)	0.022(3)	0.038(4)	–0.010(3)	0.008(3)	–0.017(3)
C(12)	1*a*	0.564(1)	0.394(1)	0.3780(7)	0.023(3)	0.017(3)	0.019(3)	–0.007(2)	0.002(2)	–0.006(2)
C(13)	1*a*	0.612(2)	0.440(1)	0.2280(9)	0.035(5)	0.027(3)	0.029(3)	–0.015(3)	0.006(3)	–0.010(3)
C(14)	1*a*	0.683(1)	0.284(1)	0.1559(7)	0.036(4)	0.028(3)	0.018(3)	–0.013(3)	0.001(3)	–0.003(2)
O(3)	1*a*	0.747(1)	0.3178(9)	0.0345(6)	0.065(4)	0.029(3)	0.031(3)	–0.016(3)	0.021(3)	–0.013(2)
O(4)	1*a*	0.689(1)	0.1212(8)	0.2152(7)	0.059(5)	0.023(3)	0.031(3)	–0.017(3)	0.004(3)	–0.008(2)
O(5)	1*a*	–0.064(1)	0.7682(9)	0.7156(5)	0.045(4)	0.033(3)	0.022(2)	–0.015(3)	0.002(2)	–0.010(2)
O(6)	1*a*	0.252(1)	1.0660(9)	0.8941(6)	0.030(3)	0.030(2)	0.035(3)	–0.015(2)	–0.001(2)	0.001(2)
O(7)	1*a*	0.355(1)	0.7594(9)	0.7419(7)	0.048(4)	0.043(3)	0.029(3)	–0.008(3)	0.003(3)	–0.017(2)
O(8)	1*a*	0.494(1)	0.175(1)	0.6947(6)	0.045(4)	0.033(3)	0.030(3)	–0.014(3)	0.001(3)	–0.004(2)
O(9)	1*a*	0.681(1)	0.678(1)	–0.0870(6)	0.041(4)	0.034(3)	0.032(3)	–0.017(3)	0.000(2)	0.000(2)
O(10)	1*a*	–0.1783(9)	1.0825(8)	0.8645(6)	0.020(3)	0.035(3)	0.034(3)	0.006(2)	–0.002(2)	–0.017(2)
O(11)	1*a*	0.513(1)	–0.095(1)	0.1144(7)	0.053(4)	0.044(3)	0.035(3)	–0.029(3)	–0.007(3)	0.008(2)
O(12)	1*a*	0.667(1)	0.9400(9)	0.4865(6)	0.078(6)	0.034(3)	0.028(3)	–0.026(3)	–0.013(3)	–0.006(2)

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Crystal structure of tetraaquamonosuberatonickel(II), $Ni(H_2O)_4(C_8H_{12}O_4)$

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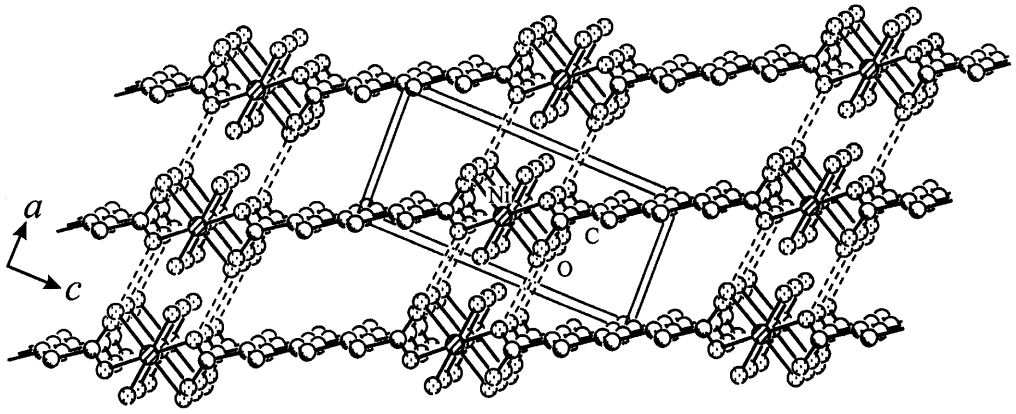

Abstract

$C_8H_{20}NiO_8$, triclinic, $P\bar{1}$ (No. 2), $a = 4.874(1)$ Å, $b = 6.329(1)$ Å, $c = 10.560(1)$ Å, $\alpha = 76.78(1)°$, $\beta = 87.79(1)°$, $\gamma = 76.97(1)°$, $V = 308.9$ Å^3, $Z = 2$, $R_{gt}(F) = 0.024$, $wR_{ref}(F^2) = 0.065$, $T = 293$ K.

Source of material

A methanolic solution of 0.44 g (2.50 mmol) suberic acid in 10 ml CH_3OH was added to a suspension of 0.30 g (2.50 mmol) $NiCO_3$ in 10 mml H_2O. The resulting mixture was then stirred for one hour. After filtration, the filtrate was allowed to stand at room temperature. Green well-shaped crystals were grown by slow evaporation for about 20 days.

Discussion

The Ni atoms in the title compound are each coordinated by four H_2O molecules and two suberato groups to complete slightly *trans* NiO_6 octahedra with d(Ni—O) = 2.044 Å – 2.080 Å. The acute cisoid O–Ni–O angles fall in the region 87.62(4)° – 89.72(5)° trivially less than 90° while the transoid O–Ni–O angles are equal to 180° due to imposition of the local $\bar{1}$ symmetry. The suberate anions function as bis-monodenate ligands with the middle C—C bond centered at the crystllographic 1*c* position. The C—O bond to the coordinating O(1) atom is 1.280(2) Å significantly longer than that of 1.245(2) Å to the uncoordinating O(2) atom and the terminal C—C bond is 1.512(2) Å considerably shorter than the remaining ones averaged to 1.522 Å. The bis-monodenate suberato groups bridge Ni atoms to generate $^1_\infty[Ni(H_2O)_4(C_8H_{12}O_4)_{2/2}]$ polymeric chains extending along [111] direction. The formed chain molecules display strong intramolecular hydrogen bonds between aqua O(3) atom and uncoordinating carboxylate O(2)$^{\#1}$ atom with d(O···O) = 2.623 Å and ∠O–H···O =157° (#1 = –*x*+1, –*y*, –*z*+1). The interchain hydrogen bonds with d(O···O) =2.763 Å – 2.942 Å and ∠O–H···O = 157° – 170° are responsible for the supramolecular assembly of the polymeric chains.

Table 1. Data collection and handling.

Crystal:	green block, size 0.178 × 0.244 × 0.267 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	15.97 cm^{-1}
Diffractometer, scan mode:	Bruker P4, $\theta/2\theta$
$2\theta_{max}$:	59.98°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	2375, 1795
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 1722
$N(param)_{refined}$:	97
Programs:	SHELXS-97 [1], SHELXL-97 [2]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	*x*	*y*	*z*	U_{iso}
H(2A)	2*i*	0.2422	–0.1148	0.1120	0.043
H(2B)	2*i*	–0.0130	–0.1572	0.2008	0.043
H(3A)	2*i*	0.1328	–0.5414	0.2105	0.043
H(3B)	2*i*	0.3866	–0.4972	0.1200	0.043
H(4A)	2*i*	–0.1824	–0.3195	0.0393	0.043
H(4B)	2*i*	0.0768	–0.2949	–0.0508	0.043
HO(4B)	2*i*	0.331(5)	–0.293(4)	0.671(2)	0.042(6)
HO(4A)	2*i*	0.143(5)	–0.113(4)	0.664(2)	0.044(7)
HO(3B)	2*i*	0.228(6)	0.348(5)	0.545(3)	0.064(8)
HO(3A)	2*i*	0.053(7)	0.255(6)	0.501(3)	0.08(1)

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Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ni	1*f*	1/2	0	1/2	0.0139(1)	0.0184(1)	0.0230(1)	–0.00080(8)	–0.00415(7)	–0.01152(8)
O(1)	2*i*	0.2680(2)	–0.0976(2)	0.3717(1)	0.0190(4)	0.0304(5)	0.0321(5)	–0.0019(4)	–0.0051(4)	–0.0205(4)
O(2)	2*i*	0.5786(2)	–0.3867(2)	0.3267(1)	0.0264(5)	0.0278(5)	0.0369(6)	0.0014(4)	–0.0099(4)	–0.0194(4)
O(3)	2*i*	0.1865(2)	0.2807(2)	0.4842(1)	0.0192(4)	0.0236(4)	0.0306(5)	0.0011(4)	–0.0048(4)	–0.0135(4)
O(4)	2*i*	0.2953(2)	–0.1598(2)	0.6569(1)	0.0231(5)	0.0244(5)	0.0338(6)	–0.0019(4)	0.0005(4)	–0.0081(4)
C(1)	2*i*	0.3571(3)	–0.2403(2)	0.3026(1)	0.0200(5)	0.0224(5)	0.0243(6)	–0.0068(4)	–0.0015(4)	–0.0119(5)
C(2)	2*i*	0.1817(3)	–0.2198(2)	0.1836(2)	0.0320(7)	0.0276(6)	0.0311(7)	0.0000(5)	–0.0115(5)	–0.0167(5)
C(3)	2*i*	0.1938(3)	–0.4346(2)	0.1402(1)	0.0324(7)	0.0269(6)	0.0249(6)	–0.0052(5)	–0.0086(5)	–0.0126(5)
C(4)	2*i*	0.0066(3)	–0.3938(2)	0.0208(1)	0.0351(7)	0.0267(6)	0.0279(7)	–0.0039(5)	–0.0108(5)	–0.0132(5)

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Crystal structure of 2,5-dimethylanilinium cyclohexaphosphate octahydrate, $(C_8H_{12}N)_6O_{18}P_6 \cdot 8H_2O$

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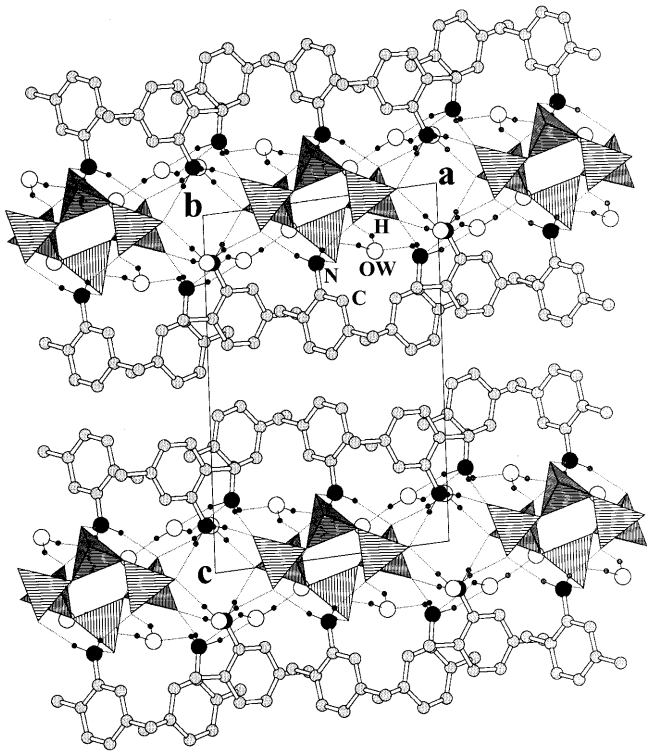

Abstract

$C_{48}H_{88}N_6O_{26}P_6$, triclinic, $P\bar{1}$ (No. 2), a = 10.759(3) Å, b = 10.351(9) Å, c = 15.914(6) Å, α = 99.82(6)°, β = 98.02(2)°, γ = 75.96(5)°, V = 1685.2 Å^3, Z = 1, $R_{gt}(F)$ = 0.060, $wR_{ref}(F)$ = 0.060, T = 296 K.

Source of material

The compound $(C_8H_{12}N)_6P_6O_{18} \cdot 8H_2O$ was prepared by an acid - base reaction. An aqueous solution of cyclohexaphosphoric acid was first obtained by passing a solution of $Li_6P_6O_{18}$ through an ion-exchange resin (amberlite IR 120) in its *H*-State. The lithium salt was prepared according to the process described by Schülke and Kayser [1]. Distilled $(CH_3)_2C_6H_3NH_2$ was added drop by drop to the $H_6P_6O_{18}$ solution, with continuous stirring until the solution exhibits a light greenish colour. The resulting solution was slowly evaporated at room temperature for several days, giving transparent thin single crystals, stable under normal conditions of temperature and humidity.

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Discussion

The projection of the crystal structure of $(C_8H_{12}N)_6O_{18}P_6 \cdot 8H_2O$ along the *b* axis shows the organization of the different components into two entities. The first one includes the inorganic components (P_6O_{18} ring, NH_3 groups and water molecules). The second one is consisted of the organic groups. The inorganic entities form parallel layers around the planes z = 0. Between these layers, the organic groups are located establishing H-bonds via their NH_3 groups with P_6O_{18} rings and water molecules. In this atomic arrangement, there are three independent organic groups having correct values of bond distances and angles. The hydrogen bonds at which they participate explains the stability of the three-dimensional network of the studied crystal structure.

Table 1. Data collection and handling.

Crystal:	colourless prism, size 0.15 × 0.35 × 0.60 mm
Wavelength:	Ag K_α radiation (0.5608 Å)
μ:	1.30 cm^{-1}
Diffractometer, scan mode:	Enraf Nonius MACH3, $\omega/2\theta$
$2\theta_{max}$:	49.92°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	10909, 10535
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 4249
$N(param)_{refined}$:	388
Programs:	SIR92 [2], teXsan [3]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(1)	2*i*	0.9074	0.6629	0.1645	0.042
H(2)	2*i*	0.8889	0.5000	0.1667	0.042
H(3)	2*i*	1.0110	0.5934	0.1878	0.042
H(4)	2*i*	1.0549	0.4030	0.2937	0.115
H(5)	2*i*	1.1585	0.4882	0.3146	0.115
H(6)	2*i*	1.1186	0.4280	0.3869	0.115
H(7)	2*i*	1.0368	0.5925	0.4772	0.042
H(8)	2*i*	0.8586	0.8108	0.5183	0.042
H(9)	2*i*	0.6615	0.9431	0.4673	0.104
H(10)	2*i*	0.6951	1.0114	0.3965	0.104
H(11)	2*i*	0.6004	0.9160	0.3736	0.104
H(12)	2*i*	0.7501	0.7860	0.2578	0.042
H(13)	2*i*	0.5030	1.1934	0.1430	0.042
H(14)	2*i*	0.3940	1.2165	0.1484	0.042
H(15)	2*i*	0.5020	1.0719	0.1727	0.042
H(16)	2*i*	0.2405	1.1795	0.2694	0.076
H(17)	2*i*	0.3486	1.0500	0.2568	0.076
H(18)	2*i*	0.2938	1.0976	0.3448	0.076

Table 2. Continued.

Atom	Site	*x*	*y*	*z*	U_{iso}
H(19)	2*i*	0.3889	1.2552	0.4549	0.042
H(20)	2*i*	0.5550	1.3771	0.4865	0.042
H(21)	2*i*	0.7295	1.4421	0.4650	0.098
H(22)	2*i*	0.7798	1.3974	0.3755	0.098
H(23)	2*i*	0.6741	1.5280	0.3918	0.098
H(24)	2*i*	0.6412	1.3151	0.2477	0.042
H(25)	2*i*	0.0785	0.9270	0.0886	0.042
H(26)	2*i*	–0.0003	1.0274	0.1296	0.042
H(27)	2*i*	–0.0474	0.9103	0.1233	0.042
H(28)	2*i*	–0.0849	1.1459	0.2645	0.099
H(29)	2*i*	–0.1604	1.0324	0.2464	0.099
H(30)	2*i*	–0.1288	1.0969	0.3400	0.099
H(31)	2*i*	0.0534	0.9718	0.4258	0.042

Table 2. Continued.

Atom	Site	*x*	*y*	*z*	U_{iso}
H(32)	2*i*	0.2430	0.8195	0.4339	0.042
H(33)	2*i*	0.4036	0.6478	0.3669	0.120
H(34)	2*i*	0.3743	0.5867	0.2723	0.120
H(35)	2*i*	0.4499	0.7001	0.2937	0.120
H(36)	2*i*	0.2295	0.7815	0.1614	0.042
H(37)	2*i*	0.7177	0.3821	0.1220	0.042
H(38)	2*i*	0.6596	0.5385	0.1438	0.042
H(39)	2*i*	0.0832	1.2192	0.1047	0.042
H(40)	2*i*	–0.0511	1.2520	0.0884	0.042
H(41)	2*i*	0.1024	0.5465	0.1256	0.203
H(42)	2*i*	0.2444	0.4693	0.1188	0.203
H(43)	2*i*	0.3379	0.4448	0.0227	0.187
H(44)	2*i*	0.4482	0.5130	0.0670	0.187

Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
P(1)	2*i*	0.52584(7)	0.80582(7)	0.10980(4)	0.0367(4)	0.0349(3)	0.0478(4)	–0.0051(3)	–0.0028(3)	0.0001(3)
P(2)	2*i*	0.30241(6)	0.86612(7)	–0.01769(4)	0.0330(3)	0.0408(4)	0.0364(3)	–0.0113(3)	0.0018(2)	–0.0030(2)
P(3)	2*i*	0.26652(7)	1.15388(7)	–0.02428(4)	0.0392(4)	0.0357(3)	0.0393(3)	–0.0076(3)	–0.0009(3)	–0.0007(3)
O(1)	2*i*	0.5286(3)	0.6687(2)	0.1219(2)	0.117(2)	0.043(1)	0.113(2)	–0.022(1)	–0.016(2)	0.015(1)
O(2)	2*i*	0.5613(2)	0.9028(2)	0.1829(1)	0.052(1)	0.049(1)	0.0382(9)	–0.0106(9)	–0.0010(8)	–0.0006(7)
O(3)	2*i*	0.3868(2)	0.8733(2)	0.0712(1)	0.039(1)	0.082(2)	0.042(1)	0.007(1)	–0.0045(8)	–0.0055(9)
O(4)	2*i*	0.1698(2)	0.8811(3)	–0.0015(1)	0.040(1)	0.132(2)	0.074(1)	–0.033(1)	0.011(1)	–0.032(1)
O(5)	2*i*	0.3626(2)	0.7557(2)	–0.0806(1)	0.055(1)	0.042(1)	0.051(1)	–0.0201(9)	0.0129(8)	–0.0110(8)
O(6)	2*i*	0.3195(3)	0.9974(2)	–0.0488(1)	0.160(3)	0.039(1)	0.065(1)	–0.004(1)	0.046(2)	0.005(1)
O(7)	2*i*	0.1640(2)	1.1997(2)	–0.0901(1)	0.045(1)	0.076(2)	0.055(1)	–0.019(1)	–0.0076(8)	0.021(1)
O(8)	2*i*	0.3915(2)	1.2033(3)	–0.0329(1)	0.045(1)	0.098(2)	0.057(1)	–0.029(1)	0.0138(9)	–0.032(1)
O(9)	2*i*	0.2429(2)	1.1890(2)	0.0668(1)	0.044(1)	0.056(1)	0.045(1)	–0.0062(9)	0.0040(8)	–0.0038(8)
O(10)	2*i*	0.7286(2)	0.4645(2)	0.1657(2)	0.071(2)	0.048(1)	0.118(2)	–0.025(1)	–0.008(1)	–0.008(1)
O(11)	2*i*	0.0111(2)	1.2169(3)	0.1339(2)	0.054(1)	0.097(2)	0.081(2)	–0.016(1)	0.008(1)	0.011(1)
O(12)	2*i*	0.1664(4)	0.4689(4)	0.1413(3)	0.152(4)	0.109(3)	0.279(5)	–0.066(3)	0.141(4)	–0.072(3)
O(13)	2*i*	0.3662(4)	0.4999(4)	0.0734(3)	0.141(3)	0.129(3)	0.204(4)	–0.085(3)	0.103(3)	–0.092(3)
N(1)	2*i*	0.9196(2)	0.5965(2)	0.1979(2)	0.054(2)	0.051(1)	0.059(1)	–0.019(1)	0.004(1)	0.007(1)
N(2)	2*i*	0.4762(2)	1.1705(2)	0.1781(1)	0.041(1)	0.041(1)	0.0312(9)	–0.0116(9)	0.0031(8)	–0.0037(8)
N(3)	2*i*	0.0336(2)	0.9403(3)	0.1364(1)	0.038(1)	0.070(2)	0.049(1)	–0.020(1)	0.0006(9)	0.010(1)
C(1)	2*i*	0.9073(3)	0.6521(3)	0.2881(2)	0.048(2)	0.046(2)	0.052(1)	–0.020(1)	–0.004(1)	0.007(1)
C(2)	2*i*	0.9882(3)	0.5891(3)	0.3530(2)	0.046(2)	0.053(2)	0.078(2)	–0.014(1)	–0.009(1)	0.021(2)
C(3)	2*i*	0.9652(4)	0.6482(4)	0.4363(2)	0.067(2)	0.075(2)	0.058(2)	–0.024(2)	–0.018(2)	0.025(2)
C(4)	2*i*	0.8685(4)	0.7573(4)	0.4543(2)	0.076(2)	0.065(2)	0.050(2)	–0.027(2)	–0.001(1)	0.009(1)
C(5)	2*i*	0.7869(3)	0.8144(3)	0.3904(2)	0.062(2)	0.056(2)	0.058(2)	–0.015(2)	0.003(1)	0.008(1)
C(6)	2*i*	0.8094(3)	0.7598(3)	0.3059(2)	0.055(2)	0.054(2)	0.050(2)	–0.011(1)	–0.011(1)	0.014(1)
C(7)	2*i*	1.0907(4)	0.4654(5)	0.3345(3)	0.081(3)	0.082(3)	0.112(3)	0.010(2)	–0.008(2)	0.019(2)
C(8)	2*i*	0.6762(4)	0.9326(4)	0.4094(3)	0.101(3)	0.083(3)	0.081(2)	0.003(2)	0.019(2)	0.006(2)
C(9)	2*i*	0.4901(2)	1.2318(2)	0.2674(1)	0.038(1)	0.033(1)	0.033(1)	–0.003(1)	0.0019(9)	–0.0027(9)
C(10)	2*i*	0.4137(3)	1.2065(3)	0.3237(2)	0.048(2)	0.038(1)	0.047(1)	–0.005(1)	0.009(1)	0.005(1)
C(11)	2*i*	0.4367(3)	1.2633(3)	0.4091(2)	0.079(2)	0.051(2)	0.038(1)	–0.008(2)	0.017(1)	0.001(1)
C(12)	2*i*	0.5298(3)	1.3358(3)	0.4345(2)	0.071(2)	0.056(2)	0.036(1)	–0.004(2)	–0.003(1)	–0.008(1)
C(13)	2*i*	0.6043(3)	1.3596(3)	0.3777(2)	0.056(2)	0.049(2)	0.047(1)	–0.008(1)	–0.007(1)	–0.008(1)
C(14)	2*i*	0.5826(3)	1.3054(3)	0.2922(2)	0.040(1)	0.044(1)	0.045(1)	–0.012(1)	0.003(1)	–0.005(1)
C(15)	2*i*	0.3155(3)	1.1257(4)	0.2962(2)	0.069(2)	0.068(2)	0.071(2)	–0.033(2)	0.028(2)	–0.005(2)
C(16)	2*i*	0.7064(4)	1.4382(4)	0.4046(2)	0.071(2)	0.094(3)	0.084(2)	–0.038(2)	–0.004(2)	–0.031(2)
C(17)	2*i*	0.0906(3)	0.9029(3)	0.2206(2)	0.045(2)	0.055(2)	0.050(1)	–0.026(1)	0.008(1)	–0.003(1)
C(18)	2*i*	0.0254(3)	0.9679(3)	0.2916(2)	0.065(2)	0.058(2)	0.063(2)	–0.025(2)	0.022(2)	–0.004(1)
C(19)	2*i*	0.0855(4)	0.9286(4)	0.3695(2)	0.098(3)	0.069(2)	0.050(2)	–0.035(2)	0.023(2)	–0.003(2)
C(20)	2*i*	0.1983(4)	0.8325(4)	0.3751(2)	0.096(3)	0.087(3)	0.046(2)	–0.035(2)	–0.000(2)	0.014(2)
C(21)	2*i*	0.2578(4)	0.7703(4)	0.3040(2)	0.072(2)	0.070(2)	0.061(2)	–0.018(2)	0.000(2)	0.017(2)
C(22)	2*i*	0.2009(3)	0.8088(3)	0.2250(2)	0.049(2)	0.057(2)	0.049(2)	–0.018(1)	0.004(1)	0.005(1)
C(23)	2*i*	–0.0982(4)	1.0708(4)	0.2843(3)	0.077(3)	0.090(3)	0.094(3)	0.001(2)	0.034(2)	0.007(2)
C(24)	2*i*	0.3844(5)	0.6670(5)	0.3096(3)	0.102(4)	0.126(4)	0.090(3)	0.021(3)	0.005(2)	0.047(3)

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Crystal structure of 1,2,3,4-tetrahydro-2,6-diphenyl-3,5,7-trimethyl-6*H*-pyrrolo[3,4-*d*]pyridazine-1,4-dione, $C_{21}H_{19}N_3O_2$

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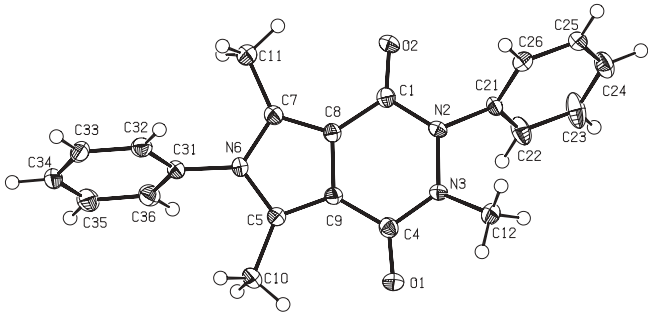

Abstract

$C_{21}H_{19}N_3O_2$, orthorhombic, *Pna*2$_1$ (No. 33), a = 8.385(1) Å, b = 23.223(2) Å, c = 8.8285(9) Å, V = 1719.0 Å^3, Z = 4, $R_{gt}(F)$ = 0.046, $wR_{ref}(F^2)$ = 0.089, T = 100 K.

Source of material

A mixture of of pyrrolopyridazinone (1.09 g), K_2CO_3 (0.6 g) and ICH_3 (0.8 ml) in 40 ml acetonitrile was stirred at 313 K for 15 hours. After reaction the mixture was filtered and the filtrate was evaporated. The residue was chromatographed [CC, ethyl acetate/cyclohexane (2:1:5)]. The fractions containing two products: A with Rf = 0.89 yielded 0.51 g (mp 577 K) and B with Rf = 0.72 (mp 453 K) yielded 0.1 g. For the B product we determined the crystal structure. For X-ray study, the crystals were obtained by slow evaporation of an ethanol solution at 296 K. After five days of growth, colorless, platelet crystals were obtained. The small single crystal used for the X-ray data collection was cut from a larger, good quality, single crystal.

Discussion

Pyrrolopyridaziones are known for their biological activity, antiproliferative and antiviral activity [1], antiulcar and antibacterial action against Helicobacter pylori [2,3], NMDA and AMPA receptor antagonistic action [4], antimicrobial and antifungal activity [5], anticancer and antimycobacterial [6] and are inhibitors of phospholipase A2 [7] or exhibit profound inhibition of lipid peroxdation in vitro [8].

The molecule is placed in the general position of the lattice. The C—C bonds inside the rings ranging from 1.372(3) Å to 1.384(3) Å. Inside the ring systems, the N3—N2 distance is 1.431(3) Å, and the C—N distances on average are 1.385(5) Å, ranging from a low value of 1.376(2) Å to a high value of 1.394(3) Å. The C1—O2 and C4—O1 bonds are 1.234(2) Å and 1.239(2) Å, respectively. The parameters of the intermolecular hydrogen bonds are: the distance d(O2···H42^i) = 2.490(3) Å, with an angle of 146° subtended at H for symmetry operation i: $-x$, $-y$, z+0.5.

Table 1. Data collection and handling.

Crystal:	colorless plate, size 0.25 × 0.10 × 0.05 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	0.88 cm^{-1}
Diffractometer, scan mode:	KUMA KM4CCD, ω
$2\theta_{max}$:	56.92°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	11072, 3977
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 3025
$N(param)_{refined}$:	238
Programs:	SHELX-97 [9], ORTEP-3 [10]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(10A)	4*a*	0.2799	0.3856	0.3049	0.037
H(10B)	4*a*	0.2829	0.4076	0.1371	0.037
H(10C)	4*a*	0.4398	0.4077	0.2337	0.037
H(11A)	4*a*	0.5244	0.1918	–0.1412	0.042
H(11B)	4*a*	0.6180	0.2490	–0.1730	0.042
H(11C)	4*a*	0.4432	0.2416	–0.2330	0.042
H(12A)	4*a*	0.0946	0.2165	0.5486	0.037
H(12B)	4*a*	0.2082	0.1663	0.5983	0.037
H(12C)	4*a*	0.0863	0.1568	0.4659	0.037
H(22)	4*a*	0.5197	0.1422	0.5346	0.035
H(23)	4*a*	0.5733	0.0583	0.6662	0.044
H(24)	4*a*	0.4601	–0.0280	0.5904	0.036
H(25)	4*a*	0.2848	–0.0292	0.3899	0.033
H(26)	4*a*	0.2274	0.0546	0.2580	0.030
H(32)	4*a*	0.2980	0.3414	–0.2429	0.026
H(33)	4*a*	0.3581	0.4141	–0.4148	0.030
H(34)	4*a*	0.5638	0.4775	–0.3658	0.033
H(35)	4*a*	0.7175	0.4666	–0.1504	0.035
H(36)	4*a*	0.6637	0.3929	0.0185	0.031

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Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(1)	4*a*	0.2389(2)	0.29723(6)	0.4679(2)	0.0366(9)	0.0196(7)	0.0230(8)	0.0052(7)	0.0068(7)	–0.0025(7)
O(2)	4*a*	0.4616(2)	0.13145(5)	0.0914(2)	0.0317(8)	0.0155(7)	0.0258(8)	0.0043(6)	0.0050(7)	–0.0013(7)
N(3)	4*a*	0.2756(2)	0.20387(7)	0.4046(2)	0.0260(9)	0.0145(8)	0.0189(9)	0.0027(7)	0.0064(8)	–0.0011(8)
N(2)	4*a*	0.3315(2)	0.15972(7)	0.3047(2)	0.027(1)	0.0134(8)	0.021(1)	0.0045(7)	0.0040(8)	–0.0003(8)
N(6)	4*a*	0.4367(2)	0.31671(7)	0.0156(2)	0.0258(9)	0.0154(9)	0.0176(9)	0.0004(7)	0.0019(8)	0.0030(8)
C(1)	4*a*	0.4046(2)	0.17137(8)	0.1662(2)	0.018(1)	0.019(1)	0.020(1)	0.0002(9)	–0.0013(9)	0.001(1)
C(4)	4*a*	0.2894(2)	0.26181(9)	0.3745(2)	0.021(1)	0.019(1)	0.021(1)	0.0013(9)	–0.002(1)	0.002(1)
C(5)	4*a*	0.3788(2)	0.32793(9)	0.1604(2)	0.022(1)	0.018(1)	0.018(1)	0.0018(9)	0.0007(9)	0.0003(9)
C(7)	4*a*	0.4523(2)	0.25770(8)	–0.0078(2)	0.021(1)	0.018(1)	0.021(1)	0.0010(9)	0.0004(9)	0.001(1)
C(8)	4*a*	0.4038(2)	0.23172(8)	0.1248(2)	0.020(1)	0.017(1)	0.018(1)	0.0013(8)	–0.0008(9)	0.0014(9)
C(9)	4*a*	0.3588(2)	0.27562(9)	0.2289(2)	0.022(1)	0.016(1)	0.016(1)	0.0011(9)	–0.0010(9)	–0.0008(9)
C(10)	4*a*	0.3421(3)	0.38751(8)	0.2138(3)	0.032(1)	0.016(1)	0.025(1)	0.0012(9)	–0.000(1)	0.0015(9)
C(11)	4*a*	0.5151(3)	0.23278(9)	–0.1515(2)	0.036(1)	0.023(1)	0.024(1)	0.004(1)	0.008(1)	0.002(1)
C(12)	4*a*	0.1558(2)	0.18417(9)	0.5138(2)	0.029(1)	0.024(1)	0.022(1)	0.001(1)	0.007(1)	0.003(1)
C(21)	4*a*	0.3693(2)	0.10649(8)	0.3831(2)	0.022(1)	0.013(1)	0.021(1)	0.0010(8)	0.0026(9)	0.0030(9)
C(22)	4*a*	0.4724(3)	0.10772(9)	0.5051(3)	0.029(1)	0.022(1)	0.038(1)	–0.009(1)	–0.008(1)	0.008(1)
C(23)	4*a*	0.5049(3)	0.0575(1)	0.5833(3)	0.027(1)	0.035(1)	0.048(2)	–0.006(1)	–0.013(1)	0.024(1)
C(24)	4*a*	0.4362(2)	0.0059(1)	0.5391(3)	0.027(1)	0.021(1)	0.041(2)	0.006(1)	0.008(1)	0.011(1)
C(25)	4*a*	0.3325(3)	0.00524(9)	0.4187(2)	0.044(1)	0.017(1)	0.023(1)	–0.004(1)	0.008(1)	–0.001(1)
C(26)	4*a*	0.2978(3)	0.05540(9)	0.3395(2)	0.034(1)	0.023(1)	0.018(1)	–0.001(1)	0.001(1)	–0.001(1)
C(31)	4*a*	0.4738(2)	0.36069(8)	–0.0938(2)	0.023(1)	0.016(1)	0.020(1)	0.0017(9)	0.0033(9)	0.0013(9)
C(32)	4*a*	0.3822(2)	0.36647(9)	–0.2243(2)	0.022(1)	0.022(1)	0.022(1)	0.0009(9)	0.002(1)	–0.002(1)
C(33)	4*a*	0.4180(3)	0.41021(9)	–0.3267(2)	0.030(1)	0.026(1)	0.019(1)	0.006(1)	0.004(1)	0.003(1)
C(34)	4*a*	0.5419(3)	0.44782(9)	–0.2981(3)	0.038(1)	0.018(1)	0.027(1)	0.002(1)	0.013(1)	0.003(1)
C(35)	4*a*	0.6335(3)	0.44140(9)	–0.1690(3)	0.032(1)	0.023(1)	0.033(1)	–0.009(1)	0.006(1)	–0.002(1)
C(36)	4*a*	0.6007(3)	0.39760(9)	–0.0674(2)	0.029(1)	0.022(1)	0.025(1)	–0.001(1)	–0.002(1)	–0.000(1)

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Crystal structure of diaqua-bis[*N*-(2-pyridyl)carbonylaniline]copper(II) dinitrate, $Cu(C_{12}H_{16}N_2O)_2(H_2O)_2(NO_3)_2$

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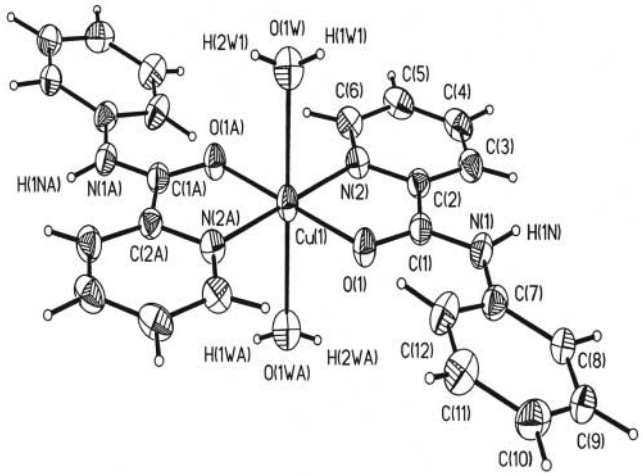

Abstract

$C_{24}H_{24}CuN_6O_{10}$, monoclinic, $P12_1/c1$ (No. 14), a = 7.441(2) Å, b = 11.458(2) Å, c = 14.850(3) Å, β = 95.941(5)°, V = 1259.4 Å^3, Z = 2, $R_{gt}(F)$ = 0.049, $wR_{ref}(F^2)$ = 0.126, T = 120 K.

Source of material

N-(2-pyridyl)carbonylaniline was synthesized in accordance with published procedure [1]. The green crystals of the title compound were obtained from the reaction of a solution of *N*-(2-pyridyl)carbonylaniline (0.396 g, 2 mmol) in hot acetonitrile (5 ml) and a hot aqueous solution of copper(II)nitrate (0.188 g, 1 mmol) with *N*-(2-pyridyl)-carbonylaniline (0.200 g, 2 mmol) in 15 ml acetonitrile. The final solution was brought to the boil and allowed to cool slowly overnight, depositing green crystals (0.372 g, yield 60%; mp 563 K). The green single crystals suitable for X-rax analysis were obtained by slow diffusion (2 days) of diethyl ether in methanolic solution of title compound. Elemental analyses were consistent with the composition $C_{24}H_{24}CuN_6O_{10}$ (found: C, 45.38%; H, 3.75%; N, 13.41%; calc.: C, 46.45.%; H, 3.87.%; N, 13.54%).

Discussion

Numerous copper(II) complexes with nitrogen or oxygen donor ligands have been synthesized and studied. Some of these complexes serve as structural models for the active site in enzymes [2]. In the recent years the interest in the determination of X-ray crystal structures of biologically active compounds increased [3]. In this work, we describe the crystal structure of diaqua-bis[*N*-(2-pyridyl)-carbonylaniline]copper(II) dinitrate, $Cu(C_{12}H_{16}N_2O)_2(H_2O)_2(NO_3)_2$. The cationic complex is mononuclear and occupies special positions in the inversion centers. In the cation, the metal atom is coordinated to two *N*-(2-pyridyl)carbonylaniline (L), via one pyridine nitrogen and one carbonyl oxygen, and to two H_2O molecules. The *N*-(2-pyridyl)carbonylaniline (L) ligand behaves as a bidentate ligands, forming a five-membered metallcycle. The coordination of Cu is a distorted octahedral. The molecules have an inversion center with approximate C_{2h} symmetry and are formed by two bidentate *N*-(2-pyridyl)carbonylaniline ligands through their O and N atoms and two water molecules. Two oxygen atoms from amide and two nitrogen atoms from pyridyl are in *trans* positions [the angles ∠O(amide)–Cu–O(amide) and ∠N(pyridyl)–Cu–O(pyridyl) are 180°], and also the two coordinated water molecules are *trans* [∠O(water)–Cu–O(water) is 180°]. The bond distances Cu—N (1.977 Å) Cu—O(amide) (1.965 Å) and Cu—O(water) (2.405 Å) are consistent with previously described values [2]. The bite angles of ∠O1–Cu1–N2 and ∠O1#1–Cu1–N2#1 are 82.06° and 82.06°, respectively, being similar to previously reported [2]. The nitrate anions in this compound show rotational disorder over two positions with unequal occupancies. Cations are linked by hydrogen bonding. The coordinated *N*-(2-pyridyl)carbonylaniline (L) molecules and the two coordinated water molecules are involved in hydrogen bonding acting as hydrogen-bond donors with coordinated O and N atoms as potential hydrogen-bond acceptors. The hydrogen bonding yields infinite chains parallel to the crystallgraphic vectors *a* and *b*. Each cation is bonded to four neighbors and assembles the molecules into a one-dimensional chain.

Table 1. Data collection and handling.

Crystal:	deep green prism, size 0.3 × 0.4 × 0.6 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	9.39 cm^{-1}
Diffractometer, scan mode:	Bruker SMART 1000 CCD, φ/ω
$2\theta_{max}$:	59.16°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	14185, 3521
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2611
$N(param)_{refined}$:	214
Programs:	SHELXTL-plus [4], SHELXTL-97 [5], SADABS [6]

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Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	*x*	*y*	*z*	U_{iso}
H(3A)	4*e*	0.3158	0.3985	0.0413	0.037
H(4A)	4*e*	0.0204	0.3837	–0.0267	0.041
H(5A)	4*e*	–0.0886	0.2042	–0.0796	0.041
H(6A)	4*e*	0.1042	0.0451	–0.0701	0.036
H(8A)	4*e*	0.8289	0.4931	0.1488	0.040
H(9A)	4*e*	1.1239	0.5163	0.2099	0.047
H(10A)	4*e*	1.2991	0.3555	0.2537	0.045
H(11A)	4*e*	1.1777	0.1692	0.2339	0.044
H(12A)	4*e*	0.8809	0.1457	0.1716	0.039
H(1W1)	4*e*	0.4105	–0.0219	0.1870	0.046
H(2W1)	4*e*	0.4031	–0.1236	0.1498	0.057
H(1N)	4*e*	0.5822	0.3645	0.1219	0.047

Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	Occ.	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu(1)	2*b*		1/2	0	0	0.0237(2)	0.0213(2)	0.0333(2)	0.0025(1)	–0.0055(1)	–0.0074(1)
O(1W)	4*e*		0.3877(2)	–0.0604(1)	0.1389(1)	0.0416(9)	0.0353(9)	0.0334(8)	0.0030(7)	–0.0034(7)	–0.0012(7)
O(1)	4*e*		0.6485(2)	0.1236(1)	0.0619(1)	0.0266(7)	0.0228(7)	0.0347(8)	0.0015(6)	–0.0044(6)	–0.0069(6)
N(1)	4*e*		0.6446(2)	0.3096(1)	0.1122(1)	0.0340(9)	0.0184(8)	0.0311(9)	–0.0025(7)	0.0029(7)	–0.0017(7)
N(2)	4*e*		0.3156(2)	0.1248(2)	–0.0087(1)	0.0245(8)	0.0254(8)	0.0267(8)	0.0016(7)	–0.0010(6)	–0.0024(7)
C(1)	4*e*		0.5671(3)	0.2188(2)	0.0682(1)	0.030(1)	0.0210(9)	0.0238(9)	–0.0003(8)	0.0032(8)	–0.0013(7)
C(2)	4*e*		0.3771(3)	0.2283(2)	0.0254(1)	0.029(1)	0.023(1)	0.0228(9)	0.0001(8)	0.0036(7)	–0.0002(7)
C(3)	4*e*		0.2705(3)	0.3273(2)	0.0190(1)	0.038(1)	0.025(1)	0.029(1)	0.0048(9)	0.0056(9)	0.0030(8)
C(4)	4*e*		0.0946(3)	0.3183(2)	–0.0214(1)	0.036(1)	0.036(1)	0.031(1)	0.014(1)	0.0065(9)	0.0074(9)
C(5)	4*e*		0.0301(3)	0.2120(2)	–0.0538(2)	0.025(1)	0.046(1)	0.030(1)	0.0090(9)	0.0003(8)	0.0030(9)
C(6)	4*e*		0.1461(3)	0.1168(2)	–0.0471(1)	0.027(1)	0.033(1)	0.029(1)	0.0007(9)	0.0001(8)	–0.0026(8)
C(7)	4*e*		0.8261(3)	0.3168(2)	0.1525(1)	0.034(1)	0.025(1)	0.0247(9)	–0.0054(8)	0.0029(8)	–0.0029(8)
C(8)	4*e*		0.8992(3)	0.4279(2)	0.1653(2)	0.038(1)	0.025(1)	0.040(1)	–0.0063(9)	0.011(1)	–0.0081(9)
C(9)	4*e*		1.0753(3)	0.4417(2)	0.2024(2)	0.041(1)	0.035(1)	0.044(1)	–0.015(1)	0.013(1)	–0.017(1)
C(10)	4*e*		1.1804(3)	0.3457(2)	0.2284(2)	0.036(1)	0.047(1)	0.029(1)	–0.013(1)	0.0007(9)	–0.008(1)
C(11)	4*e*		1.1076(3)	0.2342(2)	0.2166(1)	0.042(1)	0.038(1)	0.027(1)	–0.006(1)	–0.0052(9)	0.0017(9)
C(12)	4*e*		0.9300(3)	0.2201(2)	0.1790(1)	0.042(1)	0.026(1)	0.028(1)	–0.0080(9)	–0.0053(9)	0.0022(8)
N(3)	4*e*		0.4339(2)	0.6171(1)	0.1534(1)	0.0264(8)	0.0204(8)	0.0325(9)	0.0002(7)	0.0034(7)	0.0001(7)
O(2)	4*e*	0.80	0.5109(3)	0.5224(2)	0.1802(1)	0.036(1)	0.025(1)	0.037(1)	0.0061(8)	–0.0047(9)	0.0004(8)
O(3)	4*e*	0.80	0.3458(3)	0.6197(2)	0.0775(1)	0.039(1)	0.035(1)	0.032(1)	0.0035(9)	–0.0039(8)	0.0071(8)
O(4)	4*e*	0.80	0.4401(4)	0.7011(2)	0.2049(2)	0.072(2)	0.027(1)	0.047(1)	0.008(1)	–0.001(1)	–0.0109(9)
O(2A)	4*e*	0.20	0.376(1)	0.7142(6)	0.1240(5)	0.039(4)	0.022(4)	0.038(4)	0.012(3)	–0.004(3)	0.007(3)
O(3A)	4*e*	0.20	0.461(1)	0.5410(7)	0.0958(6)	0.040(5)	0.027(4)	0.043(4)	0.000(4)	0.006(4)	–0.012(3)
O(4A)	4*e*	0.20	0.489(1)	0.6056(7)	0.2339(5)	0.046(5)	0.039(5)	0.028(4)	0.001(4)	–0.012(3)	0.011(3)

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Crystal structure of triaquabis(vanillin-*O*,*O′*)nitritoerbium(III), $Er(C_8H_7O_3)_2(NO_2)(H_2O)_3$

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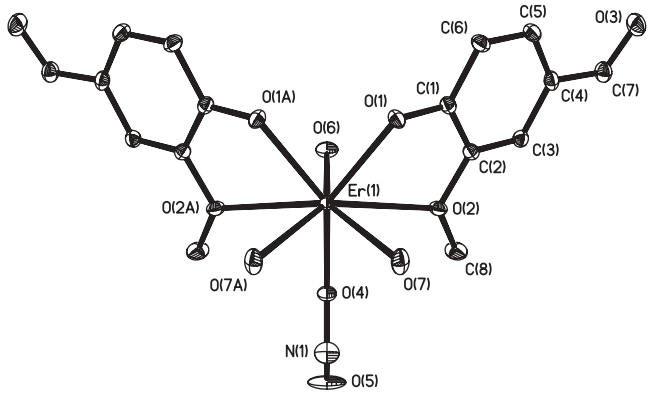

Abstract

$C_{16}H_{20}ErNO_{11}$, orthorhombic, *Pnma* (No. 62), a = 7.744(2) Å, b = 21.929(4) Å, c = 11.013(2) Å, V = 1870.2 Å^3, Z = 4, $R_{gt}(F)$ = 0.020, $wR_{ref}(F^2)$ = 0.083, T = 293 K.

Source of material

Adamantaneamine (2.0 mmol) in 15.0 ml CH_3OH was added to a solution of $Er(NO_3)_3 \cdot 5H_2O$ (1.0 mmol) dissolved in 10.0 ml CH_3OH, producing a colorless solution, to which 2.2 mmol vanillin was added under continuous stirring. The mixture was then further stirred for 5 h. Slow evaporation afforded the title complex crystals for the X-ray structure determination.

Discussion

The crystal structure of the title compound is built up by triaquabis(vanillin-*O*,*O′*)nitritoerbium(III) complex molecules, within which the Er atoms are each surrounded by four O atoms from two vanillin ligands, three H_2O molecules and one O atom of nitrito ligand, to which nitrato group was reduced by adamantaneimine. The geometry around Er atom can be described as a distorted square antiprism with O1, O7, O7*a*, O1*a* (plane I) and O2, O4, O2*a*, O6 (plane II) (symmetry code: *a*: *x*, –*y*+1/2, *z*) at the tetragonal bases (dihedral angle between their mean planes is 3.3(1)°). The distances between Er and the two planes are –1.075(2) Å and 1.344(2) Å, respectively. The bond lengths of Er—O(phenato), Er—O(methyloxy) and Er—O(nitrito) are 2.260(3) Å, 2.585(3) Å and 2.236(4) Å, respectively. The average bond length of Er—O(water) is 2.330 Å. To form the three-dimensional structure, the complex molecules are connected to each orther through strong intramolecular hydrogen bonds with d(O6–H···O5*b*) = 2.677(5) Å and ∠O6–H···O5*b* = 172.2°, d(O6–H···O5*c*) = 2.677(6) Å and ∠O6–H···O5c = 179.6°, d(O7–H···O1*d*) = 2.688(4) Å and ∠O7–H···O1*d* = 167.8°, d(O7–H···O3e) = 2.839(5) Å and ∠O7–H···O3*e* = 170.6° (symmetry codes: *b*: *x*–1, *y*, *z*; *c*: *x*–1/2, *y*, –*z*+1/2; *d*: *x*+1/2, *y*, –*z*+3/2; *e*: –x, –y+1, –z+1, respectively).

Table 1. Data collection and handling.

Crystal:	colourless prism, size 0.12 × 0.20 × 0.25 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	45.50 cm^{-1}
Diffractometer, scan mode:	Rigaku R-AXIS RAPID, φ/ω
$2\theta_{max}$:	54.96°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	3792, 2125
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 1902
$N(param)_{refined}$:	139
Programs:	SHELXS-97 [1], SHELXL-97 [2]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(61)	4*c*	–0.0958	1/4	0.3522	0.032
H(62)	4*c*	0.0698	1/4	0.2958	0.032
H(71)	8*d*	0.3470	0.3113	0.7481	0.039
H(72)	8*d*	0.3099	0.3531	0.6667	0.039
H(3)	8*d*	0.0760	0.4564	0.3305	0.027
H(5)	8*d*	–0.3939	0.4643	0.4987	0.031
H(6)	8*d*	–0.3295	0.3760	0.6060	0.032
H(7)	8*d*	–0.1108	0.5404	0.2874	0.035
H(8A)	8*d*	0.2492	0.3772	0.2778	0.054
H(8B)	8*d*	0.4070	0.3517	0.3528	0.054
H(8C)	8*d*	0.3449	0.4184	0.3740	0.054

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Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Er(1)	4*c*	0.17306(3)	1/4	0.54339(2)	0.0141(2)	0.0158(2)	0.0143(2)	0	0.00056(8)	0
O(1)	8*d*	–0.0436(4)	0.3136(1)	0.5968(3)	0.024(1)	0.020(1)	0.025(1)	0.006(1)	0.008(1)	0.006(1)
O(2)	8*d*	0.1876(3)	0.3571(2)	0.4460(3)	0.017(1)	0.024(2)	0.029(2)	0.003(1)	0.004(1)	0.007(1)
O(3)	8*d*	–0.3292(4)	0.5573(2)	0.3531(3)	0.041(2)	0.025(2)	0.047(2)	0.009(1)	–0.009(2)	0.006(2)
O(4)	4*c*	0.4204(5)	1/4	0.4387(4)	0.017(2)	0.029(2)	0.033(2)	0	0.007(2)	0
O(5)	4*c*	0.6779(5)	1/4	0.3555(4)	0.016(2)	0.119(6)	0.021(2)	0	0.003(2)	0
O(6)	4*c*	0.0235(5)	1/4	0.3619(3)	0.018(2)	0.045(3)	0.018(2)	0	0.000(2)	0
O(7)	8*d*	0.3190(4)	0.3143(2)	0.6791(3)	0.051(2)	0.019(2)	0.028(2)	0.001(1)	–0.020(1)	–0.002(1)
N(1)	4*c*	0.5819(8)	1/4	0.4444(5)	0.037(3)	0.047(4)	0.030(3)	0	0.002(2)	0
C(1)	8*d*	–0.0848(5)	0.3629(2)	0.5367(3)	0.022(2)	0.018(2)	0.021(2)	0.003(2)	–0.000(1)	–0.002(2)
C(2)	8*d*	0.0333(5)	0.3884(2)	0.4517(3)	0.020(2)	0.020(2)	0.020(2)	0.002(2)	–0.003(1)	–0.002(2)
C(3)	8*d*	–0.0059(5)	0.4402(2)	0.3874(4)	0.022(2)	0.020(2)	0.024(2)	–0.001(2)	–0.002(2)	0.002(2)
C(4)	8*d*	–0.1658(5)	0.4695(2)	0.4047(4)	0.028(2)	0.017(2)	0.028(2)	0.003(2)	–0.008(2)	–0.002(2)
C(5)	8*d*	–0.2843(6)	0.4447(2)	0.4868(4)	0.023(2)	0.024(2)	0.032(2)	0.006(2)	–0.002(2)	–0.002(2)
C(6)	8*d*	–0.2460(6)	0.3927(2)	0.5509(4)	0.022(2)	0.025(2)	0.032(2)	0.005(2)	0.006(2)	0.002(2)
C(7)	8*d*	–0.1980(6)	0.5260(2)	0.3424(4)	0.035(2)	0.022(2)	0.030(2)	0.002(2)	–0.006(2)	0.002(2)
C(8)	8*d*	0.3075(6)	0.3778(2)	0.3551(5)	0.026(2)	0.037(3)	0.046(3)	0.003(2)	0.014(2)	0.018(2)

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Crystal structure of 2,2-dibenzyl-1,3-dimethyloxypropane, $C_{19}H_{24}O_2$

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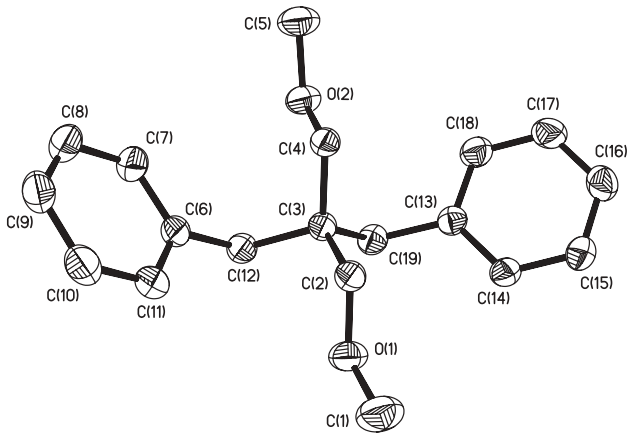

Abstract

$C_{19}H_{24}O_2$, monoclinic, $P12_1/n1$ (No. 14), a = 8.408(2) Å, b = 13.915(3) Å, c = 14.456(3) Å, β = 93.15(3)°, V = 1688.8 Å^3, Z = 4, $R_{gt}(F)$ = 0.042, $wR_{ref}(F^2)$ = 0.111, T = 293 K.

Source of material

The title compound was synthesized similarly to a method described in the literature [1]. Alkylation of $CH_2(COOEt)_2$ by $C_6H_5CH_2Br$ in EtOH containing EtONa gave $(C_6H_5CH_2)_2C(COOEt)_2$, which was reduced by $LiAlH_4$ in Et_2O to give $(C_6H_5CH_2)_2C(CH_2OH)_2$. Methylation of the diol by MeI in THF gave 2,2-dibenzyl-1,3-dimethoxypropane. Colourless prismatic crystals for the X-ray structure determination were obtained by recrystallization from methanol.

Discussion

Electron donors play a fundamental role in modern Ziegler-Natta catalyst systems for the polymerization of propene [2]. A novel and simplified generation of $MgCl_2$-supported catalysts used as internal donors was developed with the discovery of 1,3-diethers [2]. These donors are known for having the property to produce highly active and stereospecific catalysts without any external donors. Herein we report the structure of a diether moleculse of 2,2-dibenzyl-1,3-dimethyloxypropane. In the title compound, the centre C(3) atom which links two methoxymethyl groups and benzyl groups has sp^3 hybrid geometry with C–C–C at 107° – 111°. The atoms C(1), O(1), C(2), C(3), C(4), O(2) and C(5) are coplanar with rms deviation being 0.03 Å. The molecule exhibits essentially butterfly shape with dihedreal angle of 59.28(5)° between wings of benzyl groups. The distance between the O atoms of methoxy groups is 4.789(2) Å, which is longer the one of 3.662(2) Å between the O atoms of β-diol in 2-(hydroxymethyl)-1,3-propanediol [3].

Table 1. Data collection and handling.

Crystal:	colourless prism, size 0.10 × 0.21 × 0.32 mm
Wavelength:	Mo K_α radiation (0.71069 Å)
μ:	0.71 cm^{-1}
Diffractometer, scan mode:	Rigaku R-AXIS RAPID, ω
$2\theta_{max}$:	54.96°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	3870, 3870
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 2098
$N(param)_{refined}$:	190
Programs:	SHELXS-97 [4], SHELXL-97 [5]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(1A)	4*e*	–0.3622	0.0509	–0.3324	0.162
H(1B)	4*e*	–0.2946	–0.0224	–0.2578	0.162
H(1C)	4*e*	–0.4229	0.0532	–0.2318	0.162
H(2A)	4*e*	–0.1254	0.0340	–0.1326	0.070
H(2B)	4*e*	–0.2452	0.1155	–0.1078	0.070
H(4A)	4*e*	–0.0584	0.1734	0.0137	0.067
H(4B)	4*e*	0.0583	0.0900	–0.0105	0.067
H(5A)	4*e*	0.2954	0.2569	0.1078	0.144
H(5B)	4*e*	0.1180	0.2366	0.1298	0.144
H(5C)	4*e*	0.2341	0.1508	0.1138	0.144
H(7)	4*e*	–0.0375	0.3849	0.0018	0.094
H(8)	4*e*	–0.2253	0.4466	0.0967	0.111
H(9)	4*e*	–0.4904	0.4141	0.0678	0.111
H(10)	4*e*	–0.5713	0.3233	–0.0590	0.106
H(11)	4*e*	–0.3859	0.2623	–0.1548	0.091
H(12A)	4*e*	0.0271	0.3130	–0.1413	0.076
H(12B)	4*e*	–0.1084	0.2768	–0.2112	0.076
H(14)	4*e*	0.0487	–0.0234	–0.2726	0.078
H(15)	4*e*	0.1498	–0.1756	–0.2505	0.090
H(16)	4*e*	0.3506	–0.2038	–0.1403	0.096
H(17)	4*e*	0.4502	–0.0791	–0.0510	0.106
H(18)	4*e*	0.3519	0.0735	–0.0730	0.094
H(19A)	4*e*	0.0847	0.1506	–0.2512	0.074
H(19B)	4*e*	0.2060	0.1884	–0.1737	0.074

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Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(1)	4*e*	–0.2097(1)	0.10728(7)	–0.24063(6)	0.0924(7)	0.0774(6)	0.0600(6)	–0.0116(5)	–0.0164(5)	0.0039(5)
O(2)	4*e*	0.1614(1)	0.21653(6)	–0.00020(6)	0.0800(6)	0.0743(6)	0.0559(5)	–0.0112(5)	–0.0050(4)	–0.0023(4)
C(1)	4*e*	–0.3322(2)	0.0421(1)	–0.2679(1)	0.115(1)	0.105(1)	0.100(1)	–0.029(1)	–0.030(1)	–0.007(1)
C(2)	4*e*	–0.1582(2)	0.09951(9)	–0.14639(8)	0.0694(8)	0.0541(7)	0.0524(7)	0.0022(6)	0.0012(6)	0.0036(6)
C(3)	4*e*	–0.0191(1)	0.16772(8)	–0.12549(8)	0.0650(8)	0.0481(6)	0.0447(6)	0.0014(6)	0.0054(5)	0.0042(5)
C(4)	4*e*	0.0300(2)	0.15638(8)	–0.02346(8)	0.0673(8)	0.0521(7)	0.0490(7)	0.0004(6)	0.0016(6)	0.0023(5)
C(5)	4*e*	0.2059(2)	0.2152(1)	0.0955(1)	0.112(1)	0.107(1)	0.0649(9)	–0.011(1)	–0.0208(9)	–0.0052(9)
C(6)	4*e*	–0.1908(2)	0.31499(9)	–0.08676(8)	0.087(1)	0.0485(7)	0.0531(7)	0.0111(7)	–0.0015(7)	0.0066(6)
C(7)	4*e*	–0.1448(2)	0.3716(1)	–0.0110(1)	0.100(1)	0.0595(8)	0.075(1)	0.0085(8)	–0.0029(8)	–0.0077(7)
C(8)	4*e*	–0.2579(3)	0.4087(1)	0.0461(1)	0.130(2)	0.073(1)	0.073(1)	0.023(1)	0.002(1)	–0.0161(8)
C(9)	4*e*	–0.4157(2)	0.3900(1)	0.0288(1)	0.112(2)	0.085(1)	0.081(1)	0.042(1)	0.009(1)	0.0031(9)
C(10)	4*e*	–0.4636(2)	0.3356(1)	–0.0463(1)	0.086(1)	0.096(1)	0.084(1)	0.0300(9)	–0.0002(9)	0.0063(9)
C(11)	4*e*	–0.3517(2)	0.2988(1)	–0.1037(1)	0.088(1)	0.0754(9)	0.0637(8)	0.0198(8)	–0.0112(8)	0.0007(7)
C(12)	4*e*	–0.0677(2)	0.27324(9)	–0.14721(8)	0.0847(9)	0.0533(7)	0.0508(7)	0.0016(6)	0.0028(6)	0.0064(6)
C(13)	4*e*	0.1878(2)	0.04263(9)	–0.17449(8)	0.0612(8)	0.0619(7)	0.0487(7)	0.0015(6)	0.0113(6)	–0.0012(6)
C(14)	4*e*	0.1299(2)	–0.03381(9)	–0.22741(9)	0.0709(9)	0.0715(9)	0.0528(7)	0.0083(7)	–0.0008(6)	–0.0072(7)
C(15)	4*e*	0.1907(2)	–0.1252(1)	–0.2143(1)	0.083(1)	0.0674(9)	0.075(1)	0.0115(8)	0.0031(8)	–0.0153(7)
C(16)	4*e*	0.3099(2)	–0.1421(1)	–0.1489(1)	0.087(1)	0.078(1)	0.076(1)	0.0266(9)	0.0107(8)	–0.0012(8)
C(17)	4*e*	0.3691(2)	–0.0679(1)	–0.0961(1)	0.080(1)	0.106(1)	0.077(1)	0.0306(9)	–0.0150(8)	–0.0128(9)
C(18)	4*e*	0.3093(2)	0.0235(1)	–0.1091(1)	0.0701(9)	0.085(1)	0.078(1)	0.0102(8)	–0.0098(7)	–0.0192(8)
C(19)	4*e*	0.1207(2)	0.14254(9)	–0.18681(8)	0.0739(9)	0.0593(7)	0.0519(7)	–0.0033(6)	0.0115(6)	0.0025(6)

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Crystal structure of ethylenediaminesilver(I) 4-nitrobenzoate hemi-hydrate, $Ag(C_2H_8N_2)(C_7H_4NO_4) \cdot 0.5H_2O$

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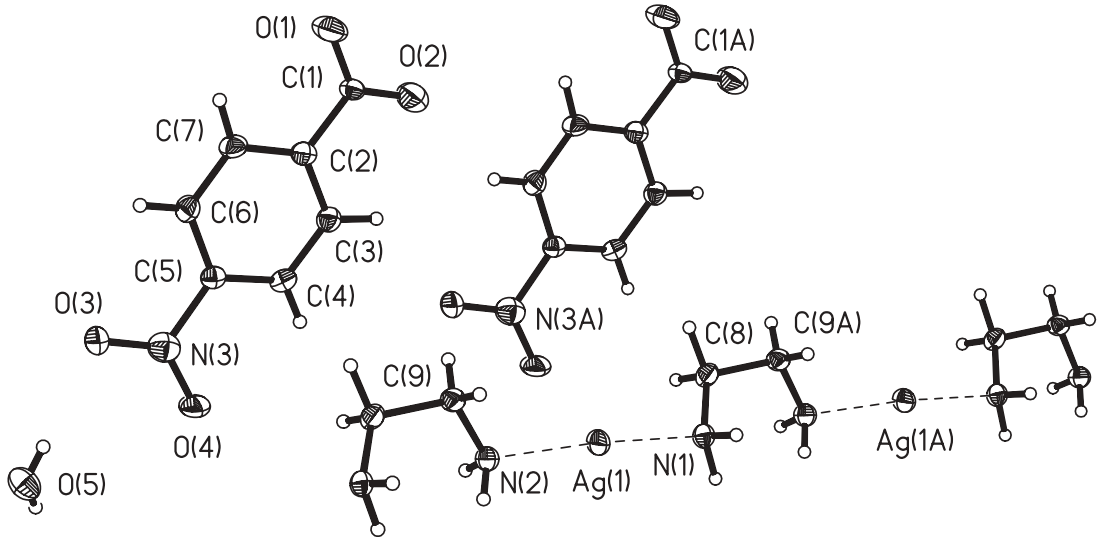

Abstract

$C_9H_{13}AgN_3O_{4.50}$, monoclinic, *C*12/*c*1 (No. 15), $a = 8.331(2)$ Å, $b = 11.645(2)$ Å, $c = 23.947(5)$ Å, $\beta = 94.845(3)°$, $V = 2314.8$ Å^3, $Z = 8$, $R_{gt}(F) = 0.030$, $wR_{ref}(F^2) = 0.072$, $T = 298$ K.

Source of material

Ag_2O (0.5 mmol, 116 mg) and 4-nitrobenzoate (1 mmol, 167 mg) were dissolved in a 1 : 1 solution of acetonitrile and concentrated ammonium solution (v/v, 10 ml), stirring for ca. 10 min ethylenediamine (1 mmol, 60 mg) was added to obtain a clear solution. After standing still the solution in air for two days with the ammium gas escaping large colorless prism crystals were crystallized, isolated, washed with water for three times, and dried in a vacuum desiccator under drying $CaCl_2$ (yield 45%). Elemental analysis: found – C, 31.70%; H, 3.90%; N, 12.14%; calc. for $C_9H_{13}AgN_3O_{4.5}$ – C, 31.51%; H, 3.82%; N, 12.25%.

Discussion

Coordination chemistry of coinage metal(I) monovalent ions have received considerable attention in the past three decades. The research on different uses and ideas of various silver(I) compounds is being in the ascendant. We have been interested in the investigation on silver(I) complexes with various organic ligands containing N and/or O atoms. Reported here is a silver(I)carboxylato complex with ethylenediamine.

The title complex crystallizes with the asymmetric unit consisting of one Ag ions, one 4-nitrobenzoate anion, one ethylenediamine molecule, and half a crystal water molecule. The Ag(1) ion is coordinated by two nitrogen atoms from two ethylenediamines. The Ag—N distances are 2.138(3) Å and 2.148(3) Å and the N–Ag–N angle is 173.1(2)°, indicating a linear coordination of Ag(1). Besides, there is a ligand unsupported Ag—Ag bond with a *d*(Ag···Ag) distance of 2.934(3) Å. The nitrobenzoate anion is pendent and functions as a counterion to maintain charge balance. The amine ligands bridge adjacent Ag ions to form one-dimensional chain and the chains are linked by Ag—Ag bonds to form two-dimensional layer with (4,4) topology. The four-connected nodes are provided by pairs of Ag ions. In addition, there are a variety of hydrogen bonds N–H···O, O–H···O and C–H···O [*d*(N1···O3) = 3.070(3) Å; *d*(N1···O4) = 2.968(4) Å; *d*(N2···O5) = 3.060(2) Å; *d*(N2···O4) = 3.022(4) Å; *d*(O5···O3) = 2.803(1) Å, *d*(C3···O2) = 2.714(0) Å; *d*(C4···O4) = 2.784(7) Å; *d*(C7···O1) = 2.726(8) Å] which extend the two-dimensional layer into three-dimensional supramolecular array.

Table 1. Data collection and handling.

Crystal:	colorless prism, size 0.20 × 0.30 × 0.30 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	17.55 cm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD, φ/ω
$2\theta_{max}$:	52.72°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	6470, 2309
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 1862
$N(param)_{refined}$:	211
Programs:	SHELXTL [1], SHELXTL-plus [2]

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Table 2. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	*x*	*y*	*z*	U_{iso}
H(1)	8*f*	0.334(5)	0.016(3)	0.572(2)	0.05(1)
H(2)	8*f*	0.287(4)	0.135(3)	0.649(2)	0.039(9)
H(3)	8*f*	–0.020(4)	0.320(3)	0.552(1)	0.040(9)
H(4)	8*f*	0.020(5)	0.194(3)	0.479(2)	0.06(1)
H(5)	8*f*	1.230(4)	–0.104(3)	0.669(2)	0.04(1)
H(6)	8*f*	1.207(4)	–0.143(3)	0.724(2)	0.040(9)
H(7)	8*f*	0.739(6)	0.102(4)	0.728(2)	0.08(2)
H(8)	8*f*	0.836(4)	0.186(3)	0.719(2)	0.05(1)
H(9)	8*f*	1.008(4)	–0.256(3)	0.684(1)	0.035(9)
H(10)	8*f*	1.011(4)	–0.219(2)	0.625(2)	0.037(9)
H(11)	8*f*	0.642(4)	0.129(3)	0.634(1)	0.033(9)
H(12)	8*f*	0.771(3)	0.210(2)	0.628(1)	0.023(8)
H(13)	8*f*	0.000(6)	0.492(3)	0.725(2)	0.05(1)

Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ag(1)	8*f*	0.97424(3)	0.00715(2)	0.68864(1)	0.0430(2)	0.0342(2)	0.0402(2)	0.0154(1)	–0.0026(1)	–0.0033(1)
N(1)	8*f*	1.1547(3)	–0.1241(2)	0.6862(1)	0.032(2)	0.030(1)	0.037(2)	0.006(1)	0.000(1)	–0.001(1)
N(2)	8*f*	0.7937(4)	0.1327(3)	0.7014(1)	0.039(2)	0.030(1)	0.038(2)	0.010(1)	–0.004(1)	–0.003(1)
N(3)	8*f*	0.1047(4)	0.3182(3)	0.6592(1)	0.054(2)	0.055(2)	0.045(2)	–0.007(2)	0.008(2)	0.001(2)
O(1)	8*f*	0.1338(4)	0.0425(2)	0.4281(1)	0.086(2)	0.060(2)	0.035(2)	0.009(2)	–0.001(1)	–0.010(1)
O(2)	8*f*	0.3045(4)	–0.0546(3)	0.4803(1)	0.091(2)	0.084(2)	0.055(2)	0.037(2)	–0.008(2)	–0.020(2)
O(3)	8*f*	0.0006(3)	0.3947(2)	0.6519(1)	0.045(1)	0.048(1)	0.046(2)	0.015(1)	–0.000(1)	–0.007(1)
O(4)	8*f*	0.1955(3)	0.3020(2)	0.7027(1)	0.073(2)	0.066(2)	0.032(2)	0.020(1)	–0.016(1)	–0.011(1)
O(5)	4*e*	0	0.5259(4)	3/4	0.068(3)	0.040(2)	0.049(3)	0	0.015(2)	0
C(1)	8*f*	0.2074(4)	0.0237(2)	0.4732(1)	0.038(2)	0.030(2)	0.027(2)	–0.000(1)	–0.000(1)	–0.004(1)
C(2)	8*f*	0.1769(4)	0.0964(3)	0.5209(1)	0.036(2)	0.037(2)	0.031(2)	–0.003(1)	0.003(1)	–0.002(1)
C(3)	8*f*	0.2584(4)	0.0736(3)	0.5722(1)	0.037(2)	0.034(2)	0.037(2)	0.003(1)	–0.000(1)	0.001(1)
C(4)	8*f*	0.2311(4)	0.1445(3)	0.6171(2)	0.035(2)	0.035(2)	0.032(2)	–0.003(1)	–0.004(1)	0.003(1)
C(5)	8*f*	0.1270(3)	0.2376(2)	0.6103(1)	0.030(2)	0.032(2)	0.029(2)	–0.006(1)	0.003(1)	0.001(1)
C(6)	8*f*	0.0454(4)	0.2569(3)	0.5578(1)	0.039(2)	0.038(2)	0.037(2)	0.009(2)	0.001(2)	0.004(1)
C(7)	8*f*	0.0692(4)	0.1859(3)	0.5134(1)	0.043(2)	0.046(2)	0.026(2)	0.001(2)	–0.003(1)	0.004(2)
C(8)	8*f*	1.0820(4)	–0.2317(3)	0.6631(2)	0.029(2)	0.034(2)	0.042(2)	0.002(1)	–0.004(2)	–0.000(1)
C(9)	8*f*	0.7014(4)	0.1768(3)	0.6509(2)	0.036(2)	0.030(2)	0.037(2)	0.002(1)	–0.002(2)	–0.004(1)

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Crystal structure of (1-cyclopropyl-6-fluoro-7-chloro-1,4-dihydro-4-oxo-3-quinolinecarboxylato)chloro(2,2′-bipyridine)copper(II) dihydrate, $CuCl(C_{10}H_8N_2)(C_{13}H_8NClFO_3) \cdot 2H_2O$

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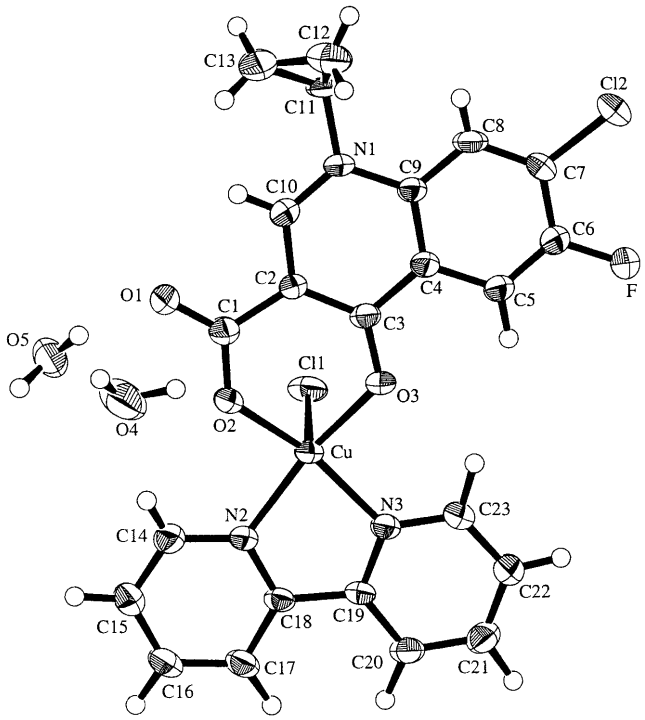

Abstract

$C_{23}H_{20}Cl_2CuFN_3O_5$, triclinic, $P\bar{1}$ (No. 2), a = 10.329(2) Å, b = 11.417(4) Å, c = 10.225(3) Å, α = 95.77(3)°, β = 99.10(2)°, γ = 98.65(2)°, V = 1167.5 Å^3, Z = 2, $R_{gt}(F)$ = 0.050, $wR_{obs}(F)$ = 0.061, T = 293 K.

Source of material

The compound was obtained in water/ethanol media, by mixing solutions containing 2,2-bipyridine (bipy, 1 mmol), $Cu(NO_3)_2 \cdot 3H_2O$ (1 mmol), Hcip (1-cyclopropyl-6-fluoro-7-chloro-1,4-dihydro-4-oxo-3-quinolinecarboxylic acid, 1 mmol) and NaOH (1 mmol). The pH of the resulting solution was adjusted to about 7.5 with dilute HCl. Then the solution was slowly evaporated at room temperature, and blue crystals were formed in a period of two months. Elemental analysis: found – C, 48.47%; N, 7.58%; H, 3.54%; calculated for $C_{23}H_{20}O_5N_3FCuCl_2$ – C, 48.30%; N, 7.35%; H, 3.52%;

Discussion

Quinolones, such as ciprofloxacin, norfloxacin and ofloxacin, are representatives of a class of synthetic antimicrobial drugs, which exhibit excellent activity against many Gram-positive and Gram-negative bacterial pathogens [1-3]. The coordination chemistry of quinolines with transition and non-transition metal ions has been the subject of a number of literature reports [4]. In this paper, we report a quaternary complex of copper(II) with a quinolone ligand, $[CuCl(C_{10}H_8N_2)(C_{13}H_8NClFO_3)] \cdot 2H_2O$ (**I**). In the title complex, the copper atom is five-coordinated with a square pyramidal environment, involving two nitrogen atoms from one 2,2′-bipy, one chloride anion and two oxygen atoms from one cip$^-$ ligand. Atoms O2, O3, N2 and N3 are sitting in a basal plane, while Cl1 is in apical position with a longer Cu—Cl1 distance. The cip$^-$ ligand is coordinated to Cu^{II} ion via the *keto* and the oxygen atom of the carboxylate group to form a six-membered ring. Compared with complex $[Cu(Hcpf)(bipy)(Cl)_{0.7}(NO_3)_{0.3}](NO_3) \cdot 2H_2O$ (**II**) [5], the Cl$^-$ anion (Cl2) in **I** could be replaced by other anions, such as acetate and nitrate. As expected, the distance Cu—O(COO$^-$) of 1.923(3) Å is similar to those in previous structures, such as **II**, $[Cu(phen)(nal)(H_2O)](NO_3) \cdot 3H_2O$ (**III**), $[Cu(phen)(cnx)(H_2O)](NO_3) \cdot H_2O$ (**IV**) and $[Cu(bpy)(oxo)](NO_3) \cdot H_2O$ (**V**) [6,7]. The Cu—O(*keto*) distance in **I** (1.976(3) Å) is longer than those observed in **II**, **III**, **IV** and **V**. The Cu—N distances (1.992(4) Å and 2.020(4) Å) are as observed in the structures of the analogous **II** and **III**. Interestingly, the distances between π-π stacked cip$^-$ rings from neighboring molecules and between cip$^-$ ring and bipy ring from another molecule are about 3.68 Å and 3.5 Å, respectively. The latter distance indicates a strong stacking interaction.

Table 1. Data collection and handling.

Crystal:	blue prismatic, size 0.20 × 0.23 × 0.30 mm
Wavelength:	Mo K_α radiation (0.7107 Å)
μ:	12.13 cm^{-1}
Diffractometer, scan mode:	AFC7R, $\omega/2\theta$
$2\theta_{max}$:	50.0°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	3882, 2918
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2918
$N(param)_{refined}$:	317
Programs:	SHELXS-86 [8], teXsan [9]

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Table 2. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	*x*	*y*	*z*	U_{iso}
H(1)	2*i*	0.5205	0.2526	0.7377	0.050
H(2)	2*i*	0.2433	0.5107	0.5851	0.050
H(3)	2*i*	0.3482	0.3398	0.2129	0.050
H(4)	2*i*	0.2953	0.5742	0.3751	0.050
H(5)	2*i*	0.0582	0.4013	0.3573	0.050
H(6)	2*i*	0.0563	0.5298	0.3542	0.050
H(7)	2*i*	0.1537	0.5297	0.1650	0.050
H(8)	2*i*	0.1505	0.3982	0.1544	0.050
H(9)	2*i*	0.6860	–0.0389	0.1352	0.050
H(10)	2*i*	0.7919	–0.1690	0.0328	0.050
H(11)	2*i*	0.9508	–0.2573	0.1744	0.050
H(12)	2*i*	0.9783	–0.2080	0.4189	0.050
H(13)	2*i*	0.9795	–0.1676	0.6212	0.050
H(14)	2*i*	0.9697	–0.1057	0.8450	0.050
H(15)	2*i*	0.8264	0.0445	0.8967	0.050
H(16)	2*i*	0.6948	0.1167	0.7145	0.050
H(17)	2*i*	0.7677	0.1947	0.0396	0.050
H(18)	2*i*	0.8179	0.2228	0.1806	0.050
H(19)	2*i*	0.5235	0.1427	0.9707	0.050
H(20)	2*i*	0.5570	0.0539	0.8780	0.050

Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu	2*i*	0.65888(6)	0.07378(5)	0.41371(6)	0.0385(4)	0.0263(3)	0.0294(3)	0.0159(3)	0.0016(3)	0.0023(2)
Cl(1)	2*i*	0.8225(1)	0.2603(1)	0.4166(1)	0.0472(8)	0.0242(6)	0.0548(8)	0.0120(6)	0.0052(6)	0.0055(6)
Cl(2)	2*i*	0.2671(2)	0.5448(1)	0.8623(1)	0.102(1)	0.0554(9)	0.0430(8)	0.0465(9)	0.0148(8)	–0.0043(7)
F	2*i*	0.4374(3)	0.3710(3)	0.9242(3)	0.082(2)	0.046(2)	0.029(2)	0.029(2)	0.002(2)	0.000(1)
O(1)	2*i*	0.4302(4)	0.1811(3)	0.1090(3)	0.071(3)	0.056(2)	0.029(2)	0.038(2)	0.004(2)	0.004(2)
O(2)	2*i*	0.5420(3)	0.0820(3)	0.2498(3)	0.052(2)	0.034(2)	0.030(2)	0.022(2)	0.000(2)	–0.002(1)
O(3)	2*i*	0.5466(3)	0.1553(3)	0.5196(3)	0.046(2)	0.034(2)	0.033(2)	0.023(2)	0.007(2)	0.007(1)
O(4)	2*i*	0.8572(5)	0.2104(4)	0.0924(5)	0.073(3)	0.078(3)	0.077(3)	0.038(3)	–0.005(2)	–0.020(3)
O(5)	2*i*	0.5989(4)	0.1343(3)	0.9312(4)	0.059(3)	0.054(2)	0.045(2)	0.014(2)	0.012(2)	–0.006(2)
N(1)	2*i*	0.3237(4)	0.4041(3)	0.3870(4)	0.041(2)	0.025(2)	0.033(2)	0.015(2)	0.004(2)	0.007(2)
N(2)	2*i*	0.7526(4)	–0.0438(3)	0.3201(4)	0.038(2)	0.023(2)	0.029(2)	0.010(2)	0.003(2)	0.002(2)
N(3)	2*i*	0.7551(4)	0.0153(3)	0.5723(4)	0.033(2)	0.024(2)	0.032(2)	0.009(2)	0.003(2)	0.002(2)
C(1)	2*i*	0.4758(5)	0.1666(4)	0.2240(5)	0.036(3)	0.036(3)	0.033(3)	0.015(2)	0.002(2)	0.003(2)
C(2)	2*i*	0.4460(5)	0.2457(4)	0.3371(4)	0.037(3)	0.026(2)	0.026(2)	0.011(2)	0.002(2)	0.004(2)
C(3)	2*i*	0.4796(5)	0.2320(4)	0.4741(5)	0.031(3)	0.022(2)	0.032(3)	0.007(2)	–0.001(2)	0.004(2)
C(4)	2*i*	0.4304(5)	0.3110(4)	0.5673(5)	0.038(3)	0.021(2)	0.030(3)	0.006(2)	0.004(2)	0.003(2)
C(5)	2*i*	0.4599(5)	0.3051(4)	0.7062(5)	0.042(3)	0.026(3)	0.031(3)	0.009(2)	0.002(2)	0.005(2)
C(6)	2*i*	0.4104(5)	0.3776(4)	0.7930(5)	0.052(3)	0.030(3)	0.030(3)	0.010(2)	0.002(2)	0.005(2)
C(7)	2*i*	0.3317(5)	0.4597(4)	0.7485(5)	0.057(4)	0.026(3)	0.034(3)	0.013(2)	0.007(2)	–0.004(2)
C(8)	2*i*	0.3035(5)	0.4697(4)	0.6155(5)	0.043(3)	0.025(2)	0.042(3)	0.015(2)	–0.002(2)	0.005(2)
C(9)	2*i*	0.3516(5)	0.3960(4)	0.5242(4)	0.035(3)	0.021(2)	0.030(3)	0.007(2)	0.002(2)	0.004(2)
C(10)	2*i*	0.3714(5)	0.3326(4)	0.3023(5)	0.044(3)	0.031(3)	0.030(3)	0.010(2)	0.003(2)	0.007(2)
C(11)	2*i*	0.2462(5)	0.4945(4)	0.3400(5)	0.043(3)	0.029(3)	0.046(3)	0.021(2)	0.001(2)	0.010(2)
C(12)	2*i*	0.1014(6)	0.4737(5)	0.3299(7)	0.052(4)	0.042(3)	0.072(4)	0.019(3)	0.003(3)	0.004(3)
C(13)	2*i*	0.1586(8)	0.4716(7)	0.2091(6)	0.108(6)	0.084(5)	0.049(4)	0.068(5)	–0.005(4)	0.006(3)
C(14)	2*i*	0.7454(5)	–0.0683(4)	0.1874(5)	0.042(3)	0.032(3)	0.033(3)	0.009(2)	–0.001(2)	0.003(2)
C(15)	2*i*	0.8125(5)	–0.1490(5)	0.1323(5)	0.048(3)	0.037(3)	0.035(3)	0.011(3)	0.005(2)	–0.003(2)
C(16)	2*i*	0.8937(5)	–0.2062(4)	0.2151(5)	0.051(3)	0.033(3)	0.045(3)	0.017(3)	0.009(3)	–0.004(2)
C(17)	2*i*	0.9062(5)	–0.1811(4)	0.3530(5)	0.044(3)	0.025(3)	0.041(3)	0.010(2)	0.005(2)	–0.003(2)
C(18)	2*i*	0.8312(5)	–0.0999(4)	0.4019(5)	0.031(3)	0.019(2)	0.034(3)	0.006(2)	0.001(2)	0.000(2)
C(19)	2*i*	0.8339(4)	–0.0658(4)	0.5452(5)	0.031(3)	0.020(2)	0.035(3)	0.008(2)	0.005(2)	0.003(2)
C(20)	2*i*	0.9099(5)	–0.1124(4)	0.6457(5)	0.038(3)	0.028(3)	0.041(3)	0.012(2)	0.001(2)	0.005(2)
C(21)	2*i*	0.9043(5)	–0.0729(5)	0.7787(5)	0.044(3)	0.040(3)	0.036(3)	0.011(3)	–0.001(2)	0.009(2)
C(22)	2*i*	0.8252(5)	0.0100(5)	0.8056(5)	0.047(3)	0.043(3)	0.033(3)	0.018(3)	0.006(2)	0.002(2)
C(23)	2*i*	0.7530(5)	0.0531(4)	0.7012(5)	0.042(3)	0.033(3)	0.036(3)	0.015(2)	0.007(2)	0.002(2)

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Crystal structure of ethylenediammonium di(4-chlor-benzoate), $(C_2H_{10}N_2)(C_7H_4O_2Cl)_2$

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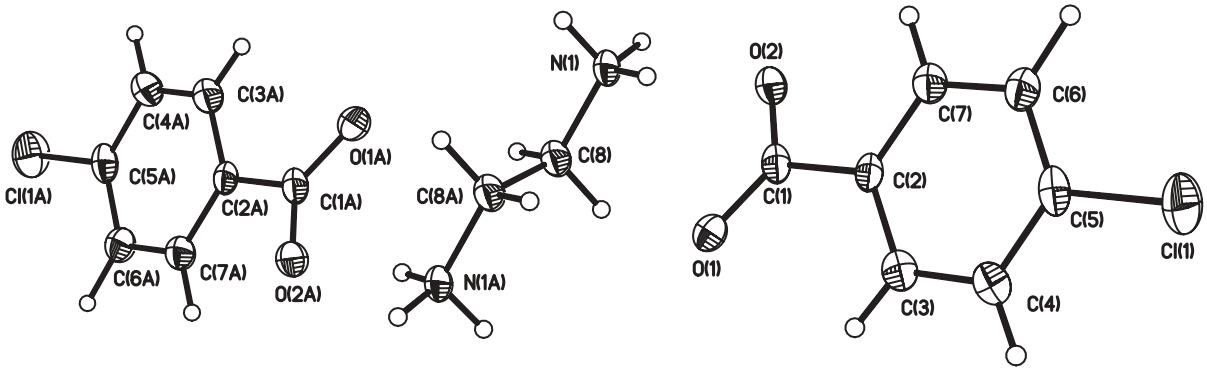

Abstract

$C_{16}H_{18}Cl_2N_2O_4$, monoclinic, *C*12/*c*1 (No. 15), a = 21.92(1) Å, b = 9.015(5) Å, c = 8.620(5) Å, β = 96.151(9)°, V = 1693.3 Å^3, Z = 4, $R_{gt}(F)$ = 0.064, $wR_{ref}(F^2)$ = 0.186, T = 298 K.

Source of material

The crystals suitable for X-ray diffraction were obtained by the following method. Ethylenediamine (1 mmol, 60 mg) and 4-chlor-benzoic acid (2 mmol, 313 mg) were dissolved in concentrated ammonium solution and kept in air for three days. Colorless prism crystals were precipitated, collected, washed with water, and dried in a vacuum over $CaCl_2$ (yield 41%). Elemental analysis: found – C, 51.26%; H, 4.90%; N, 7.38%; calc. for $C_{16}H_{18}Cl_2N_2O_4$ – C, 51.49%; H, 4.86%; N, 7.51%.

Experimental details

The compound is sensitive to air, to light and to X-ray exposure. This explain the relative low quality of the collected intensity data, resulting in a $N(hkl)_{gt}/N(param)$ ratio of about 4.8.

Discussion

The most study among the investigation on quaternary ammonium salts are that they are widely used and studied as phase-transfer catalysts [1,2], and as effective antimicrobials [3,4]. Recently, we have studied and reported some antimicrobial properties of several quaternary ammonium salts.

The title compound crystallizes with one ethylenediamine dication and two 4-chlor-benzoate anions. The cation shows a *trans*-conformation, and is fully extended in two different directions. All the bond parameters in the cation are in the normal ranges. The dication is located between two anions. The hydrogen bonds between the nitrogen atoms and the oxygen atoms join the compound along *c*-axis into one-dimensional chains, which are further linked by the weak interaction between the chlorine atoms with d(Cl···Cl) = 3.303(3) Å into a two-dimensional network in *ac*-plane.

Table 1. Data collection and handling.

Crystal:	colorless prism, size 0.05 × 0.40 × 0.50 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	4.06 cm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD, φ/ω
$2\theta_{max}$:	52.86°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	4620, 1748
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 699
$N(param)_{refined}$:	145
Programs:	SHELXTL [5], SHELXTL-plus [6]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(1)	8*f*	0.369(2)	0.950(5)	0.596(5)	0.07(2)
H(2)	8*f*	0.427(2)	0.976(5)	0.847(5)	0.05(1)
H(3)	8*f*	0.440(2)	0.512(5)	0.873(4)	0.05(1)
H(4)	8*f*	0.381(2)	0.507(5)	0.626(5)	0.06(1)
H(5)	8*f*	0.199(3)	0.503(8)	0.130(7)	0.15(3)
H(6)	8*f*	0.269(2)	0.586(5)	0.187(6)	0.05(2)
H(7)	8*f*	0.270(2)	0.514(5)	0.045(6)	0.06(2)
H(8)	8*f*	0.197(2)	0.772(6)	0.098(6)	0.09(2)
H(9)	8*f*	0.188(2)	0.693(4)	–0.058(5)	0.05(1)

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Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cl(1)	8*f*	0.47922(7)	0.7653(2)	1.0601(1)	0.089(1)	0.091(1)	0.0366(7)	–0.0056(9)	–0.0144(6)	–0.0047(7)
N(1)	8*f*	0.2450(2)	0.5697(5)	0.1077(4)	0.070(3)	0.041(2)	0.020(2)	0.001(2)	–0.001(2)	0.002(2)
O(1)	8*f*	0.3266(2)	0.8278(3)	0.3470(3)	0.092(3)	0.040(2)	0.028(2)	0.003(2)	–0.001(2)	0.008(2)
O(2)	8*f*	0.3054(2)	0.5953(3)	0.4008(3)	0.089(3)	0.044(2)	0.025(2)	–0.009(2)	–0.004(2)	–0.004(2)
C(1)	8*f*	0.3308(2)	0.7185(5)	0.4350(5)	0.056(3)	0.045(3)	0.025(2)	0.003(2)	0.009(2)	–0.004(2)
C(2)	8*f*	0.3688(2)	0.7300(5)	0.5905(4)	0.050(3)	0.041(3)	0.021(2)	0.003(2)	0.007(2)	0.000(2)
C(3)	8*f*	0.3838(2)	0.8673(6)	0.6567(5)	0.060(3)	0.044(3)	0.035(3)	0.002(3)	0.007(2)	–0.004(2)
C(4)	8*f*	0.4177(2)	0.8800(6)	0.7999(5)	0.069(4)	0.047(3)	0.039(3)	–0.006(3)	0.004(2)	–0.009(3)
C(5)	8*f*	0.4378(2)	0.7521(6)	0.8774(5)	0.051(3)	0.063(3)	0.026(2)	–0.001(3)	0.003(2)	–0.008(2)
C(6)	8*f*	0.4253(2)	0.6137(5)	0.8145(5)	0.065(3)	0.047(3)	0.030(2)	0.004(3)	0.002(2)	0.003(2)
C(7)	8*f*	0.3904(2)	0.6037(5)	0.6712(5)	0.060(3)	0.042(3)	0.031(2)	0.003(3)	0.003(2)	–0.001(2)
C(8)	8*f*	0.2233(2)	0.7098(5)	0.0308(5)	0.055(3)	0.041(3)	0.029(2)	–0.002(2)	0.002(2)	0.005(2)

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Crystal structure of 1,2-diaminopropanesilver(I) 4-nitrobenzoate dihydrate, $Ag(C_3H_6N_2H_6)(C_7H_3NO_4) \cdot 2H_2O$

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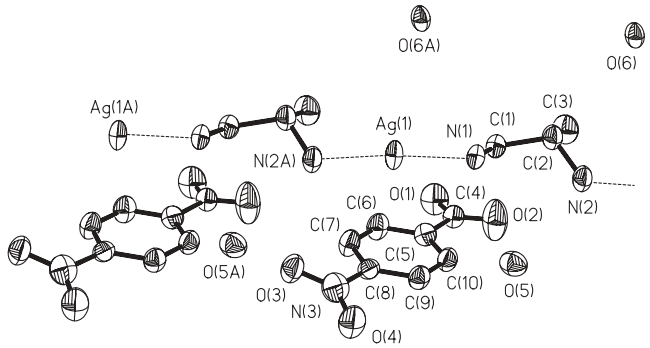

Abstract

$C_{10}H_{18}AgN_3O_6$, triclinic, $P\bar{1}$ (No. 2), a = 7.139(2) Å, b = 7.509(2) Å, c = 14.007(4) Å, α = 78.505(5)°, β = 78.789(4)°, γ = 82.023(4)°, V = 717.8 Å^3, Z = 2, $R_{gt}(F)$ = 0.036, $wR_{ref}(F^2)$ = 0.096, T = 298 K.

Source of material

Ag_2O (0.5 mmol, 116 mg) and 4-nitrobenzoic acid (1 mmol, 167 mg) were dissolved in ammonium solution (10 ml), stirring for ca. 10 min and 1,2-diaminopropane (1 mmol, 74 mg) was added to obtain a clear solution. After standing the solution in air for two days with the ammonium gas escaping, large colorless prism crystals were crystallized, isolated, washed with water for three times, and dried in a vacuum desiccator under drying $CaCl_2$ (yield 62%). Elemental analysis: found – C, 31.36%; H, 4.89%; N, 10.68%; calc. for $C_{10}H_{18}AgN_3O_6$ – C, 31.27%; H, 4.72%; N, 10.94%.

Discussion

The coordination chemistry of the coinage metals has been the subject of investigation for decades. Historically, the interest in this area grew out of the diverse structural motifs displayed by these superficially similar monovalent cations. More recently, interest has been renewed by practical concerns. The complexes of silver(I) with carboxylic acids represent a group of metal compounds which, despite their usage in synthetic organic chemistry. We have been interested in the investigation on silver(I) complexes with various organic ligands containing N and/or O atoms. Reported here is a silver(I)carboxylato complex with 1,2-diamino propane.

The title complex crystallizes with the asymmetric unit consisting of one Ag ions, one 1,2-diaminopropane molecule, one 4-nitrobenzoate anion, and two crystal water molecules. The Ag(1) ion has a linear coordination geometry, being coordinated by two nitrogen atoms from two amine molecules. The Ag—N distances are 2.124(3) Å and 2.132(3) Å and the N–Ag–N angle is 175.5(1)°. The anion is pendent and acts as a counterion to maitain charge balance. The structure of the complex is simple one-dimensional chain constructed from Ag atoms and the amine ligands. In addition, there are a variety of N–H···O, O–H···O and C–H···O hydrogen bonds [d(N1···O5) = 2.996(4) Å; d(N1···O6) = 3.117(4) Å; d(N2···O3) = 3.037(4) Å; d(N2···O5) = 3.020(4) Å; d(O5···O3) = 2.721(4) Å; d(O5···O6) = 2.723(4) Å; d(O6···O4) = 2.722(4) Å; d(O6···O4) = 2.730(4) Å; d(C7···O2) = 3.376(4) Å; d(C10···O3) = 3.348(4) Å] which extend the two-dimensional layers into three-dimensional supramolecular array.

Table 1. Data collection and handling.

Crystal:	colorless prism, size 0.16 × 0.35 × 0.54 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	14.32 cm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD, φ/ω
$2\theta_{max}$:	52.9°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	4158, 2873
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 2353
$N(param)_{refined}$:	253
Programs:	SHELXTL [1], SHELXTL-plus [2]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(1)	2*i*	0.716(4)	0.468(3)	0.902(2)	0.03(1)
H(2)	2*i*	0.760(5)	0.283(3)	0.923(2)	0.03(1)
H(3)	2*i*	0.405(6)	0.549(6)	0.811(3)	0.04(1)
H(4)	2*i*	0.410(7)	0.435(6)	0.909(4)	0.06(1)
H(5)	2*i*	0.814(5)	0.261(4)	0.759(3)	0.07(1)
H(6)	2*i*	0.730(7)	0.478(3)	0.739(3)	0.06(1)
H(7)	2*i*	0.501(6)	0.205(6)	0.844(3)	0.06(1)
H(8)	2*i*	0.558(6)	0.208(5)	0.667(3)	0.07(2)
H(9)	2*i*	0.485(5)	0.421(2)	0.654(2)	0.019(8)
H(10)	2*i*	0.343(2)	0.292(6)	0.707(4)	0.07(1)
H(11)	2*i*	1.206(7)	0.724(6)	0.505(4)	0.07(1)
H(12)	2*i*	1.356(7)	0.789(6)	0.614(3)	0.06(1)
H(13)	2*i*	0.846(5)	0.903(5)	0.786(3)	0.04(1)
H(14)	2*i*	0.699(6)	0.838(5)	0.660(3)	0.04(1)
H(15)	2*i*	0.515(5)	0.769(5)	0.890(2)	0.04(1)
H(16)	2*i*	0.620(6)	0.810(4)	0.956(3)	0.06(1)
H(17)	2*i*	0.108(3)	0.052(5)	0.056(3)	0.04(1)
H(18)	2*i*	0.195(8)	0.030(7)	–0.037(2)	0.08(2)

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Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ag(1)	2*i*	1.08961(4)	0.39630(4)	0.86104(2)	0.0231(2)	0.0611(2)	0.0674(3)	–0.0056(1)	–0.0119(1)	–0.0111(2)
N(1)	2*i*	0.7907(4)	0.3784(4)	0.8756(2)	0.022(1)	0.043(2)	0.049(2)	–0.002(1)	–0.006(1)	–0.010(2)
N(2)	2*i*	0.3843(4)	0.4365(5)	0.8469(3)	0.027(2)	0.050(2)	0.048(2)	–0.004(1)	–0.010(1)	–0.011(2)
N(3)	2*i*	1.2132(6)	0.9037(5)	0.7892(3)	0.057(2)	0.063(2)	0.058(2)	–0.009(2)	–0.013(2)	–0.010(2)
O(1)	2*i*	0.9511(5)	0.6871(5)	0.4215(2)	0.071(2)	0.096(3)	0.048(2)	–0.012(2)	–0.012(2)	–0.024(2)
O(2)	2*i*	0.6818(5)	0.7207(7)	0.5135(3)	0.058(2)	0.165(4)	0.073(2)	–0.022(2)	–0.011(2)	–0.057(3)
O(3)	2*i*	1.3866(4)	0.8477(4)	0.7854(2)	0.038(2)	0.066(2)	0.060(2)	0.004(1)	–0.018(1)	–0.018(2)
O(4)	2*i*	1.1152(4)	0.9926(5)	0.8515(2)	0.048(2)	0.097(2)	0.061(2)	–0.001(2)	–0.004(2)	–0.052(2)
O(5)	2*i*	0.5732(4)	0.7166(4)	0.9411(2)	0.054(2)	0.043(2)	0.048(2)	–0.007(1)	–0.017(1)	–0.011(1)
O(6)	2*i*	0.2259(4)	0.0290(5)	0.0220(2)	0.046(2)	0.076(2)	0.057(2)	–0.016(2)	–0.010(2)	–0.026(2)
C(1)	2*i*	0.7298(5)	0.3610(5)	0.7833(3)	0.029(2)	0.042(2)	0.047(2)	–0.004(2)	–0.002(2)	–0.011(2)
C(2)	2*i*	0.5253(5)	0.3104(6)	0.7969(3)	0.031(2)	0.047(2)	0.045(2)	–0.005(2)	–0.010(2)	–0.009(2)
C(3)	2*i*	0.4791(7)	0.3035(7)	0.6966(4)	0.055(3)	0.070(3)	0.048(3)	–0.009(2)	–0.014(2)	–0.020(2)
C(4)	2*i*	0.8524(5)	0.7246(5)	0.4966(3)	0.039(2)	0.049(2)	0.028(2)	–0.005(2)	–0.006(2)	–0.015(2)
C(5)	2*i*	0.9438(5)	0.7747(5)	0.5707(3)	0.042(2)	0.043(2)	0.037(2)	–0.004(2)	–0.009(2)	–0.007(2)
C(6)	2*i*	1.1398(6)	0.7617(6)	0.5573(3)	0.038(2)	0.065(3)	0.037(2)	–0.003(2)	0.003(2)	–0.018(2)
C(7)	2*i*	1.2249(6)	0.8044(6)	0.6278(3)	0.033(2)	0.063(3)	0.047(2)	0.000(2)	–0.005(2)	–0.016(2)
C(8)	2*i*	1.1168(5)	0.8622(5)	0.7108(3)	0.035(2)	0.033(2)	0.039(2)	0.000(1)	–0.006(2)	–0.006(2)
C(9)	2*i*	0.9181(5)	0.8765(5)	0.7218(3)	0.035(2)	0.050(2)	0.038(2)	–0.002(2)	–0.002(2)	–0.017(2)
C(10)	2*i*	0.8303(5)	0.8320(5)	0.6522(3)	0.031(2)	0.049(2)	0.044(2)	–0.002(2)	–0.002(2)	–0.014(2)

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Crystal structure of aqua-bis(4-nitrobenzoato)disilver(I), $Ag_2(C_7H_4NO_4)_2(H_2O)$

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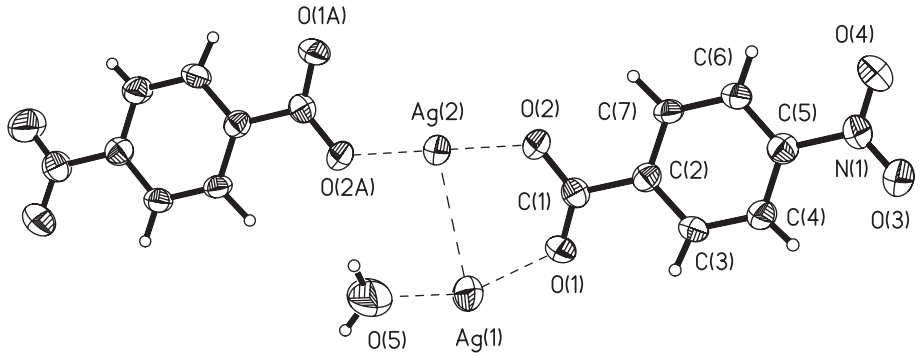

Abstract

$C_{14}H_{10}Ag_2N_2O_9$, monoclinic, *C*12/*c*1 (No. 15), $a = 21.164(6)$ Å, $b = 6.451(2)$ Å, $c = 12.219(4)$ Å, $\beta = 104.646(4)°$, $V = 1614.1$ Å^3, $Z = 4$, $R_{gt}(F) = 0.035$, $wR_{ref}(F^2) = 0.074$, $T = 298$ K.

Source of material

Ag_2O (0.5 mmol, 116 mg) and 4-nitrobenzoic acid (1 mmol, 167 mg) were dissolved in ammonium solution (10 ml) and stirred for ca. 10 min to obtain a clear solution. After standing still the solution in air for two days with the ammonium gas escaping, large colorless prism crystals were crystallized, isolated, washed with water for three times, and dried in a vacuum desiccator under drying $CaCl_2$ (yield 41%). Elemental analysis: found – C, 30.10%; H, 1.81%; N, 5.00%; calc. for $C_7H_5AgNO_{4.5}$ – C, 29.71%; H, 1.78%; N, 4.95%.

Discussion

Silver is by far the less investigated coinage metal in coordination chemistry, which can possibly be attributed to the poor solubility of silver(I) compounds in common solvents and the sensitivity toward photodecomposition [1]. On the other hand, it has been found that many factors such as the nature of the ligands, solvents, counter-anions, etc., appear to modulate the stereochemistry of silver complexes [2]. Our previous studies on the coordination of various silver(I) salts to a macrocyclic Schiff Base have clearly shown their versatility [3].

X-ray single crystal diffraction reveals the title complex crystallizes with two crystallographically different Ag ions, two 4-nitrobenzoate anions and one coordinated water molecule. The Ag(1), Ag(2) and O(5) are localized at special positions. The Ag(1) ion is coordinated by two oxygen atoms from two nitrobenzoate anions and one water molecule. The Ag1—O distances are 2.311(4) Å and 2.328(4) Å and the O–Ag1–O angles are 95.4(2)° and 132.3(2)°. Ag(2) ion is localized at a two-fold rotation axis and has an exactly linear environment, being coordinated by two oxygen atom with Ag—O distance of 2.097(4) Å and O–Ag–O angle of 180°. Such a linking way results in chain-like structure in which there are ligand supported Ag···Ag interactions [d(Ag···Ag) = 3.151(3) Å].

Table 1. Data collection and handling.

Crystal:	colorless prism, size 0.06 × 0.35 × 0.40 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	12.41 cm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD, φ/ω
$2\theta_{max}$:	52.9°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	4127, 1522
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 1137
$N(param)_{refined}$:	145
Programs:	SHELXTL [4], SHELXTL-plus [5]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(1)	8*f*	0.357(2)	0.642(7)	0.103(4)	0.06(1)
H(2)	8*f*	0.303(2)	0.949(7)	0.024(4)	0.05(1)
H(3)	8*f*	0.359(2)	0.862(7)	–0.252(4)	0.06(1)
H(4)	8*f*	0.412(2)	0.546(7)	–0.179(4)	0.06(2)
H(5)	8*f*	0.515(4)	–0.28(1)	0.318(3)	0.13(3)

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Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ag(1)	4*e*	1/2	0.11959(7)	1/4	0.0910(4)	0.0367(3)	0.0729(4)	0	0.0394(3)	0
Ag(2)	4*b*	1/2	0	0	0.0566(3)	0.0369(3)	0.0406(3)	0.0118(2)	0.0152(2)	0.0023(2)
N(1)	8*f*	0.2949(2)	1.1294(6)	–0.1631(3)	0.052(2)	0.046(2)	0.042(2)	0.014(2)	0.008(2)	0.007(2)
O(1)	8*f*	0.4386(2)	0.3607(5)	0.1283(2)	0.076(2)	0.055(2)	0.032(2)	0.023(2)	0.018(2)	0.013(2)
O(2)	8*f*	0.4469(2)	0.2749(4)	–0.0445(2)	0.068(2)	0.036(1)	0.038(2)	0.013(1)	0.016(2)	–0.004(1)
O(3)	8*f*	0.2618(2)	1.2179(6)	–0.1117(3)	0.121(3)	0.082(3)	0.060(2)	0.062(2)	0.034(2)	0.016(2)
O(4)	8*f*	0.3033(2)	1.1913(5)	–0.2517(3)	0.083(2)	0.056(2)	0.050(2)	0.013(2)	0.019(2)	0.018(2)
O(5)	4*e*	1/2	–0.210(1)	1/4	0.164(7)	0.085(4)	0.055(4)	0	0.030(4)	0
C(1)	8*f*	0.4281(2)	0.3896(6)	0.0249(4)	0.037(2)	0.033(2)	0.038(2)	–0.002(2)	0.009(2)	0.002(2)
C(2)	8*f*	0.3905(2)	0.5780(6)	–0.0261(3)	0.033(2)	0.033(2)	0.035(2)	–0.002(2)	0.009(2)	–0.004(2)
C(3)	8*f*	0.3568(2)	0.6960(7)	0.0361(4)	0.053(3)	0.047(2)	0.033(2)	0.013(2)	0.020(2)	0.012(2)
C(4)	8*f*	0.3249(2)	0.8740(7)	–0.0090(4)	0.042(2)	0.049(2)	0.038(3)	0.014(2)	0.014(2)	0.004(2)
C(5)	8*f*	0.3272(2)	0.9356(6)	–0.1150(4)	0.037(2)	0.040(2)	0.035(2)	–0.001(2)	0.007(2)	–0.002(2)
C(6)	8*f*	0.3590(2)	0.8197(6)	–0.1801(4)	0.040(2)	0.040(2)	0.028(2)	0.001(2)	0.011(2)	0.002(2)
C(7)	8*f*	0.3900(2)	0.6401(6)	–0.1353(3)	0.039(2)	0.040(2)	0.024(2)	0.004(2)	0.009(2)	–0.002(2)

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