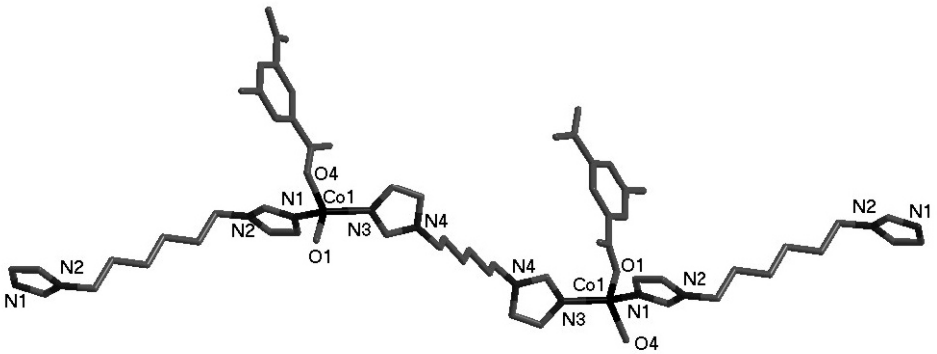
Crystal structure of *catena*-{[μ_2-5-methylisophthalato][μ_2-1,6-bis(imidazol-1-yl)-hexane]cobalt(II)}, $Co(C_9H_6O_4)(C_{12}H_{18}N_4)$

Min-Le Han*, Rui Zhang and Zu-Qiang Zhang

Luoyang Normal University, College of Chemistry and Chemical Engineering, Luoyang 471022, Henan, P. R. China

Received March 9, 2011, accepted and available on-line August 9, 2011; CCDC no. 1267/3433



Abstract

$C_{21}H_{24}CoN_4O_4$, triclinic, $P\bar{1}$ (no. 2), a = 9.782(1) Å, b = 10.135(1) Å, c = 11.277(1) Å, α = 94.587(1)°, β = 99.261(1)°, γ = 101.145(1)°, V = 1075.5 Å^3, Z = 2, $R_{gt}(F)$ = 0.033, $wR_{ref}(F^2)$ = 0.077, T = 296 K.

Source of material

1,6-bis(imidazol-1-yl)-hexane (bih, 22 mg, 0.1 mmol), 5-methyliso- phthalic acid (mip, 17.9 mg, 0.1 mmol), $Co(OAc)_2 \cdot 4H_2O$ (24 mg, 0.1 mmol) and KOH (11.2 mg, 0.2 mmol) were added to water (12 ml) in a Teflon-lined stainless steel vessel. The mixture was heated at 433 K for 3 d, and then slowly cooled down to room temperature. Pink block-like crystals of the title complex were obtained.

Discussion

Metal-organic hybrid materials are studied because of their intriguing structural architectures and topologies, as well as their potential applications as functional materials in the fields of molecular recognition, ion exchange, adsorption, fluorescence, catalysis, and magnetism [1-5]. Multicarboxylate ligands have been widely used to construct various coordination structures. For example, 1,3-benzenedicarboxylic acid, 1,2,3-benzenetricarboxylic acid as well as their derivatives [6-7] have been widely investigated for constructing novel coordination polymeric frameworks.

The crystal structure of the title complex comprises a 5-methylisophthalato molecule, a Co(II) ion and a 1,6-bis(imidazol-1-yl)-hexane molecule per asymmetric unit. Both carboxylate groups of the acid are deprotonated. The Co(II) ion has the distorted tetrahedral coordination which is composed of two nitrogen atoms from the bih ligands and two oxygen atoms from the carboxyl groups of mip. The Co—O distances are 1.981(1) Å and 2.010(2) Å, the Co—N distances are 2.016(2) Å and 2.036(2) Å. The bond angles around the central Co(II) ion range from 97.85(6)° to 114.93(8)°. Four Co(II) ions are interlinked by the two bih and the two mip ligands, thus affording a square grid (puckered 4^4 net) with a large window of 10.14 × 15.88 Å^2. The single nets are interlocked and form a 2-fold interpenetrated architecture.

* Correspondence author (e-mail: minle_han@163.com)

Table 1. Data collection and handling.

Crystal:	pink block, size 0.18 × 0.23 × 0.29 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	8.32 cm^{-1}
Diffractometer, scan mode:	CCD area detector, φ/ω
$2\theta_{max}$:	51°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	8239, 3984
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 3377
$N(param)_{refined}$:	272
Programs:	SHELXS-97, SHELXL-97, SHELXTL [8]

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

Atom	Site	x	y	z	U_{iso}
H(2)	2*i*	0.7438	1.1049	0.6920	0.043
H(4)	2*i*	0.3870	1.2478	0.6506	0.046
H(6)	2*i*	0.3665	0.8485	0.6289	0.049
H(9A)	2*i*	0.1600	1.0918	0.6536	0.098
H(9B)	2*i*	0.1516	0.9352	0.6391	0.098
H(9C)	2*i*	0.1565	1.0157	0.5262	0.098
H(10)	2*i*	0.6353	0.4479	0.4325	0.053
H(11)	2*i*	0.9900	0.7135	0.5369	0.067
H(12)	2*i*	0.9845	0.6257	0.3286	0.072
H(13A)	2*i*	0.6650	0.3560	0.2221	0.074
H(13B)	2*i*	0.8012	0.4228	0.1744	0.074
H(14A)	2*i*	0.7086	0.6049	0.1240	0.070
H(14B)	2*i*	0.5865	0.5676	0.1977	0.070
H(15A)	2*i*	0.6022	0.4251	–0.0235	0.074
H(15B)	2*i*	0.4845	0.3771	0.0522	0.074
H(16)	2*i*	0.9699	0.8664	0.7932	0.057
H(17)	2*i*	0.8632	0.5406	0.9486	0.067
H(18)	2*i*	1.0587	0.6912	1.0880	0.070

Table 2. Continued.

Atom	Site	*x*	*y*	*z*	U_{iso}
H(19A)	2*i*	1.1781	0.9620	1.0840	0.074
H(19B)	2*i*	1.1565	1.0127	0.9557	0.074
H(20A)	2*i*	1.2971	0.8632	0.8937	0.079
H(20B)	2*i*	1.3287	0.8312	1.0278	0.079
H(21A)	2*i*	1.4360	1.0633	1.0856	0.082
H(21B)	2*i*	1.4150	1.0855	0.9483	0.082

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(1)	2*i*	0.72398(3)	0.61827(3)	0.68291(3)	0.0413(2)	0.0209(2)	0.0447(2)	0.0053(1)	0.0007(1)	0.0033(1)
O(1)	2*i*	0.5704(2)	0.7253(1)	0.6735(2)	0.057(1)	0.0206(7)	0.067(1)	0.0102(7)	0.0015(8)	0.0065(7)
O(2)	2*i*	0.7689(2)	0.8617(2)	0.6571(2)	0.053(1)	0.0337(9)	0.066(1)	0.0169(8)	0.0015(9)	0.0065(8)
O(3)	2*i*	0.7970(2)	1.3576(2)	0.7398(2)	0.044(1)	0.0318(8)	0.073(1)	0.0033(7)	–0.0025(8)	0.0014(8)
O(4)	2*i*	0.6037(2)	1.4372(1)	0.6837(2)	0.0473(9)	0.0201(7)	0.064(1)	0.0077(6)	0.0091(8)	0.0063(7)
N(1)	2*i*	0.7965(2)	0.5871(2)	0.5277(2)	0.043(1)	0.0296(9)	0.047(1)	0.0058(8)	0.0040(9)	0.0045(8)
N(2)	2*i*	0.7904(2)	0.5085(2)	0.3390(2)	0.055(1)	0.048(1)	0.047(1)	0.014(1)	0.011(1)	0.0024(9)
N(3)	2*i*	0.8771(2)	0.6855(2)	0.8320(2)	0.050(1)	0.032(1)	0.046(1)	0.0054(8)	–0.0003(9)	0.0044(8)
N(4)	2*i*	1.0530(2)	0.8215(2)	0.9565(2)	0.046(1)	0.046(1)	0.053(1)	0.0061(9)	–0.004(1)	–0.005(1)
C(1)	2*i*	0.5659(2)	0.9583(2)	0.6595(2)	0.050(1)	0.021(1)	0.037(1)	0.0100(9)	–0.000(1)	0.0032(8)
C(2)	2*i*	0.6455(2)	1.0899(2)	0.6785(2)	0.040(1)	0.028(1)	0.039(1)	0.0083(9)	0.0008(9)	0.0036(9)
C(3)	2*i*	0.5790(2)	1.1993(2)	0.6774(2)	0.043(1)	0.021(1)	0.036(1)	0.0069(9)	0.0029(9)	0.0035(8)
C(4)	2*i*	0.4319(2)	1.1749(2)	0.6542(2)	0.046(1)	0.025(1)	0.047(1)	0.0126(9)	0.008(1)	0.0064(9)
C(5)	2*i*	0.3501(2)	1.0440(2)	0.6362(2)	0.041(1)	0.032(1)	0.049(1)	0.0048(9)	0.004(1)	0.008(1)
C(6)	2*i*	0.4195(2)	0.9366(2)	0.6399(2)	0.048(1)	0.023(1)	0.048(1)	0.0026(9)	0.000(1)	0.0064(9)
C(7)	2*i*	0.6410(3)	0.8428(2)	0.6626(2)	0.055(2)	0.025(1)	0.043(1)	0.013(1)	–0.003(1)	0.0018(9)
C(8)	2*i*	0.6687(2)	1.3408(2)	0.7025(2)	0.044(1)	0.024(1)	0.038(1)	0.0054(9)	0.008(1)	0.0035(9)
C(9)	2*i*	0.1899(3)	1.0194(3)	0.6115(3)	0.046(2)	0.046(2)	0.101(2)	0.005(1)	0.007(2)	0.016(2)
C(10)	2*i*	0.7231(2)	0.5035(2)	0.4333(2)	0.044(1)	0.036(1)	0.049(1)	0.004(1)	0.007(1)	0.003(1)
C(11)	2*i*	0.9172(3)	0.6484(3)	0.4897(2)	0.046(1)	0.050(2)	0.065(2)	–0.002(1)	0.005(1)	0.007(1)
C(12)	2*i*	0.9150(3)	0.6008(3)	0.3747(3)	0.051(2)	0.065(2)	0.067(2)	0.007(1)	0.019(1)	0.013(1)
C(13)	2*i*	0.7269(3)	0.4416(3)	0.2166(2)	0.079(2)	0.060(2)	0.048(2)	0.019(2)	0.014(1)	–0.004(1)
C(14)	2*i*	0.6429(3)	0.5300(3)	0.1458(2)	0.067(2)	0.059(2)	0.048(2)	0.016(1)	0.012(1)	–0.004(1)
C(15)	2*i*	0.5455(3)	0.4561(3)	0.0316(2)	0.073(2)	0.059(2)	0.050(2)	0.014(1)	0.008(1)	–0.005(1)
C(16)	2*i*	0.9669(2)	0.8035(2)	0.8490(2)	0.051(1)	0.039(1)	0.046(1)	0.004(1)	–0.003(1)	0.004(1)
C(17)	2*i*	0.9091(3)	0.6257(3)	0.9344(2)	0.065(2)	0.045(1)	0.054(2)	0.005(1)	–0.000(1)	0.014(1)
C(18)	2*i*	1.0172(3)	0.7082(3)	1.0121(2)	0.065(2)	0.057(2)	0.048(2)	0.011(1)	–0.005(1)	0.013(1)
C(19)	2*i*	1.1722(3)	0.9360(3)	0.9984(3)	0.053(2)	0.054(2)	0.066(2)	0.002(1)	–0.006(1)	–0.011(1)
C(20)	2*i*	1.3080(3)	0.9005(3)	0.9774(3)	0.058(2)	0.063(2)	0.067(2)	0.003(1)	0.003(1)	–0.011(1)
C(21)	2*i*	1.4308(3)	1.0201(3)	1.0046(3)	0.061(2)	0.069(2)	0.062(2)	–0.004(2)	0.006(1)	–0.009(1)

References

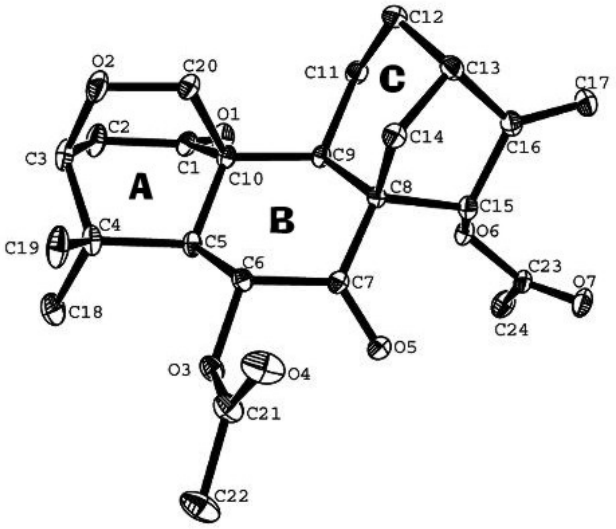
1. Mukherjee, P. S.; Dalai, S.; Chaudhuri, N. R.; Zangrando, E.; Lloret, F.: The first metamagnetic one-dimensional molecular material with nickel(II) and end-to-end azido bridges. Chem. Commun. **16** (2001) 1444-1445.
2. Kido, J.; Okamoto, Y.: Organo Lanthanide Metal Complexes for Electroluminescent Materials. Chem. Rev. **102** (2002) 2357-2368.
3. Kolotilov, S. V.; Cador, O.; Golhen, S.; Shvets, O.; Ilyin, V. G.; Pavlishchuk, V. V.; Ouahab, L.: Synthesis, structure, sorption and magnetic properties of Ni(II) and Cu(II) complexes with thiosemicarbazone of 2-hydroxybenzaldehyde, bridged by 4,4′-bipyridine. Inorg. Chim. Acta. **360** (2007) 1883-1889.
4. Alldendorf, M. D.; Bauer, C. A.; Bhakta, R. K.: Luminescent Metal-Organic Frameworks. Chem. Soc. Rev. **38** (2009) 1330-1352.
5. Zheng, N.; Bu, X.; Lu, H.; Zhang, Q.; Feng, P.: Crystalline Superlattices from Single-Sized Quantum Dots. J. Am. Chem. Soc. **127** (2005) 11963-11965.
6. Ma, L. F.; Meng, Q. L.; Li, C. P.; Li, B.; Wang, L. Y.; Du, M.; Liang, F. P.: Delicate Substituent Effect of Benzene-1,2,3-Tricarboxyl Tectons on Structural Assembly of Unusual Self-Penetrating Coordination Frameworks. Cryst. Growth Des. **10** (2010) 3036-3043.
7. Liu, G. X.; Zhu, K.; Nishihara, S.; Huang, R. Y.; Ren, X. M.: Syntheses, structures and photoluminescent properties of two zinc(II) coordination polymers based on aromatic polycarboxylate and 1,4-bis(imidazol-1-ylmethyl)benzene. Inorg. Chem. Acta. **362** (2009) 5103-5108.
8. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. **A64** (2008) 112-122.

Refinement of the crystal structure of 3,20-epoxy-6b,15b-diacetoxy-ent-kaurene-1,7-dione, $C_{24}H_{30}O_7$

Jing-Jie Zhang[I], Qi-Ji Li[I], Qi-Long Zhang[II] and Lu-Tai Pan[*,I]

[I] Guiyang College of Traditional Chinese Medicine, Guiyang 550002, P. R. China
[II] Department of Chemistry, Guiyang Medical College, Guiyang 550004, P. R. China

Received January 22, 2011, accepted and available on-line July 18, 2011; CCDC no. 1267/3373



Abstract

$C_{24}H_{30}O_7$, monoclinic, $P2_1$ (no. 4), a = 6.7733(5) Å, b = 14.662(1) Å, c = 11.4365(9) Å, β = 95.770(3)°, V = 1130.0 Å^3, Z = 2, $R_{gt}(F)$ = 0.040, $wR_{ref}(F^2)$ = 0.102, T = 293 K.

Source of material

The dried and powdered leaves of Isodon eriocalyx were extracted with 95% methanol and filtered. The filtrate was concentrated and extracted with diethyl ether to give a residue, which was applied to silica gel column chromatography eluting with chloroform/acetone (1:0-0:1). The fraction [chloroform/acetone (8:1)] produced colorless needles by recrystallization from methanol; m.p. 500-502 K; $[\alpha]_D^{13}$ = –175.5 (c = 0.98, C_5H_5N).

Experimental details

The molecule contains no heavy atoms, therefore a meaningful Flack parameter could not be determined with Mo K_α radiation (x = –0.5(10)) and the absolute structure could not be made sure.

Discussion

The title compound was first isolated from Rabdosia nervosa. Its crystal structure has not been analyzed completely [1-3]. We used a larger data set and achieved better residual values compared to the previous publications, e.g. in [3].

The compound crystallizes with one molecule in the asymmetric unit of the acentric space group $P2_1$. The bond distances and bond angles are all in normal range. The carbonyl distances are d(C1—O1) = 1.201(3) Å and d(C7—O5) = 1.198(3) Å. The distances in the acetoxy groups are d(C23—O7) = 1.189(3) Å, d(C23—O6) = 1.350(3) Å, and d(C15—O6) = 1.453(3) Å, with an angle of ∠C23–O6–C15 = 117.84(18)°, and d(C21—O4) = 1.198(4) Å, d(C21—O3) = 1.351(3) Å and d(C6—O3) = 1.445(3) Å, with an angle of ∠C21–O3–C6 = 116.4(2)°. The compound contains three six-membered rings, ring A(C1/C2/C3/C4/C5/C10) is in boat conformation, ring B(C5/C6/C7/C8/C9/C10) is in chair conformation, and ring C(C8/C9/C11/C12/C13/C14) is in a distorted chair conformation.

Table 1. Data collection and handling.

Crystal:	colourless block, size 0.21 × 0.25 × 0.29 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	0.92 cm^{-1}
Diffractometer, scan mode:	Bruker CCD, φ/ω
$2\theta_{max}$:	50°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	12084, 3929
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 3096
$N(param)_{refined}$:	281
Program:	SHELXL-97 [4]

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

Atom	Site	x	y	z	U_{iso}
H(2A)	2*a*	0.3424	0.3019	0.5571	0.092
H(2B)	2*a*	0.2968	0.1971	0.5413	0.092
H(3)	2*a*	0.6198	0.2177	0.6319	0.078
H(5)	2*a*	0.4903	0.1126	0.3268	0.056
H(6)	2*a*	0.8838	0.1662	0.2934	0.054
H(9)	2*a*	0.3562	0.2342	0.1688	0.052
H(11A)	2*a*	0.3069	0.3685	0.0950	0.070
H(11B)	2*a*	0.3574	0.3970	0.2264	0.070
H(12A)	2*a*	0.6586	0.4518	0.1938	0.081
H(12B)	2*a*	0.5177	0.4865	0.0858	0.081
H(13)	2*a*	0.8043	0.4262	0.0111	0.072
H(14A)	2*a*	0.8637	0.3194	0.1828	0.063
H(14B)	2*a*	0.9094	0.2770	0.0612	0.063
H(15)	2*a*	0.6228	0.2013	–0.0680	0.057
H(17A)	2*a*	0.5463	0.4361	–0.1772	0.090
H(17B)	2*a*	0.4359	0.3420	–0.2163	0.090
H(18A)	2*a*	0.6033	0.0030	0.4894	0.156
H(18B)	2*a*	0.4179	0.0623	0.5111	0.156
H(18C)	2*a*	0.5905	0.0494	0.6118	0.156
H(19A)	2*a*	0.9523	0.1855	0.4927	0.146
H(19B)	2*a*	0.9369	0.0790	0.4838	0.146
H(19C)	2*a*	0.9139	0.1278	0.6036	0.146
H(20A)	2*a*	0.8052	0.3138	0.3575	0.067
H(20B)	2*a*	0.6316	0.3819	0.3740	0.067

* Correspondence author (e-mail: ltpan@yahoo.cn)

Table 2. Continued.

Atom	Site	*x*	*y*	*z*	U_{iso}
H(22A)	2*a*	0.8956	–0.1197	0.3054	0.154
H(22B)	2*a*	1.1261	–0.1087	0.3313	0.154
H(22C)	2*a*	1.0307	–0.1228	0.2019	0.154
H(24A)	2*a*	0.0225	0.1533	–0.0527	0.114
H(24B)	2*a*	0.0618	0.0709	–0.1346	0.114
H(24C)	2*a*	–0.0222	0.1627	–0.1894	0.114

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)	2*a*	0.3389(4)	0.2602(2)	0.3854(2)	0.043(1)	0.072(2)	0.047(1)	0.001(1)	0.007(1)	–0.009(1)
C(2)	2*a*	0.3773(4)	0.2469(3)	0.5166(2)	0.060(2)	0.129(3)	0.043(2)	0.010(2)	0.012(1)	–0.006(2)
C(3)	2*a*	0.5942(4)	0.2256(2)	0.5467(2)	0.053(2)	0.109(2)	0.033(1)	–0.009(2)	0.003(1)	–0.002(1)
C(4)	2*a*	0.6618(4)	0.1402(2)	0.4862(2)	0.053(2)	0.093(2)	0.040(1)	0.000(2)	0.005(1)	0.013(1)
C(5)	2*a*	0.6025(3)	0.1533(2)	0.3490(2)	0.037(1)	0.066(2)	0.038(1)	–0.005(1)	0.0022(9)	0.005(1)
C(6)	2*a*	0.7662(3)	0.1286(2)	0.2715(2)	0.039(1)	0.050(1)	0.045(1)	0.003(1)	0.002(1)	0.006(1)
C(7)	2*a*	0.6982(3)	0.1418(2)	0.1423(2)	0.039(1)	0.052(2)	0.043(1)	–0.003(1)	0.0077(9)	–0.003(1)
C(8)	2*a*	0.6301(3)	0.2373(2)	0.1082(2)	0.039(1)	0.047(1)	0.035(1)	0.001(1)	0.0026(9)	0.002(1)
C(9)	2*a*	0.4751(3)	0.2710(2)	0.1905(2)	0.039(1)	0.055(1)	0.036(1)	0.002(1)	0.0008(9)	–0.003(1)
C(10)	2*a*	0.5282(3)	0.2530(2)	0.3229(2)	0.035(1)	0.060(2)	0.038(1)	0.001(1)	0.0022(9)	–0.003(1)
C(11)	2*a*	0.4121(4)	0.3702(2)	0.1592(2)	0.063(2)	0.061(2)	0.052(2)	0.016(1)	–0.000(1)	–0.005(1)
C(12)	2*a*	0.5765(5)	0.4324(2)	0.1238(2)	0.087(2)	0.049(2)	0.064(2)	0.007(1)	0.000(2)	0.002(1)
C(13)	2*a*	0.7071(4)	0.3845(2)	0.0400(2)	0.067(2)	0.056(2)	0.058(2)	–0.009(1)	0.007(1)	0.008(1)
C(14)	2*a*	0.8069(4)	0.3030(2)	0.1044(2)	0.047(1)	0.059(2)	0.054(1)	–0.003(1)	0.008(1)	–0.001(1)
C(15)	2*a*	0.5460(3)	0.2422(2)	–0.0222(2)	0.046(1)	0.058(2)	0.039(1)	0.004(1)	0.0065(9)	0.003(1)
C(16)	2*a*	0.5793(4)	0.3395(2)	–0.0596(2)	0.062(2)	0.062(2)	0.049(2)	0.006(1)	0.009(1)	0.008(1)
C(17)	2*a*	0.5142(5)	0.3761(2)	–0.1609(2)	0.098(2)	0.072(2)	0.054(2)	0.008(2)	0.007(2)	0.015(2)
C(18)	2*a*	0.5589(7)	0.0560(3)	0.5285(3)	0.149(4)	0.103(3)	0.065(2)	–0.013(3)	0.029(2)	0.026(2)
C(19)	2*a*	0.8875(5)	0.1324(3)	0.5197(3)	0.068(2)	0.174(4)	0.047(2)	0.025(2)	–0.012(1)	0.004(2)
C(20)	2*a*	0.6777(4)	0.3199(2)	0.3884(2)	0.055(2)	0.068(2)	0.043(1)	–0.007(1)	0.001(1)	–0.009(1)
C(21)	2*a*	0.9923(4)	0.0055(2)	0.2618(3)	0.050(2)	0.072(2)	0.085(2)	0.015(2)	0.008(2)	0.015(2)
C(22)	2*a*	1.0130(5)	–0.0954(3)	0.2764(4)	0.077(2)	0.078(2)	0.155(3)	0.029(2)	0.024(2)	0.037(2)
C(23)	2*a*	0.2721(4)	0.1695(2)	–0.1350(2)	0.067(2)	0.061(2)	0.034(1)	0.003(1)	0.000(1)	–0.001(1)
C(24)	2*a*	0.0650(4)	0.1361(2)	–0.1272(2)	0.067(2)	0.097(2)	0.063(2)	–0.009(2)	–0.002(1)	–0.019(2)
O(1)	2*a*	0.1764(3)	0.2747(1)	0.3369(2)	0.038(1)	0.102(2)	0.062(1)	0.0058(9)	0.0042(8)	–0.001(1)
O(2)	2*a*	0.7019(3)	0.3035(2)	0.5123(2)	0.087(2)	0.111(2)	0.045(1)	–0.030(1)	–0.010(1)	–0.009(1)
O(3)	2*a*	0.8141(2)	0.0335(1)	0.2917(2)	0.046(1)	0.061(1)	0.061(1)	0.0093(8)	0.0054(8)	0.0148(8)
O(4)	2*a*	1.1123(3)	0.0564(2)	0.2277(2)	0.057(1)	0.085(2)	0.168(2)	0.009(1)	0.042(2)	0.012(2)
O(5)	2*a*	0.7050(3)	0.0810(1)	0.0729(2)	0.095(2)	0.056(1)	0.050(1)	0.009(1)	0.0016(9)	–0.0073(9)
O(6)	2*a*	0.3397(2)	0.2135(1)	–0.0353(1)	0.047(1)	0.072(1)	0.0365(9)	0.0013(8)	0.0006(7)	–0.0073(8)
O(7)	2*a*	0.3657(3)	0.1588(2)	–0.2165(2)	0.091(2)	0.096(2)	0.041(1)	–0.011(1)	0.017(1)	–0.011(1)

Acknowledgment. This research is funded by the Science and Technology Fund of Guiyang [grant nos. (2008) 36 and (2009) 3].

References

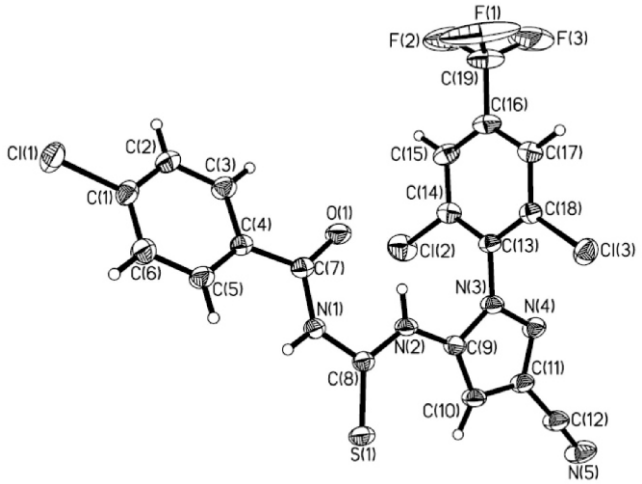
1. Sun, H.-D.; Zhao, Q.-Z.; Cha, J.-H: Studies on the diterpenoids from Rabdosia nervosa. Acta Botan. Yunnan. **6** (1984) 235-236.
2. Sun, H.-D.; Lin, Z.-W.; Wan, D.-Z.: The structure of Neorabdosin. Acta Chim. Sin. **43** (1985) 481-483.
3. Zhai, Y.; Ju X.; Zhai J.: Study on the Crystal Structure and Electronic Sturcture for Neorabdosin. J. Zhengzhou University **31** (1999) 84-88.
4. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. **A64** (2008) 112-122.

Crystal structure of *N*-[1-(2,6-dichloro-4-trifluoromethyl)-phenyl-3-cyano-1*H*-pyrazol-5-yl]-*N′*-4-chlorobenzoyl-thiourea, $C_{19}H_9Cl_3F_3N_5OS$

Jun Dai[I], Xiao-Hong Zhang[*,II], Chenghai Wu[I], Mingmin Wang[I] and Ping Zhong[*,I]

[I] Oujiang College, Wenzhou University, Wenzhou 325027, P. R. China
[II] College of Chemisty and Materials Science, Wenzhou University, Wenzhou 325027, P. R. China

Received March 1, 2011, accepted and available on-line June 23, 2011; CCDC no. 1267/3421



Abstract

$C_{19}H_9Cl_3F_3N_5OS$, monoclinic, $P2_1/n$ (no. 14), a = 16.973(2) Å, b = 7.3779(7) Å, c = 17.346(2) Å, β = 94.280(2)°, V = 2166.0 Å^3, Z = 4, $R_{gt}(F)$ = 0.074, $wR_{ref}(F^2)$ = 0.177, T = 298 K.

Source of material

Following the method in [1], reaction of 2,6-dichloro-4-trifluoromethylamine (0.01 mol) with a suspension of nitrosyl sulfuric acid, followed by reaction with a solution of ethyl 2,3-dicyanopropionate (0.01 mol) in acetic acid, gave 5-amino-3-cyano-1-(2,6-dichloro-4-trifluoromethylphenyl)-pyrazole (about 0.005 mol, product 1). Furthermore, according to the method in [2], 4-chlorobenzoyl chloride (0.007 mol) with dry potassium thiocyanate (0.1mol) was refluxed in anhydrous CH_3CN for two hours at 80 °C and was then filtrated to obtain acylisothiocyanate solution (product 2). The products 1 and 2 were then reacted in anhydrous CH_3CN for about four hours to get the title compound.

Experimental Details

Single crystals suitable for X-ray analysis were obtained by slow evaporation of the solution of acetone (m.p. 482 - 483 K).
IR and NMR data are available in the CIF file.

Discussion

Acyl-thiourea derivatives have attracted much attention due to their chemical properties and biological activity. For example, some thiourea derivatives have been found to be useful as herbicides, inhibitors, anti-HIV and plant-growth regulators [3-6]. Futhermore, the pyrazoles with the functional groups of chloride and trifluoromethyl, like 5-amino-3-cyano-1-(2,6-dichloro-4-trifluoromethylphenyl)-4 trifluoromethylsulphenylpyrazole or 5-amino-3-cyano-1-(2,6-dichloro-4-trifluoromethylphenyl)-4-trifluoromethylsulfonyl pyrazole, show good bioactivity [1]. So we envisioned the acylthiourea derivatives bearing pyrazole moiety might have high biological activity.
The title compound is an acyl-thiourea with an overall U-shape. In the crystal structure, the dihedral angles between the pyrazole and attached phenyl ring and the chlorophenyl are 73.04(1)° and 29.51(1)°, respectively. An intramolecular N2–H2···O1 hydrogen bond with an d(N2···O1) = 2.604(4) Å additionally stabilizes the molecule.

Table 1. Data collection and handling.

Crystal:	colorless block, size 0.24 × 0.25 × 0.34 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	5.68 cm^{-1}
Diffractometer, scan mode:	Bruker APEX, φ and ω
$2\theta_{max}$:	50.04°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	10964, 3810
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 3387
$N(param)_{refined}$:	289
Programs:	SHELXS-97, SHELXL-97, SHELXTL [7]

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

Atom	Site	x	y	z	U_{iso}
H(1)	4*e*	0.8603	0.6914	0.0592	0.050
H(2)	4*e*	0.9411	0.7291	0.2298	0.053
H(2A)	4*e*	1.1568	0.7770	–0.0690	0.061
H(3)	4*e*	1.1085	0.7436	0.0509	0.058
H(5)	4*e*	0.8873	0.7737	–0.0447	0.058
H(6)	4*e*	0.9350	0.8150	–0.1644	0.067
H(10)	4*e*	0.7701	0.5039	0.3135	0.057
H(15)	4*e*	1.1825	0.7134	0.3189	0.064
H(17)	4*e*	1.0899	1.1616	0.4066	0.054

* Correspondence author (e-mail: kamenzxh@163.com, zhongp0512@163.com)

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(1)	4*e*	0.76040(6)	0.5722(2)	0.15844(7)	0.0323(6)	0.089(1)	0.0489(7)	–0.0124(6)	0.0022(5)	0.0012(6)
O(1)	4*e*	1.0141(2)	0.7530(5)	0.1520(2)	0.039(2)	0.087(2)	0.043(2)	–0.015(2)	–0.001(1)	0.006(2)
F(1)	4*e*	1.2254(3)	1.1789(9)	0.3240(6)	0.066(3)	0.180(6)	0.49(1)	–0.040(3)	0.015(5)	0.204(8)
F(2)	4*e*	1.2817(2)	0.9446(7)	0.3424(4)	0.045(2)	0.143(4)	0.301(8)	–0.016(2)	0.043(3)	–0.004(5)
F(3)	4*e*	1.2521(4)	1.087(2)	0.4293(5)	0.138(5)	0.46(2)	0.198(7)	–0.204(8)	0.032(5)	–0.117(8)
N(1)	4*e*	0.8896(2)	0.6918(5)	0.1018(2)	0.035(2)	0.057(2)	0.032(2)	–0.007(2)	0.000(1)	0.003(2)
N(2)	4*e*	0.8958(2)	0.6797(5)	0.2341(2)	0.037(2)	0.056(2)	0.039(2)	–0.018(2)	0.004(2)	0.004(2)
N(3)	4*e*	0.9288(2)	0.6895(5)	0.3684(2)	0.039(2)	0.058(2)	0.037(2)	–0.015(2)	0.001(2)	0.007(2)
N(4)	4*e*	0.9045(2)	0.6374(5)	0.4380(2)	0.044(2)	0.067(2)	0.037(2)	–0.010(2)	0.006(2)	0.008(2)
N(5)	4*e*	0.7537(3)	0.4135(7)	0.5217(3)	0.055(3)	0.112(4)	0.064(3)	–0.018(3)	0.009(2)	0.031(3)
C(1)	4*e*	1.0499(3)	0.7993(6)	–0.1276(2)	0.056(3)	0.038(2)	0.044(2)	–0.004(2)	0.017(2)	–0.001(2)
C(2)	4*e*	1.1027(3)	0.7774(7)	–0.0639(3)	0.036(2)	0.064(3)	0.054(3)	–0.003(2)	0.011(2)	–0.001(2)
C(3)	4*e*	1.0735(2)	0.7563(6)	0.0073(3)	0.037(2)	0.058(3)	0.049(3)	0.002(2)	0.004(2)	0.003(2)
C(4)	4*e*	0.9930(2)	0.7534(5)	0.0155(2)	0.034(2)	0.033(2)	0.045(2)	0.000(2)	0.006(2)	0.000(2)
C(5)	4*e*	0.9416(2)	0.7752(6)	–0.0494(2)	0.033(2)	0.065(3)	0.046(2)	0.000(2)	0.002(2)	0.003(2)
C(6)	4*e*	0.9698(3)	0.7991(7)	–0.1209(3)	0.046(3)	0.079(3)	0.042(2)	–0.001(2)	0.001(2)	0.003(2)
C(7)	4*e*	0.9676(2)	0.7335(5)	0.0954(2)	0.036(2)	0.037(2)	0.047(2)	–0.002(2)	0.006(2)	0.002(2)
C(8)	4*e*	0.8513(2)	0.6498(5)	0.1681(2)	0.034(2)	0.038(2)	0.043(2)	–0.000(2)	0.003(2)	–0.001(2)
C(9)	4*e*	0.8767(2)	0.6398(6)	0.3084(2)	0.037(2)	0.046(2)	0.040(2)	–0.007(2)	–0.000(2)	0.003(2)
C(10)	4*e*	0.8152(3)	0.5529(6)	0.3393(3)	0.039(2)	0.056(3)	0.047(2)	–0.016(2)	0.003(2)	0.006(2)
C(11)	4*e*	0.8361(2)	0.5550(6)	0.4188(2)	0.037(2)	0.056(3)	0.045(2)	–0.009(2)	0.005(2)	0.010(2)
C(12)	4*e*	0.7918(3)	0.4768(7)	0.4778(3)	0.044(2)	0.074(3)	0.048(3)	–0.013(2)	0.002(2)	0.012(2)
C(13)	4*e*	1.0026(2)	0.7800(6)	0.3654(2)	0.031(2)	0.052(2)	0.033(2)	–0.006(2)	–0.002(2)	0.010(2)
C(14)	4*e*	1.0675(2)	0.6890(6)	0.3401(3)	0.045(2)	0.044(2)	0.049(2)	–0.002(2)	–0.001(2)	0.008(2)
C(15)	4*e*	1.1398(3)	0.7738(7)	0.3375(3)	0.037(2)	0.060(3)	0.063(3)	0.005(2)	0.008(2)	0.012(2)
C(16)	4*e*	1.1469(2)	0.9499(7)	0.3632(3)	0.034(2)	0.062(3)	0.059(3)	–0.008(2)	–0.002(2)	0.016(2)
C(17)	4*e*	1.0838(2)	1.0429(6)	0.3891(2)	0.042(2)	0.045(2)	0.048(2)	–0.006(2)	–0.003(2)	0.006(2)
C(18)	4*e*	1.0116(2)	0.9583(6)	0.3887(2)	0.037(2)	0.049(2)	0.034(2)	–0.001(2)	–0.003(2)	0.008(2)
C(19)	4*e*	1.2252(3)	1.043(1)	0.3624(5)	0.039(3)	0.086(4)	0.126(6)	–0.018(3)	0.001(3)	0.014(4)
Cl(1)	4*e*	1.08635(8)	0.8338(2)	–0.21759(7)	0.0733(8)	0.0760(9)	0.0493(7)	–0.0058(7)	0.0248(6)	0.0004(6)
Cl(2)	4*e*	1.05809(9)	0.4668(2)	0.3107(1)	0.0751(9)	0.0455(7)	0.103(1)	0.0027(6)	0.0030(8)	–0.0033(7)
Cl(3)	4*e*	0.93154(7)	1.0775(2)	0.41736(7)	0.0466(6)	0.0748(8)	0.0493(6)	0.0103(5)	0.0046(5)	–0.0030(6)

Acknowledgments. This work was supported by the National Natural Science Foundation of China (grant no. 20972114), Nature Science Foundation of Zhejiang Province (grant nos. Y4080027 and Y4100578) and Zhejiang Scientific Activities of College Students Plan (Emerging Artists Talents Scheme) project (no. 2010R424041).

References

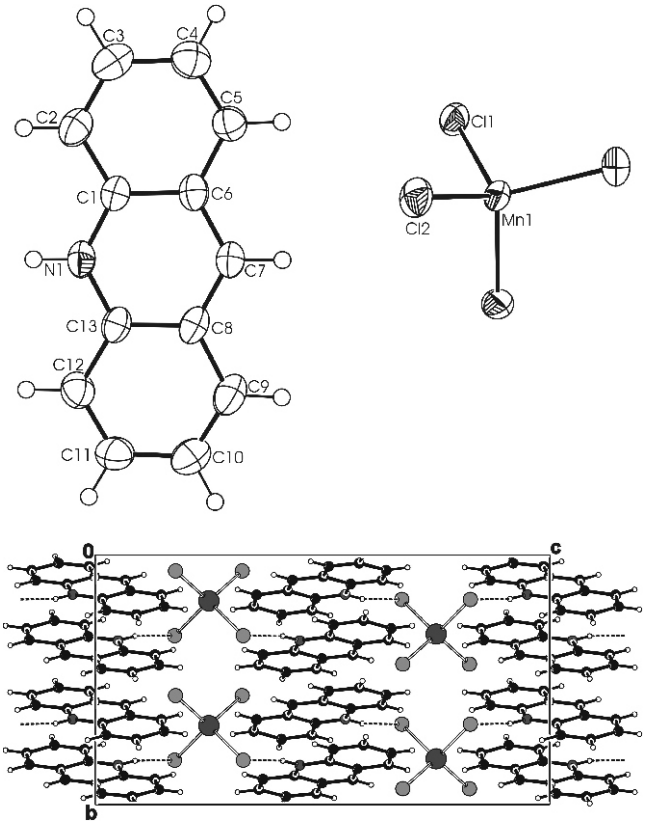
1. Hatton, L. R.; Buntain, I. G.; Hawkins, D. W.; Parnell, E. W.; Pearson, C. J.; Roberts, D. A.: Derivatives of N-phenylpyrazoles. US Patent 5232940 (1993).
2. Gong, Y.; Wang, Z.; Zhang, Z.; Chen, C.; Wang, Y.: Synthesis and Biological Activity of *N*-(2-Carboxyl-1,3,4-thiadiazol-5-yl)-*N′*-aroyl Thioureas and Aryloxyacetyl Thioureas. Chin. J. Org. Chem. **3** (2006) 360-363.
3. Xue, S. J.; Duan, L. P.; Ke, S. Y.; Zhu, J. M.: Synthesis and Herbicidal Activities of Pentylchrysanthemacyl Thiourea Pyrimidine Derivatives and Related Fuse Ring Compounds. Chin. J. Org. Chem. **24** (2004) 686-689.
4. Sun, C.; Huang, H.; Feng, M.; Shi, S.; Zhang, X.; Zhou, P.: A novel class of potent influenza virus inhibitors: Polysubstituted acylthiourea and its fused heterocycle derivatives. Bioorg. Med. Chem. Lett. **16** (2006) 162-166.
5. Venkatachalam,T. K.; Mao, C.; Uckun, F. M.: Effect of stereochemistry on the anti-HIV activity of chiral thiourea compounds. Bioorg. Med. Chem. **12** (2004) 4275-4284.
6. Li, Z. H.; Wang,Y. A.: Phosphourus, Sulfur, Silicon and the Related Elements **178** (2003) 293-297.
7. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. **A64** (2008) 112-122.

Crystal structure of bis(acridinium)tetrachloromanganate(II), $[(C_{13}H_{10}N)_2][MnCl_4]$

Kwang Ha*

Chonnam National University, School of Applied Chemical Engineering, Research Institute of Catalysis, Gwangju 500-757, Republic of Korea

Received March 18, 2011, accepted and available on-line June 23, 2011; CCDC no. 1267/3455



Abstract

$C_{26}H_{20}Cl_4MnN_2$, monoclinic, *C*2/*c* (no. 15), a = 12.838(1) Å, b = 10.2435(9) Å, c = 18.730(2) Å, β = 92.553(2)°, V = 2460.8 Å^3, Z = 4, $R_{gt}(F)$ = 0.055, $wR_{ref}(F^2)$ = 0.139, T = 200 K.

Source of material

The title compound was unexpectedly obtained as a byproduct from the reaction of $MnCl_2 \cdot 4H_2O$ (0.1982 g, 1.001 mmol) with acridine (0.3538 g, 1.974 mmol) and pyridine-2-carboxylic acid (0.2464 g, 2.001 mmol) in EtOH (20 ml). After reflux of the reaction mixture for 3 h, the formed white and yellow precipitates were separated by filtration, washed with EtOH and ether, to give the main product as a white powder (0.2321 g). The yellow byproduct (0.0672 g) was obtained from the mixture of filtrate and washing solution by recrystallizing at -85 °C. Crystals suitable for X-ray diffraction analysis were obtained by slow evaporation from a CH_3NO_2 solution of the byproduct.

Experimental details

Hydrogen atoms were positioned geometrically and allowed to ride on their parent atoms with d(C—H) = 0.95 Å, d(N—H) = 0.88 Å and U_{iso}(H) = 1.2 U_{eq}(C,N). The highest peak (0.51 e Å^{-3}) and the deepest hole (–0.55 e Å^{-3}) in the difference Fourier map are located 1.13 Å and 1.76 Å from the atoms Cl1 and Cl2, respectively.

Discussion

The asymmetric unit of the title compound contains a protonated acridinium cation and half of an anionic Mn(II) complex (figure, top). In the complex, the Mn(II) ion is four-coordinated by Cl atoms in a tetrahedral environment. The complex is disposed about a twofold rotation axis running in the [010] direction passing through the Mn atom. The distances d(Mn—Cl) are nearly equal (2.339(1) Å and 2.378(1) Å) and ∠Cl–Mn–Cl (106.32(7)° – 116.50(7)°) are close to the tetrahedral angle. These values are similar to those observed in the analogous compound $(C_{10}H_{10}N_3)_2[MnCl_4]$ [1]. Two cations interact with one complex by means of intermolecular N–H···Cl hydrogen bonds with d(N···Cl) = 3.193(4) Å (figure, bottom). Moreover, the cations display numerous intermolecular π-π interactions between adjacent six-membered rings. The shortest distance between Cg1 (the centroid of ring N1–C13) and Cg2^i (ring C1–C6; symmetry code i: ½–x,½–y,–z) is 3.693(2) Å, and the dihedral angle between the ring planes is 1.0(2)°.

Table 1. Data collection and handling.

Crystal:	yellow block, size 0.09 × 0.12 × 0.22 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	9.89 cm^{-1}
Diffractometer, scan mode:	Bruker SMART 1000 CCD, φ/ω
$2\theta_{max}$:	56.58°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	8973, 3042
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 1401
$N(param)_{refined}$:	150
Programs:	SHELXS-97, SHELXL-97 [2], ORTEP-3 [3], PLATON [4]

* e-mail: hakwang@chonnam.ac.kr

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

Atom	Site	*x*	*y*	*z*	U_{iso}
H(1)	8*f*	0.4796	0.1755	–0.0875	0.046
H(2)	8*f*	0.3395	0.1205	–0.1713	0.054
H(3)	8*f*	0.1692	0.0495	–0.1872	0.061
H(4)	8*f*	0.0674	0.0044	–0.0880	0.060
H(5)	8*f*	0.1386	0.0251	0.0258	0.049
H(7)	8*f*	0.2937	0.0785	0.1069	0.042
H(9)	8*f*	0.4485	0.1380	0.1870	0.060
H(10)	8*f*	0.6160	0.2175	0.1973	0.063
H(11)	8*f*	0.7056	0.2714	0.0955	0.059
H(12)	8*f*	0.6318	0.2418	–0.0172	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}
Mn(1)	4*e*	0	0.18329(9)	¼	0.0374(6)	0.0398(6)	0.0251(5)	0	0.0046(4)	0
Cl(1)	8*f*	–0.10435(8)	0.3225(1)	0.17459(6)	0.0403(7)	0.0572(8)	0.0358(7)	0.0050(6)	0.0019(5)	0.0099(5)
Cl(2)	8*f*	0.10760(9)	0.0631(1)	0.17684(6)	0.0506(7)	0.0562(8)	0.0393(7)	0.0061(6)	0.0130(6)	–0.0080(6)
N(1)	8*f*	0.4432(3)	0.1575(3)	–0.0500(2)	0.043(2)	0.040(2)	0.033(2)	–0.004(2)	0.011(2)	0.003(2)
C(1)	8*f*	0.3437(3)	0.1155(4)	–0.0619(2)	0.042(3)	0.035(3)	0.031(3)	0.001(2)	0.006(2)	0.002(2)
C(2)	8*f*	0.2997(4)	0.1014(4)	–0.1311(2)	0.059(3)	0.042(3)	0.034(3)	–0.003(2)	0.004(2)	0.003(2)
C(3)	8*f*	0.1989(4)	0.0598(4)	–0.1402(3)	0.068(4)	0.044(3)	0.041(3)	–0.002(3)	–0.008(3)	–0.001(2)
C(4)	8*f*	0.1377(4)	0.0318(4)	–0.0807(3)	0.050(3)	0.044(3)	0.055(3)	–0.002(2)	0.000(3)	0.001(2)
C(5)	8*f*	0.1798(3)	0.0443(4)	–0.0137(3)	0.039(3)	0.041(3)	0.043(3)	0.002(2)	0.002(2)	0.003(2)
C(6)	8*f*	0.2840(3)	0.0855(4)	–0.0014(2)	0.041(3)	0.029(3)	0.037(3)	0.003(2)	0.011(2)	–0.003(2)
C(7)	8*f*	0.3321(3)	0.0996(4)	0.0662(2)	0.042(3)	0.031(3)	0.033(3)	–0.001(2)	0.009(2)	0.001(2)
C(8)	8*f*	0.4327(4)	0.1427(4)	0.0764(2)	0.053(3)	0.032(3)	0.028(3)	0.002(2)	0.006(2)	–0.001(2)
C(9)	8*f*	0.4840(4)	0.1596(4)	0.1452(3)	0.068(4)	0.050(3)	0.033(3)	–0.004(3)	0.007(3)	–0.003(2)
C(10)	8*f*	0.5830(4)	0.2062(5)	0.1513(3)	0.061(3)	0.056(3)	0.041(3)	–0.002(3)	–0.006(3)	–0.007(2)
C(11)	8*f*	0.6368(4)	0.2377(5)	0.0901(3)	0.045(3)	0.053(3)	0.049(3)	–0.009(2)	–0.005(3)	–0.002(2)
C(12)	8*f*	0.5935(4)	0.2214(4)	0.0236(3)	0.045(3)	0.043(3)	0.045(3)	–0.009(2)	0.007(2)	–0.003(2)
C(13)	8*f*	0.4906(3)	0.1737(4)	0.0155(2)	0.047(3)	0.029(3)	0.030(3)	0.002(2)	0.007(2)	0.000(2)

Acknowledgment. This work was supported by Priority Research Centers Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (grant no. 2010-0029626).

References

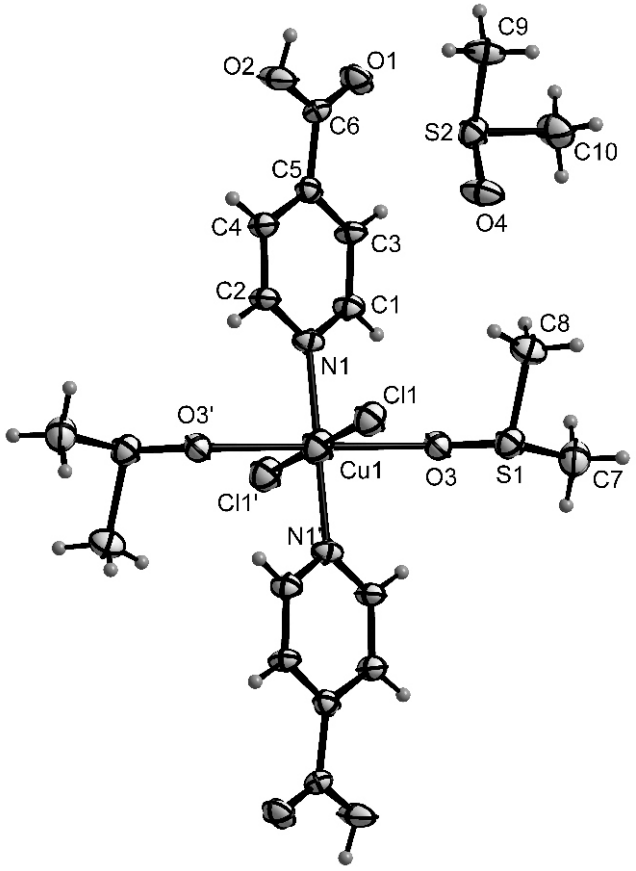
1. Ha, K.: Crystal structure of bis(2,2'-dipyridylammonium) tetrachloromanganate(II), $(C_{10}H_{10}N_3)_2[MnCl_4]$. Z. Kristallogr. NCS **225** (2010) 653-654.
2. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. **A64** (2008) 112-122.
3. Farrugia, L. J.: ORTEP-3 for Windows - a version of ORTEP-III with a Graphical User Interface (GUI) J. Appl. Crystallogr. **30** (1997) 565.
4. Spek, A. L.: Single-crystal structure validation with the program PLATON. J. Appl. Crystallogr. **36** (2003) 7-13.

Crystal structure of dichlorobis(dimethylsulfoxide-*O*)-bis-(isonicotinic acid-*N*)copper(II) — dimethylsulfoxide (1:2), $[CuCl_2(C_6H_5NO_2)_2(C_2H_6OS)_2]_2 \cdot 2C_2H_6OS$

Jaeun Kang[I], Inhae Park[I], Youngbum Kwak[I], Yeonsun Jung[I], Seonhong Kim[I], Yumi Lee[I], Hoseop Yun[II] and Junghwan Do[*, I]

[I] Department of Chemistry, Konkuk University, Seoul 147-701, Republic of Korea
[II] Division of Energy Systems Reseach and Department of Chemistry, Ajou University, Suwon 441-749, Republic of Korea

Received March 16, 2011, accepted and available on-line June 20, 2011; CCDC no. 1267/3451



Abstract

$C_{20}H_{34}Cl_2CuN_2O_8S_4$, triclinic, $P\bar{1}$ (no. 2), a = 7.105(5) Å, b = 10.578(7) Å, c = 11.007(7) Å, α = 71.58(1)°, β = 84.51(2)°, γ = 77.47(2)°, V = 765.8 Å^3, Z = 1, $R_{gt}(F)$ = 0.050, $wR_{ref}(F^2)$ = 0.155, T = 296 K.

Source of material

The title complex was synthesized from a mixture of $CuCl_2$ (0.120 g, 0.9 mmol), isonicotinic acid (0.111 g, 0.9 mmol) and DMSO (1.0 ml) sealed in a pyrex tube, heated to 100 °C for 68 hours, and then cooled to room temperature at 10 °C/h. The pH value of the solution before and after the reaction was 7 and 5, respectively. The solid products were recovered by vacuum filtration and washed with DMSO. Pale green rod-like crystals were obtained as a single phase. The product was slightly unstable in air. The yield was about 48 % based on copper. EDS analysis confirmed the presence of Cu and Cl.

Experimental details

All the hydrogen atoms associated with the isonicotinic acid and DMSO molecules were placed geometrically and refined as riding.

Discussion

The crystal structure of the title compound comprise discrete centrosymmetric mononuclear $CuCl_2$(isonicotinic acid)$_2$(DMSO)$_2$ and lattice DMSO molecules. The crystallographically unique Cu atom is coordinated by two chlorine atoms (d(Cu—Cl) = 2.335(2) Å), and two nitogen atoms from different isonicotinic acid molecules (d(Cu—N) = 1.987(4) Å). The additional oxygen atoms of two DMSO molecules (d(Cu—O) = 2.453(3) Å) complete an octahedral environment of Cu. The bond valence sum (BVS) calculation for Cu gives a value of +1.78, indicating an oxidation state of +2. The copper atom lies on a crystallographic inversion center so that ∠N–Cu–N, ∠Cl–Cu–Cl and ∠O–Cu–O are 180°. Also, two pyridine rings are coplanar, however, they are not parellel with either CuN_2Cl_2 or CuN_2O_2 planes, with the torsion angles of C2–N1–Cu1–Cl1 = 115.45(4)° and C2–N1–Cu1–O3 = 154.81(4)°. The carboxylic acid group has to be conjugated and therefore is coplanar as shown by the torsion angle C4–C5–C6–C2 = –1.3°. The lattice DMSO molecules form hydrogen bonds to the carboxyl groups in the $CuCl_2$(isonicotinic acid)$_2$(DMSO)$_2$ molecules. The DMSO molecule serves as a strong hydrogen bond acceptor, as indicated by the hydrogen bonding between the OH groups in the complex and the S=O groups in DMSO with d(H···O) = 1.712(9) Å, ∠O–H···O = 169.01(4)°, d(O···O) = 2.541(1) Å. Several coordination complexes containing isonicotinic acids and chlorine atoms are reported, and examples include Cu(I)Cl(isonicotinic acid), Pd(II)Cl$_2$- (isonicotinic acid)$_2$, and Pd(II)Cl$_2$(isonicotinic acid)$_2 \cdot$ 2DMSO [1-3]. The complex Pd(II)Cl$_2$(isonicotinic acid)$_2 \cdot$ 2DMSO has lattice DMSO molecules, and it shows similar hydrogen bonding between the isonicotinic acid in Pd(II)Cl$_2$(isonicotinic acid)$_2$ and the lattice DMSO molecules as found in the title complex [3].

* Correspondence author (e-mail: junghwan@konkuk.ac.kr)

Table 1. Data collection and handling.

Crystal:	green rod, size 0.18 × 0.20 × 0.43 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	12.03 cm^{-1}
Diffractometer, scan mode:	Rigaku R-AXIS RAPID, φ/ω
$2\theta_{max}$:	54.96°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	6323, 3417
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 1715
$N(param)_{refined}$:	174
Programs:	SHELXS-97, SHELXL-97 [4], DIAMOND [5]

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

Atom	Site	x	y	z	U_{iso}
H(2)	2*i*	0.7748	0.1626	0.4994	0.107
H(1)	2*i*	–0.0302	0.3142	0.2678	0.049
H(2A)	2*i*	0.4178	0.4003	0.0458	0.047
H(3)	2*i*	0.1629	0.2020	0.4386	0.045
H(4)	2*i*	0.6213	0.2863	0.2094	0.049
H(7A)	2*i*	0.3646	0.6098	0.2452	0.103
H(7B)	2*i*	0.4109	0.6809	0.3409	0.103
H(7C)	2*i*	0.4823	0.5238	0.3678	0.103
H(8A)	2*i*	0.8231	0.5140	0.4037	0.100
H(8B)	2*i*	0.7859	0.6693	0.3905	0.100
H(8C)	2*i*	0.9594	0.6057	0.3151	0.100
H(9A)	2*i*	–0.2565	–0.0443	0.2441	0.090
H(9B)	2*i*	–0.1015	–0.0967	0.1507	0.090
H(9C)	2*i*	–0.1871	0.0592	0.1205	0.090
H(10A)	2*i*	0.2028	0.0737	0.0877	0.112
H(10B)	2*i*	0.2376	–0.0853	0.1273	0.112
H(10C)	2*i*	0.3467	–0.0145	0.1961	0.112

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(1)	1*c*	0	½	0	0.0432(4)	0.0321(6)	0.0349(4)	–0.0074(4)	–0.0121(3)	–0.0018(3)
Cl(1)	2*i*	0.1082(2)	0.6839(1)	0.02365(9)	0.0531(7)	0.0389(8)	0.0446(5)	–0.0141(6)	–0.0072(5)	–0.0076(5)
O(1)	2*i*	0.4748(5)	0.1244(4)	0.5652(2)	0.059(2)	0.070(3)	0.031(1)	–0.015(2)	0.001(1)	–0.003(2)
O(2)	2*i*	0.7173(5)	0.1839(5)	0.4325(3)	0.037(2)	0.126(5)	0.037(2)	–0.015(2)	–0.011(1)	–0.004(2)
N(1)	2*i*	0.1711(5)	0.3768(4)	0.1398(3)	0.045(2)	0.032(3)	0.036(2)	–0.010(2)	–0.007(2)	–0.004(2)
C(1)	2*i*	0.1018(6)	0.3120(6)	0.2568(4)	0.038(2)	0.045(4)	0.040(2)	–0.013(3)	–0.003(2)	–0.009(2)
C(2)	2*i*	0.3654(6)	0.3618(5)	0.1264(3)	0.035(2)	0.048(4)	0.030(2)	–0.008(2)	–0.008(2)	–0.002(2)
C(3)	2*i*	0.2173(6)	0.2432(5)	0.3596(3)	0.035(2)	0.039(3)	0.032(2)	–0.009(2)	–0.008(2)	0.001(2)
C(4)	2*i*	0.4889(6)	0.2936(6)	0.2240(3)	0.035(2)	0.045(4)	0.037(2)	–0.006(2)	–0.007(2)	–0.005(2)
C(5)	2*i*	0.4148(6)	0.2351(5)	0.3456(3)	0.043(2)	0.034(3)	0.033(2)	–0.005(2)	–0.004(2)	–0.009(2)
C(6)	2*i*	0.5352(6)	0.1741(5)	0.4591(4)	0.037(2)	0.036(3)	0.037(2)	0.005(2)	–0.009(2)	–0.008(2)
S(1)	2*i*	0.6777(2)	0.6390(2)	0.2145(1)	0.0581(8)	0.042(1)	0.0487(6)	–0.0045(7)	–0.0060(6)	–0.0110(6)
O(3)	2*i*	–0.2606(5)	0.5244(4)	0.1590(3)	0.054(2)	0.052(3)	0.039(1)	–0.009(2)	–0.004(1)	–0.017(2)
C(7)	2*i*	0.4585(8)	0.6100(8)	0.3023(5)	0.063(4)	0.073(6)	0.076(3)	–0.009(4)	0.008(3)	–0.037(3)
C(8)	2*i*	0.8289(8)	0.6028(8)	0.3461(5)	0.064(3)	0.080(6)	0.065(3)	–0.013(4)	–0.013(3)	–0.032(3)
S(2)	2*i*	0.9636(2)	0.0078(2)	0.7260(1)	0.0573(8)	0.057(1)	0.0458(6)	–0.0167(8)	–0.0032(6)	–0.0165(6)
O(4)	2*i*	0.0843(5)	–0.1438(5)	0.3759(3)	0.064(2)	0.085(4)	0.041(2)	–0.029(3)	–0.012(2)	0.004(2)
C(9)	2*i*	–0.1482(8)	–0.0243(7)	0.1875(4)	0.071(4)	0.050(4)	0.051(2)	–0.016(3)	–0.016(2)	0.002(2)
C(10)	2*i*	0.2278(8)	–0.0086(8)	0.1580(4)	0.063(4)	0.099(7)	0.051(3)	–0.022(4)	0.005(3)	–0.005(3)

Acknowledgment. This paper was supported by Konkuk University in 2010.

References

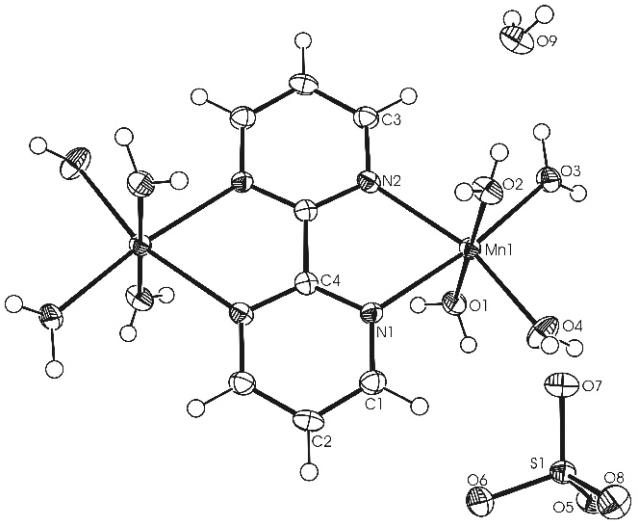
1. Pavani, K.; Ramanan, A.; Whittingham, M.S.: Hydrothermal synthesis of copper coordination polymers based on molybdates: Chemistry issues. J. Mol. Struct. **796** (2006) 179-186.
2. Qin, Z.; Jenkins, H.A.; Coles, S.J.; Muir, K.W.; Puddephatt, R.J.: Self-assembly of one-dimensional polymers by coordination and hydrogen bonding in palladium(II) complexes. Can. J. Chem. **77** (1999) 155-157.
3. Qin, Z.; Jennings, M.C.; Puddephatt, R.J.; Muir, K.W.: Self-assembly of polymer and sheet structures in palladium(II) complexes containing carboxylic acid substituents. Inorg. Chem. **41** (2002) 5174-5186.
4. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. **A64** (2008) 112-122.
5. Brandenburg, K.: DIAMOND. Visual Crystal Structure Information System. Version 3.2f. Crystal Impact, Bonn, Germany 2005.

Crystal structure of octaaqua(μ_2-2,2′-bipyrimidine)dimanganese(II) bis(sulfate) — water (1:2), $[Mn_2(H_2O)_8(C_8H_6N_4)][(SO_4)_2] \cdot 2H_2O$

Kwang Ha*

Chonnam National University, School of Applied Chemical Engineering, Research Institute of Catalysis, Gwangju 500-757, Republic of Korea

Received March 17, 2011, accepted and available on-line June 20, 2011; CCDC no. 1267/3453



Abstract

$C_8H_{26}Mn_2N_4O_{18}S_2$, monoclinic, $P12_1/c1$ (no. 14), a = 8.1522(5) Å, b = 11.6765(7) Å, c = 11.9942(7) Å, β = 91.667(1)°, V = 1141.2 Å^3, Z = 2, $R_{gt}(F)$ = 0.036, $wR_{ref}(F^2)$ = 0.104, T = 200 K.

Source of material

$MnSO_4 \cdot H_2O$ (0.1688 g, 0.999 mmol) and 2,2′-bipyrimidine (bpym; 0.1587 g, 1.003 mmol) in H_2O (20 ml) were refluxed for 1 h. After evaporation of the solvent, the residue was washed with ether and dried at 50 °C, to give a light yellow powder (0.3152 g). Crystals suitable for X-ray diffraction analysis were obtained by slow evaporation from a water solution at 50 °C.

Experimental details

The H atoms of the bipyrimidine ring were positioned geometrically and allowed to ride on their parent atoms with d(C—H) = 0.95 Å and U_{iso}(H) = 1.2 U_{eq}(C). The H atoms of the water ligands and solvent molecules were located from Fourier difference maps and refined isotropically: d(O—H) = 0.72(4) Å - 0.99(4) Å. The highest peak (0.50 eÅ^{-3}) and the deepest hole (–0.54 eÅ^{-3}) in the difference Fourier map are located 1.71 Å and 0.71 Å from the atoms H2A and S1, respectively.

Discussion

The asymmetric unit of the title crystal structure contains one half of an Mn(II) cationic complex, an SO_4^{2-} anion and a water solvent molecule. The centroid of the complex is located at a center of inversion. Each two Mn(II) ions are bridged by a bis-chelating 2,2′-bipyrimidine ligand to form a dinuclear Mn(II) complex. Each Mn atom is six-coordinated in a considerably distorted octahedral manner by two N atoms of the bridging bpym ligand and four O atoms from four water molecules. In the previously reported crystal structures of the analogous dinuclear Mn(II) complex $[Mn_2(SO_4)_2(H_2O)_6(bpym)]$, an SO_4^{2-} anion coordinates the Mn(II) ion as a monodentate ligand via one O atom, and thus each Mn atom is coordinated by two N atoms from bpym and four O atoms from one sulfato ligand and three water molecules [1,2]. The main contribution to the distortion of the ocatahedron is made by the tight chelate angle ∠N1–Mn1–N2 = 71.82(8)°, which results in non-linear *trans* axes (∠N1–Mn1–O3 = 172.02(8)° and ∠N2–Mn1–O4 = 162.25(9)°). The apical O1–Mn1–O2 bonds are almost linear with the bond angle of 179.49(9)°. The distances d(Mn—N) and d(Mn—O) are roughly equivalent: d(Mn1—N1/N2) = 2.295(2) Å and 2.307(2) Å, respectively, d(Mn1—O1/O2/O3/O4) = 2.130(2) - 2.186(2) Å). The shape of the sulfate anion is nearly tetrahedral with the O–S–O bond angles of 107.8(1)° - 110.7(1)°, and the almost equal d(S—O) = 1.460(2) - 1.491(2) Å.

In the crystal structure, the complex, the anions and the solvent molecules are linked by O–H···O hydrogen bonds with d(O···O) = 2.706(3) - 2.818(3) Å, forming a three-dimensional network. In addition, several intermolecular π–π interactions between pyrimidine rings are present. The distance between Cg1 (the centroid of ring N1–C4) and Cg1^{i} (symmetry code i: 2–x,–y,1–z) is 5.589(2) Å, and the ring planes are parallel and shifted by 4.611 Å.

Table 1. Data collection and handling.

Crystal:	light yellow block size 0.14 × 0.21 × 0.27 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	13.80 cm^{-1}
Diffractometer, scan mode:	Bruker SMART 1000 CCD, φ/ω
$2\theta_{max}$:	56.54°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	8031, 2765
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2091
$N(param)_{refined}$:	194
Programs:	SHELXS-97, SHELXL-97 [3], ORTEP-3 [4], PLATON [5]

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

Atom	Site	x	y	z	U_{iso}
H(1A)	4*e*	0.242(5)	–0.111(3)	0.299(3)	0.03(1)
H(1B)	4*e*	0.251(6)	–0.093(4)	0.196(4)	0.08(2)
H(2A)	4*e*	0.474(5)	0.301(3)	0.380(3)	0.04(1)

* e-mail: hakwang@chonnam.ac.kr

Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
H(2B)	4*e*	0.322(5)	0.312(3)	0.377(3)	0.04(1)
H(3A)	4*e*	0.005(4)	0.167(3)	0.230(3)	0.020(9)
H(3B)	4*e*	–0.021(5)	0.196(3)	0.339(4)	0.07(1)
H(4A)	4*e*	0.461(5)	0.178(3)	0.129(3)	0.05(1)
H(4B)	4*e*	0.330(5)	0.121(3)	0.086(4)	0.05(1)

Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
H(1)	4*e*	0.6682	0.0338	0.2148	0.026
H(2)	4*e*	0.9039	–0.0617	0.2769	0.028
H(3)	4*e*	0.0777	0.1180	0.5361	0.026
H(9A)	4*e*	0.164(5)	0.477(4)	0.462(4)	0.05(1)
H(9B)	4*e*	0.099(5)	0.393(3)	0.493(4)	0.04(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}
Mn(1)	4*e*	0.30433(5)	0.10957(3)	0.30717(3)	0.0169(2)	0.0179(2)	0.0176(2)	0.0010(2)	0.0013(2)	0.0010(2)
O(1)	4*e*	0.2237(3)	–0.0624(2)	0.2588(2)	0.027(1)	0.018(1)	0.025(1)	0.0017(9)	0.0006(9)	–0.001(1)
O(2)	4*e*	0.3846(3)	0.2780(2)	0.3533(2)	0.020(1)	0.021(1)	0.035(1)	0.0004(9)	–0.002(1)	–0.005(1)
O(3)	4*e*	0.0605(2)	0.1797(2)	0.2820(2)	0.015(1)	0.031(1)	0.025(1)	0.0040(9)	–0.0041(9)	–0.003(1)
O(4)	4*e*	0.3882(3)	0.1392(2)	0.1431(2)	0.028(1)	0.045(1)	0.020(1)	–0.014(1)	0.004(1)	0.003(1)
N(1)	4*e*	0.5515(3)	0.0281(2)	0.3581(2)	0.016(1)	0.019(1)	0.016(1)	0.0004(9)	0.0018(8)	–0.0001(9)
N(2)	4*e*	0.2972(3)	0.0614(2)	0.4935(2)	0.017(1)	0.019(1)	0.022(1)	0.0021(9)	0.0024(9)	0.001(1)
C(1)	4*e*	0.6770(3)	0.0085(2)	0.2900(2)	0.022(1)	0.022(1)	0.021(1)	–0.001(1)	0.004(1)	0.001(1)
C(2)	4*e*	0.8168(3)	–0.0469(2)	0.3259(3)	0.018(1)	0.025(1)	0.029(2)	0.001(1)	0.008(1)	–0.004(1)
C(3)	4*e*	0.1741(3)	0.0804(2)	0.5636(2)	0.018(1)	0.025(1)	0.023(2)	0.002(1)	0.002(1)	–0.002(1)
C(4)	4*e*	0.5707(3)	–0.0089(2)	0.4627(2)	0.019(1)	0.012(1)	0.019(1)	–0.002(1)	0.002(1)	0.000(1)
S(1)	4*e*	0.76934(8)	0.21735(6)	0.01718(6)	0.0154(3)	0.0181(3)	0.0188(4)	–0.0004(3)	0.0026(2)	–0.0007(3)
O(5)	4*e*	0.6716(2)	0.1426(2)	–0.0579(2)	0.022(1)	0.025(1)	0.027(1)	0.0001(8)	–0.0001(8)	–0.0069(9)
O(6)	4*e*	0.8920(2)	0.1443(2)	0.0784(2)	0.023(1)	0.036(1)	0.025(1)	0.0069(9)	–0.0036(8)	–0.0002(9)
O(7)	4*e*	0.6597(2)	0.2709(2)	0.0977(2)	0.023(1)	0.023(1)	0.029(1)	–0.0020(8)	0.0066(8)	–0.0063(9)
O(8)	4*e*	0.8534(2)	0.3054(2)	–0.0459(2)	0.027(1)	0.026(1)	0.032(1)	–0.0064(9)	0.0049(9)	0.005(1)
O(9)	4*e*	0.1749(3)	0.4121(2)	0.4677(2)	0.026(1)	0.021(1)	0.042(1)	0.002(1)	0.008(1)	–0.001(1)

Acknowledgment. This work was supported by Priority Research Centers Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (grant no. 2010-0029626).

References

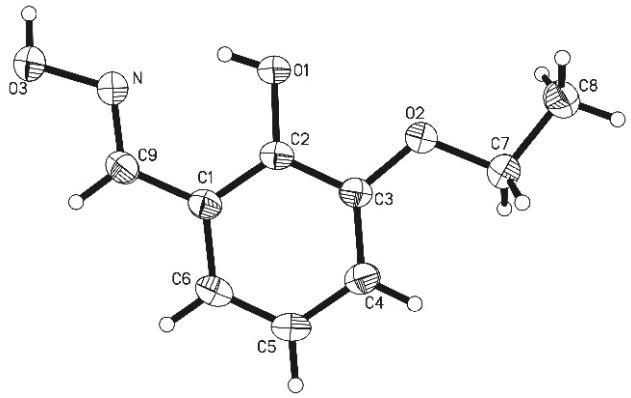
1. De Munno, G.; Ruiz, R.; Lloret, F.; Faus, J.; Sessoli, R.; Julve, M.: Oxalate and 2,2′-Bipyrimidine as Useful Tools in Designing Layered Compounds. Inorg. Chem. **34** (1995) 408-411.
2. Hong, D. M.; Chu, Y. Y.; Wei, H. H.: Structure and magnetic properties of 2,2′-bipyrimidine-(bpym)-bridged binuclear Mn(II) complex: $[Mn_2(H_2O)_6(bpym)(SO_4)_2]$. Polyhedron **15** (1996) 447-452.
3. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. **A64** (2008) 112-122.
4. Farrugia, L. J.: ORTEP-3 for Windows - a version of ORTEP-III with a Graphical User Interface (GUI) J. Appl. Crystallogr. **30** (1997) 565.
5. Spek, A. L.: Single-crystal structure validation with the program PLATON. J. Appl. Crystallogr. **36** (2003) 7-13.

Crystal structure of 3-ethoxy-2-hydroxybenzaldehyde oxime, $C_9H_{11}NO_3$

Li-Fang Cai*

Key Laboratory of Surface and Interface Science of Henan, School of Material & Chemical Engineering, Zhengzhou University of Light Industry, Zhengzhou 450002, P. R. China

Received March 22, 2011, accepted and available on-line June 20, 2011; CCDC no. 1267/3470



Abstract

$C_9H_{11}NO_3$, monoclinic, $P12_1/c1$ (no. 14), a = 9.259(2) Å, b = 14.679(3) Å, c = 7.036(1) Å, β = 108.40(2)°, V = 907.4 Å^3, Z = 4, $R_{gt(F)}$ = 0.044, $wR_{ref}(F^2)$ = 0.131, T = 293 K.

Source of material

The title compound was synthesized by the reaction of 3-ethoxy-2-hydroxybenzaldehyde (1 mmol, 0.166 g) with hydroxylamine hydrochloride (1.2 mmol, 0.084 g) in the presence of $NaHCO_3$ (1.2 mmol, 0.1 g) in methanol at room temperature (3 h). When evaporated to dryness, the product was extracted with dichloromethane and recrystallised from methanol. Colourless single crystals of the title compound were obtained over a period of one week.

Discussion

Oxime derivatives are often the source of iminoxy radicals when oxidized chemically [1], which have potential enzymatical application [2].

In the title crystal structure, the molecule adopts an *E* geometry with respect to the C=N double bond. The molecule is planar, atom C8 is displaced from the plane by –0.207(2) Å. An intramolecular O–H···N hydrogen bond is observed which helps to stablize the molecule structure. An intermolecular O–H···O hydrogen bond links the molecules into centrosymmetric dimers.

Table 1. Data collection and handling.

Crystal:	colourless block, size 0.18 × 0.21 × 0.22 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	1.00 cm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD, ω
$2\theta_{max}$:	52.76°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	3523, 1857
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 1293
$N(param)_{refined}$:	119
Program:	SHELXTL [3]

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

Atom	Site	x	y	z	U_{iso}
H(1A)	4*e*	–0.0087	0.0521	0.1343	0.087
H(3A)	4*e*	–0.2705	–0.0561	–0.2128	0.099
H(9A)	4*e*	–0.3716	0.0338	0.1284	0.061
H(6A)	4*e*	–0.3435	0.1091	0.4473	0.067
H(4A)	4*e*	0.0574	0.2021	0.7935	0.065
H(5A)	4*e*	–0.2003	0.1804	0.7325	0.074
H(7A)	4*e*	0.3060	0.1630	0.8555	0.067
H(7B)	4*e*	0.2889	0.2565	0.7409	0.067
H(8A)	4*e*	0.5442	0.2118	0.8479	0.104
H(8B)	4*e*	0.4833	0.2140	0.6132	0.104
H(8C)	4*e*	0.5002	0.1208	0.7269	0.104

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*	0.0525(1)	0.07597(9)	0.2323(2)	0.0463(7)	0.081(1)	0.0525(7)	–0.0046(6)	0.0229(5)	–0.0205(7)
O(2)	4*e*	0.2190(1)	0.15052(9)	0.5607(2)	0.0459(7)	0.0719(9)	0.0515(7)	–0.0071(6)	0.0197(5)	–0.0134(6)
C(3)	4*e*	0.0678(2)	0.1433(1)	0.5400(2)	0.0459(9)	0.044(1)	0.0483(9)	0.0012(7)	0.0206(7)	–0.0008(8)
N	4*e*	–0.2111(1)	0.0125(1)	0.0176(2)	0.0439(8)	0.063(1)	0.0476(8)	–0.0021(7)	0.0120(6)	–0.0059(7)
C(2)	4*e*	–0.0201(2)	0.1016(1)	0.3640(2)	0.0459(9)	0.044(1)	0.0450(9)	0.0056(7)	0.0207(7)	0.0019(8)
C(1)	4*e*	–0.1748(2)	0.0878(1)	0.3270(2)	0.0435(9)	0.044(1)	0.0483(9)	0.0058(7)	0.0183(7)	0.0033(8)
O(3)	4*e*	–0.3157(1)	–0.0314(1)	–0.1437(2)	0.0493(7)	0.089(1)	0.0565(7)	–0.0070(7)	0.0129(6)	–0.0192(7)
C(9)	4*e*	–0.2682(2)	0.0419(1)	0.1481(2)	0.0423(9)	0.057(1)	0.055(1)	0.0031(8)	0.0180(8)	0.0036(9)
C(6)	4*e*	–0.2401(2)	0.1180(1)	0.4693(3)	0.0477(9)	0.062(1)	0.065(1)	0.0048(9)	0.0284(8)	–0.000(1)

* e-mail: cailifang2011@126.com

Table 3. Continued.

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(4)	4*e*	–0.0003(2)	0.1732(1)	0.6767(3)	0.058(1)	0.056(1)	0.053(1)	–0.0003(9)	0.0230(8)	–0.0085(9)
C(5)	4*e*	–0.1546(2)	0.1602(1)	0.6400(3)	0.060(1)	0.073(1)	0.062(1)	0.006(1)	0.0338(9)	–0.010(1)
C(7)	4*e*	0.3158(2)	0.1929(1)	0.7373(3)	0.055(1)	0.060(1)	0.052(1)	–0.0071(9)	0.0174(8)	–0.0081(9)
C(8)	4*e*	0.4752(2)	0.1841(2)	0.7307(3)	0.052(1)	0.091(2)	0.064(1)	–0.005(1)	0.0169(9)	–0.004(1)

References

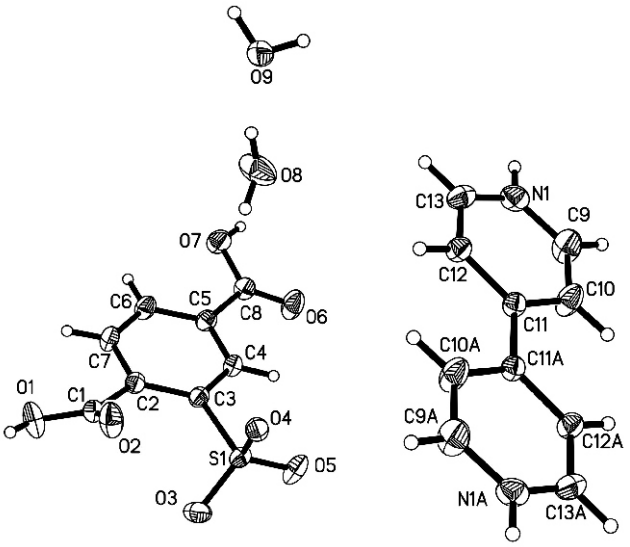
1. Thomas, J. R.: Electron-spin resonance study of iminoxy free radicals. J. Am. Chem. Soc. **86** (1964) 1446-1447.
2. Lagercrantz, C.: Oxidation of some 2-(hydroxyimino)-1-3-dioxo compounds to iminoxy radicals by horseradish peroxidase and hydrogen peroxide studied by ESR spectroscopy. Acta Chem. Scand. **B42** (1988) 414-416.
3. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. **A64** (2008) 112-122.

Crystal structure of 1,1′-dihydro[4,4′-bipyridine]-1,1′-diium-bis(2-sulfonatoterephthalic acid) — water (1:4), $(C_{10}H_{10}N_2)(C_8H_5O_7S)_2 \cdot 4H_2O$

Xin-Xiang Lei* and An-Jiang Zhang

Chengdu Institute of Biology, Chinese Academy of Sciences, Chengdu 610041, P. R. China

Received March 10, 2011, accepted and available on-line June 17, 2011; CCDC no. 1267/3436



Abstract

$C_{26}H_{28}N_2O_{18}S_2$, triclinic, $P\bar{1}$ (no. 2),
a = 8.4687(5) Å, b = 9.4670(5) Å, c = 10.4823(6) Å,
α = 73.007(1)°, β = 71.567(1)°, γ = 89.582(1)°, V = 759.1 Å^3,
Z = 1, $R_{gt}(F)$ = 0.035, $wR_{ref}(F^2)$ = 0.110, T = 298 K.

Source of material

2-sulfoterephthalic acid (0.246 g, 1.0 mmol) was dissolved in hot ethanol (5 mL, 95%), and a solution of 4,4′-bipyridine (0.156 g, 1.0 mmol) in the same solvent (5 mL) was added. After one hour of reflux the solution was filtered. After two weeks colorless crystals had formed, which were suitable for X-ray diffraction experiments.

Expermental details

All H atoms were positioned geometrically and allowed to ride on their parent atoms at distances of d(C sp^2—H) = 0.93 Å with U_{iso} = 1.2 U_{eq}(parent atom), d(N—H) = 0.86 Å with U_{iso} = 1.2 U_{eq}(parent atom) and d(O—H) = 0.82 Å with U_{iso} = 1.5 U_{eq}(parent atom).

Discussion

The design and synthesis of supramolecular compounds, especially those constructed by hydrogen bonding interactions have been more and more attractive due to their special physical properties and potential application. A well known and effective design strategy is the matching of suitable hydrogen bonding donors and acceptors [1,2]. 2-sulfoterephthalic acid may act as an excellent, readily available hydrogen bond donor. The 2-sulfoterephthalic acid possesses several interesting characteristics: (a) it has two carboxyl groups and one sulfonate group which may be completely or partially deprotonated, inducing rich coordination modes and allowing interesting structures with higher dimensions; (b) it can act not only as hydrogen-bond acceptor but also as hydrogen-bond donor, depending upon the number of deprotonated groups [3-7].

In the 2-sulfoterephthalic acid ligand, the sulfonic group is deprotonated, two carboxyl groups are protonated. The distances d(C—O) of the two carboxyl groups are 1.202(3) Å, 1.310(3) Å and 1.199(4) Å, 1.310(3) Å, which is shorter than a typical d(C—O) = 1.439(2) Å, but longer than a typical d(C=O) = 1.173(5) Å [8,9]. d(S1—O3), d(S1—O4) and d(S1—O5) are 1.446(2) Å, 1.453(2) Å and 1.440(2) Å, respectively. d(N1—C9) = 1.377(4) Å and d(N1—C13) = 1.384(4) Å are shorter than typical d(N—C) = 1.443(4) Å, but longer than typical d(N=C) = 1.269(2) Å. In order to balance the anion charge of the 2-sulfonatoterephthalatic acid, the N atoms of the 4,4′-bipyridine ligand are protonated.

The adjacent water molecules and 2-sulfonatoterephthalatic acid ligands are linked by intermolecular O—H···O bond interactions (O9—H9B···O4^{i}, O9—H9A···O5^{ii}, O9—H9A···O3^{ii}, O8—H8B···O9, O8—H8A···O2^{iii}, O8—H8A···O3^{iii}, O7—H7···O9^{iv}, O1—H1···O8^{v}, symmetry codes: (i) $-x+1,-y+1,-z+1$; (ii) $x-1,y+1,z$; (iii) $-x-2,-y+1,-z+1$; (iv) $x,y-1,z+1$; (v) $x+1,y,z$). The adjacent 4,4′-bipridinediium and 2-sulfonatoterephthalatic acid ligands are linked by N1—H1A···O2 (symmetry code: (vi) $x-1,y,z$) hydrogen-bond interactions. All above hydrogen bond interactions may enchance the stability of the solid-state structure of the title compound and generate a three-dimemsional architecture.

Table 1. Data collection and handling.

Crystal:	colorless prism, size 0.15 × 0.21 × 0.26 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	2.64 cm^{-1}
Diffractometer, scan mode:	Bruker APEX II, φ/ω
$2\theta_{max}$:	50.2°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	8997, 2686
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 2506
$N(param)_{refined}$:	220
Programs:	SHELXS-97, SHELXL-97 [10]

* Correspondence author (e-mail: xinxianglei@yahoo.com.cn)

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

Atom	Site	x	y	z	U_{iso}
H(1)	2*i*	1.3344	0.5161	0.7060	0.092
H(7)	2*i*	0.4633	0.0052	1.3277	0.082
H(8A)	2*i*	0.5717	0.6643	0.5169	0.115
H(8B)	2*i*	0.4278	0.7333	0.5560	0.115
H(9A)	2*i*	0.2705	0.9521	0.5437	0.069
H(9B)	2*i*	0.2266	0.8660	0.4787	0.069
H(1A)	2*i*	0.1187	0.4029	0.4115	0.053
H(4)	2*i*	0.7754	–0.0009	0.9106	0.043
H(6)	2*i*	0.7992	0.2327	1.1683	0.051
H(7A)	2*i*	1.0269	0.3774	0.9937	0.050
H(9)	2*i*	0.1402	0.2373	0.2982	0.069
H(10)	2*i*	0.3394	0.2850	0.0795	0.064
H(12)	2*i*	0.4739	0.6750	0.1099	0.043
H(13)	2*i*	0.2741	0.6169	0.3294	0.051

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(1)	2*i*	1.02057(6)	0.12620(5)	0.65556(5)	0.0403(3)	0.0398(3)	0.0363(3)	0.0046(2)	–0.0100(2)	–0.0194(2)
O(1)	2*i*	1.2722(2)	0.4481(2)	0.7702(2)	0.057(1)	0.061(1)	0.061(1)	–0.0227(8)	–0.0297(8)	0.0009(8)
O(2)	2*i*	1.1559(2)	0.4496(2)	0.6079(2)	0.066(1)	0.068(1)	0.0377(8)	–0.0265(8)	–0.0132(7)	–0.0063(7)
O(3)	2*i*	1.2015(2)	0.1433(2)	0.6043(2)	0.0398(8)	0.078(1)	0.0594(9)	0.0167(7)	–0.0117(7)	–0.0363(8)
O(4)	2*i*	0.9487(2)	0.2313(2)	0.5621(1)	0.0385(7)	0.0493(8)	0.0323(7)	–0.0004(6)	–0.0088(5)	–0.0146(6)
O(5)	2*i*	0.9510(2)	–0.0235(2)	0.6900(2)	0.088(1)	0.0414(8)	0.0523(9)	–0.0011(7)	–0.0208(8)	–0.0247(7)
O(6)	2*i*	0.5592(2)	–0.1061(2)	1.1565(2)	0.075(1)	0.058(1)	0.058(1)	–0.0269(8)	0.0022(8)	–0.0251(8)
O(7)	2*i*	0.5444(2)	0.0609(2)	1.2698(2)	0.0543(9)	0.0516(9)	0.0471(8)	–0.0055(7)	0.0020(7)	–0.0188(7)
O(8)	2*i*	0.4797(2)	0.6612(2)	0.5755(2)	0.0435(9)	0.055(1)	0.100(1)	–0.0017(7)	–0.0076(9)	0.0046(9)
O(9)	2*i*	0.3060(2)	0.8983(2)	0.4942(1)	0.0377(7)	0.0572(9)	0.0478(8)	0.0055(6)	–0.0111(6)	–0.0257(7)
N(1)	2*i*	0.1935(2)	0.4229(2)	0.3294(2)	0.0379(8)	0.056(1)	0.0312(8)	0.0025(7)	–0.0027(6)	–0.0105(7)
C(1)	2*i*	1.1611(2)	0.3997(2)	0.7257(2)	0.0349(9)	0.0359(9)	0.043(1)	0.0010(7)	–0.0121(8)	–0.0151(8)
C(2)	2*i*	1.0299(2)	0.2863(2)	0.8415(2)	0.0365(9)	0.0319(9)	0.0371(9)	0.0030(7)	–0.0142(7)	–0.0117(7)
C(3)	2*i*	0.9545(2)	0.1691(2)	0.8185(2)	0.0362(9)	0.0328(9)	0.0345(9)	0.0054(7)	–0.0140(7)	–0.0135(7)
C(4)	2*i*	0.8233(2)	0.0782(2)	0.9257(2)	0.0404(9)	0.0313(9)	0.0372(9)	0.0008(7)	–0.0138(8)	–0.0129(7)
C(5)	2*i*	0.7610(2)	0.1031(2)	1.0565(2)	0.042(1)	0.0327(9)	0.0346(9)	0.0030(7)	–0.0122(8)	–0.0101(7)
C(6)	2*i*	0.8382(3)	0.2162(2)	1.0808(2)	0.054(1)	0.042(1)	0.0336(9)	–0.0004(8)	–0.0123(8)	–0.0157(8)
C(7)	2*i*	0.9729(3)	0.3043(2)	0.9752(2)	0.051(1)	0.0367(9)	0.041(1)	–0.0041(8)	–0.0155(8)	–0.0168(8)
C(8)	2*i*	0.6117(2)	0.0064(2)	1.1660(2)	0.045(1)	0.040(1)	0.038(1)	0.0009(8)	–0.0117(8)	–0.0110(8)
C(9)	2*i*	0.2098(3)	0.3254(3)	0.2590(2)	0.059(1)	0.053(1)	0.045(1)	–0.021(1)	0.001(1)	–0.012(1)
C(10)	2*i*	0.3287(3)	0.3538(2)	0.1287(2)	0.062(1)	0.046(1)	0.042(1)	–0.019(1)	0.0020(9)	–0.0193(9)
C(11)	2*i*	0.4334(2)	0.4844(2)	0.0696(2)	0.0336(9)	0.0316(8)	0.0310(9)	0.0004(7)	–0.0099(7)	–0.0097(7)
C(12)	2*i*	0.4087(2)	0.5846(2)	0.1470(2)	0.0395(9)	0.0317(9)	0.0367(9)	0.0027(7)	–0.0098(7)	–0.0122(7)
C(13)	2*i*	0.2888(2)	0.5506(2)	0.2773(2)	0.047(1)	0.046(1)	0.038(1)	0.0124(8)	–0.0114(8)	–0.0190(8)

References

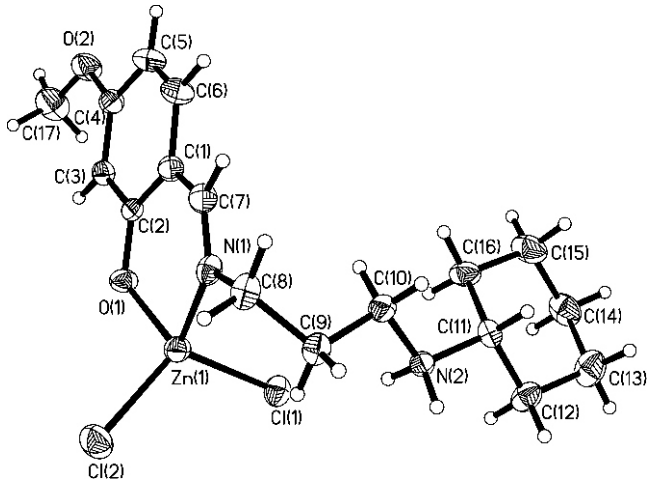
1. Cooke, G.; Rotello, V. M.: Methods of modulating hydrogen bonded interactions in synthetic host–guest systems. Chem. Soc. Rev. **31** (2002) 275-286.
2. Fan, S. R.; Xiao, H. P.; Zhu, L. G.: A cation-anion complex: 1,10-phenanthrolin-1-ium 5-sulfonatosalicylic acid. Acta Crystallogr. E **61** (2005) o253-o255.
3. Horike, S.; Matsuda, R.; Tanaka, D.; Matsubara, S.; Mizuno, M.; Endo, K.; Kitagawa, S.: Dynamic Motion of Building Blocks in Porous Coordination Polymers. Angew. Chem. Int. Ed. **45** (2006) 7226-7230.
4. Horike, S.; Matsuda, R.; Tanaka, D.; Matsubara, S.; Mizuno, M.; Endo, K.; Kitagawa, S.: Immobilization of Sodium Ions on the Pore Surface of a Porous Coordination Polymer. J. Am. Chem. Soc. **128** (2006) 4222-4223.
5. Zhao, N.; Zhang, J. M.; Lian, Z. X.; Gu, Y. Q.; Lou, T. J.: Crystal structure of bis(4-carboxy-2-sulfonatobenzoato)-bis[aqua(2,2′-bipyridyl)copper(II)]hexahydrate, $[Cu(H_2O)(C_{10}H_8N_2)(C_8H_4O_7S)]_2 \cdot 6H_2O$. Z. Kristallogr. NCS **224** (2009) 73-75.
6. Xiao, H. P.; Zheng, Y. X.; Liang, X. Q.; Zuo, J. L.; You, X. Z.: Hydrothermal synthesis,crystal structures, and luminescent properties of two lanthaninde(III) complexes containing 2-sulfoterephthalate. J. Mol. Struct. **888** (2008) 55-61.
7. Horike, S.; Breekaew, S.; Kitagawa, S.: Coordination pillared-layer type compounds having pore surface functionalization by anionic sulfonate groups. Chem. Commun. (2008) 471-473.
8. Ji, M. J.; Zhao, Z. L.; Yan, D. Y.: Crystal and molecular structure of *N*,*N*′-(dihiodi-2,1-phenylene)bis(benzamide). Chin. J. Struct. Chem. **18** (2009) 150-153.
9. Ji, Z. M.; Li, L.; Li, M. C.; Hu, M. L.; Shen, L.: Diethyl-3,8-di-methyl-4,7-diazadeca-2,8-dienedioate. Acta Crystallogr. C **60** (2004) o642-o643.
10 Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. **A64** (2008) 112-122.

Crystal structure of dichloro-2-[(3-cyclohexylaminopropylimino)-methyl]-5-methoxyphenolatozinc(II), $Zn(C_{17}H_{26}N_2O_2)Cl_2$

Shu-Jing Li* and Ke Li

Zhoukou Normal University, Department of Chemistry, Henan 466000, P. R. China

Received February 17, 2011, accepted and available on-line June 17, 2011; CCDC no. 1267/3406



Abstract

$C_{17}H_{26}Cl_2N_2O_2Zn$, monoclinic, *C*12/*c*1 (no. 15), a = 25.102(4) Å, b = 10.540(2) Å, c = 14.994(2) Å, β = 91.445(2)°, V = 3965.9 Å^3, Z = 8, $R_{gt}(F)$ = 0.034, $wR_{ref}(F^2)$ = 0.092, T = 298 K.

Source of material

A methanol solution of $ZnCl_2$ (0.14 g, 1 mmol) was added to a methanol solution (30 ml) of the Schiff base ligand (0.29 g, 1 mmol) with stirring. The resulting solution was allowed to stand at room temperature for a few days, yielding colorless block-shaped single crystals.

Experimental details

H atoms were constrained to ideal bonding parameters, with d(C—H) = 0.93 - 0.97 Å, d(N—H) = 0.90 Å, and with U_{iso}(H) = 1.2 U_{eq}(C, N) and 1.5 U_{eq}(C17).

Discussion

Schiff bases and their complexes have been attracted much attention for the interesting structures and applications [1-4]. The zinc(II) complexes with Schiff bases have been widely investigated for their biological properties [5-7].

The Zn atom in the title complex is coordinated by the phenolic O atom and the imino N atom of the Schiff base ligand, and by two chloride atoms in a tetrahedral environment. The distortion of the tetrahedral coordination can be observed from the coordinate bond angles, ranging from 95.69(6)° to 116.37(5)°. The bond lengths are comparable to those observed in similar zinc(II) complexes with Schiff bases [8-11]. The crystal structure is stabilized by intermolecular hydrogen bonds: d(N2–H2A···Cl1) = 3.210(2) Å, ∠N2–H2A···Cl1 = 159.7° and d(N2–H2B···O1) = 2.777(2) Å, ∠N2–H2B···O1 = 173.2°.

Table 1. Data collection and handling.

Crystal:	colorless block, size 0.30 × 0.30 × 0.32 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	15.19 cm^{-1}
Diffractometer, scan mode:	Bruker SMART 1000 CCD, ω
$2\theta_{max}$:	54°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	11323, 4327
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 3324
$N(param)_{refined}$:	218
Programs:	SHELXS-97, SHELXL-97 [12]

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

Atom	Site	x	y	z	U_{iso}
H(2A)	8*f*	0.0999	0.4225	0.3297	0.040
H(2B)	8*f*	0.1262	0.4406	0.4161	0.040
H(3)	8*f*	0.1158	0.3056	–0.1475	0.044
H(5)	8*f*	0.1693	–0.0415	–0.0821	0.066
H(6)	8*f*	0.2059	0.0371	0.0457	0.064
H(7)	8*f*	0.2303	0.1963	0.1419	0.051
H(8A)	8*f*	0.2673	0.4461	0.2261	0.054
H(8B)	8*f*	0.2576	0.3040	0.2525	0.054
H(9A)	8*f*	0.2283	0.4477	0.3639	0.049
H(9B)	8*f*	0.1861	0.5018	0.2950	0.049
H(10A)	8*f*	0.1574	0.2721	0.2892	0.049
H(10B)	8*f*	0.1827	0.2719	0.3860	0.049
H(11)	8*f*	0.0977	0.2403	0.4614	0.044
H(12A)	8*f*	0.0170	0.4184	0.4165	0.060
H(12B)	8*f*	0.0507	0.4192	0.5062	0.060
H(13A)	8*f*	0.0125	0.2277	0.5495	0.079
H(13B)	8*f*	–0.0333	0.3250	0.5279	0.079
H(14A)	8*f*	–0.0521	0.1254	0.4620	0.074
H(14B)	8*f*	–0.0496	0.2321	0.3892	0.074
H(15A)	8*f*	–0.0012	0.0601	0.3404	0.077
H(15B)	8*f*	0.0327	0.0576	0.4297	0.077
H(16A)	8*f*	0.0841	0.1520	0.3203	0.058
H(16B)	8*f*	0.0387	0.2504	0.2979	0.058
H(17A)	8*f*	0.0610	0.1808	–0.2410	0.111
H(17B)	8*f*	0.0817	0.0959	–0.3187	0.111
H(17C)	8*f*	0.1144	0.2153	–0.2874	0.111

* Correspondence author (e-mail: lishujinghuaxue@126.com)

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)	8*f*	0.15905(1)	0.50171(2)	0.10734(2)	0.0468(2)	0.0383(2)	0.0326(2)	0.0034(1)	–0.0020(1)	–0.00047(9)
Cl(1)	8*f*	0.08295(2)	0.50684(5)	0.18661(4)	0.0431(3)	0.0577(3)	0.0409(3)	0.0054(2)	0.0003(2)	0.0050(2)
Cl(2)	8*f*	0.19581(3)	0.68995(6)	0.08635(4)	0.0743(4)	0.0539(3)	0.0616(4)	–0.0206(3)	0.0001(3)	–0.0009(3)
N(1)	8*f*	0.20743(6)	0.3650(2)	0.1547(1)	0.0319(8)	0.050(1)	0.0334(8)	0.0054(7)	0.0020(7)	0.0029(7)
N(2)	8*f*	0.11695(6)	0.3820(1)	0.3749(1)	0.0359(8)	0.0333(8)	0.0297(8)	–0.0035(6)	–0.0021(7)	–0.0021(6)
O(1)	8*f*	0.14587(6)	0.4231(1)	–0.00911(8)	0.0602(9)	0.0335(7)	0.0341(7)	0.0104(6)	–0.0050(7)	–0.0001(6)
O(2)	8*f*	0.12106(6)	0.0706(1)	–0.2049(1)	0.073(1)	0.0403(8)	0.057(1)	–0.0146(8)	–0.0044(8)	–0.0083(7)
C(1)	8*f*	0.18227(7)	0.2203(2)	0.0330(1)	0.034(1)	0.039(1)	0.041(1)	0.0068(8)	0.0029(9)	0.0044(8)
C(2)	8*f*	0.15371(7)	0.3019(2)	–0.0263(1)	0.0307(9)	0.0325(9)	0.035(1)	0.0035(7)	0.0077(8)	0.0011(7)
C(3)	8*f*	0.13352(7)	0.2522(2)	–0.1072(1)	0.036(1)	0.037(1)	0.039(1)	–0.0029(8)	0.0040(9)	0.0018(8)
C(4)	8*f*	0.13941(8)	0.1257(2)	–0.1282(1)	0.041(1)	0.036(1)	0.048(1)	–0.0066(9)	0.008(1)	–0.0040(9)
C(5)	8*f*	0.1661(1)	0.0443(2)	–0.0690(2)	0.065(2)	0.031(1)	0.068(2)	0.005(1)	0.001(1)	–0.005(1)
C(6)	8*f*	0.18717(9)	0.0918(2)	0.0076(2)	0.055(1)	0.041(1)	0.064(2)	0.014(1)	–0.005(1)	0.006(1)
C(7)	8*f*	0.20897(8)	0.2579(2)	0.1145(1)	0.034(1)	0.047(1)	0.045(1)	0.0110(9)	0.0014(9)	0.008(1)
C(8)	8*f*	0.23999(8)	0.3830(2)	0.2366(1)	0.032(1)	0.065(1)	0.039(1)	–0.0004(9)	–0.0023(9)	0.002(1)
C(9)	8*f*	0.20555(8)	0.4260(2)	0.3130(1)	0.036(1)	0.051(1)	0.035(1)	–0.0075(9)	–0.0022(8)	–0.0026(9)
C(10)	8*f*	0.16629(8)	0.3252(2)	0.3403(1)	0.041(1)	0.040(1)	0.042(1)	–0.0008(9)	0.0080(9)	–0.0022(9)
C(11)	8*f*	0.07851(7)	0.2906(2)	0.4160(1)	0.035(1)	0.038(1)	0.037(1)	–0.0023(8)	–0.0005(9)	0.0076(8)
C(12)	8*f*	0.03508(8)	0.3649(2)	0.4604(2)	0.041(1)	0.057(1)	0.052(1)	–0.008(1)	0.010(1)	–0.014(1)
C(13)	8*f*	–0.00497(9)	0.2757(3)	0.5020(2)	0.050(1)	0.084(2)	0.064(2)	–0.010(1)	0.017(1)	–0.004(1)
C(14)	8*f*	–0.02862(9)	0.1848(2)	0.4330(2)	0.046(1)	0.055(1)	0.085(2)	–0.012(1)	0.011(1)	0.011(1)
C(15)	8*f*	0.0147(1)	0.1129(2)	0.3869(2)	0.059(2)	0.040(1)	0.095(2)	–0.012(1)	0.010(1)	–0.000(1)
C(16)	8*f*	0.05563(9)	0.2016(2)	0.3456(2)	0.047(1)	0.036(1)	0.062(1)	–0.0067(9)	0.006(1)	–0.010(1)
C(17)	8*f*	0.0922(1)	0.1469(2)	–0.2682(2)	0.100(2)	0.062(2)	0.059(2)	–0.021(2)	–0.018(2)	–0.005(1)

Acknowledgment. The financial support from Zhoukou Normal University is greatly acknowledged.

References

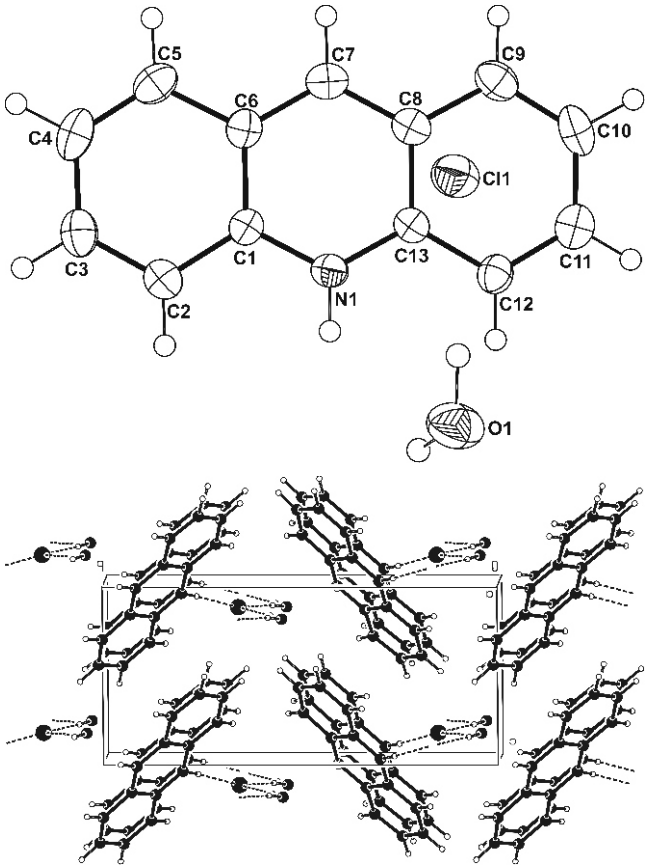
1. Nejo, A. A.; Kolawole, G. A.; Nejo, A. O.: Synthesis, characterization, antibacterial, and thermal studies of unsymmetrical Schiff-base complexes of cobalt(II). J. Coord. Chem. **63** (2010) 4398-4410.
2. Camp, C.; Mougel, V.; Horeglad, P.; Pecaut, J.; Mazzanti, M.: Multielectron Redox Reactions Involving C-C Coupling and Cleavage in Uranium Schiff Base Complexes. J. Am. Chem. Soc. **132** (2010) 17374-17377.
3. Nishat, N.; Khan, S. A.; Parveen, S.; Rasool, R.: Antimicrobial agents: synthesis, spectral, thermal, and biological aspects of a polymeric Schiff base and its polymer metal(II) complexes. J. Coord. Chem. **63** (2010) 3944-3955.
4. Kumar, K. S.; Ganguly, S.; Veerasamy, R.; De Clercq, E.: Synthesis, antiviral activity and cytotoxicity evaluation of Schiff bases of some 2-phenyl quinazoline-4(3)H-ones. Eur. J. Med. Chem. **45** (2010) 5474-5479.
5. Joseyphus, R. S.; Nair, M. S.: Antibacterial and antifungal studies on some Schiff base complexes of zinc(II). Mycobiology **36** (2008) 93-98.
6. Chohan, Z. H.; Rauf, A.; Noreen, S.; Scozzafava, A.; Supuran, C. T.: Antibacterial cobalt(II), nickel(II) and zinc(II) complexes of nicotinic acid-derived Schiff-bases. J. Enzym. Inhib. Med. Chem. **17** (2002) 101-106.
7. Ran, X. G.; Wang, L. Y.; Lin, Y. C.; Hao, J.; Cao, D. R.: Syntheses, characterization and biological studies of zinc(II), copper(II) and cobalt(II) complexes with Schiff base ligand derived from 2-hydroxy-1-naphthaldehyde and selenomethionine. Appl. Organomet. Chem. **24** (2010) 741-747.
8. Chattopadhyay, T.; Mukherjee, M.; Banu, K. S.; Banerjee, A.; Suresh, E.; Zangrando, E.; Das, D.: Mono- and dinuclear Zn(II) complexes of Schiff-base ligands: syntheses, characterization and studies of photoluminescence. J. Coord. Chem. **62** (2009) 967-979.
9. Qiu, X. Y.; Liu, Y.: Crystal structure of dichlorido-chloro-2-[(3-diethylammoniopropylimino)methyl]phenolatozinc(II), $[Zn(C_{14}H_{21}ClN_2O)]Cl_2$. Z. Kristallogr. NCS **223** (2008) 459-460.
10. Qiu, X. Y.: {4-Bromo-2-[3-(dimethylamino)propyliminomethyl]phenolato}dichlorozinc(II). Acta Crystallogr. **E62** (2006) m2173-m2174.
11. Han, X.; You, Z. L.; Xu, Y. T.; Wang, X. M.: Synthesis, characterization and crystal structure of a mononuclear zinc(II) complex derived from 2-methoxy-6-[(3-cyclohexylaminopropylimino)methyl]phenol. J. Chem. Crystallogr. **36** (2006) 743-746.
12. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. **A64** (2008) 112-122.

Crystal structure of acridinium chloride monohydrate, $[C_{13}H_{10}N]Cl \cdot H_2O$

Kwang Ha*

Chonnam National University, School of Applied Chemical Engineering, Research Institute of Catalysis, Gwangju 500-757, Republic of Korea

Received February 28, 2011, accepted and available on-line June 17, 2011; CCDC no. 1267/3418



Abstract

$C_{13}H_{12}ClNO$, monoclinic, $P2_1$ (no. 4), a = 5.442(2) Å, b = 14.935(5) Å, c = 6.931(2) Å, β = 99.016(8)°, V = 556.4 Å^3, Z = 2, $R_{gt}(F)$ = 0.057, $wR_{ref}(F^2)$ = 0.131, T = 200 K.

Source of material

To a solution of acridine (0.201 g, 1.12 mmol) in acetone (20 ml) were added five drops of hydrochloric acid (37%) and stirred for 5 min at room temperature. The formed precipitate was separated by filtration, washed with ether and dried under vacuum, to give a yellow powder (0.232 g). Crystals suitable for X-ray diffraction analysis were obtained by slow evaporation from a CH_3CN solution.

Experimental details

Hydrogen atoms were positioned geometrically and allowed to ride on their parent atoms with d(C—H) = 0.95 Å and U_{iso}(H) = 1.2 U_{eq}(C). The H atoms at the N and O atoms were located from Fourier difference maps and refined isotropically: d(N—H) = 0.87(5) Å and d(O—H) = 0.91(5) Å and 0.94(7) Å. The highest peak (0.42 e·Å^{-3}) and the deepest hole (–0.47 e·Å^{-3}) in the difference Fourier map are located 1.03 Å and 0.80 Å from the Cl1 atom, respectively. The Flack parameter is 0.33(11) in the refinement. Because the compound is a weak anomalous scatterer, the parameter is meaningless and the absolute crystal structure cannot be determined reliably.

Discussion

The title compound consists of a protonated acridinium cation, a Cl^- anion and a solvent water molecule (figure, top). In the crystal structure, the component ions and the water molecule interact by means of intermolecular N–H···Cl and O–H···Cl hydrogen bonds with d(N···Cl) = 3.095(4) Å and d(O···Cl) = 3.234(4) Å and 3.233(4) Å, forming chains along [100] (figure, bottom). The nearly planar cations are arranged in a V-shaped packing pattern along [001] and stacked in columns along [100]. In the columns, numerous intermolecular π-π interactions between adjacent six-membered rings are present. The centroid-centroid distance between Cg1 (the centroid of ring C1-C6) and $Cg2^i$ (ring C8-C13, symmetry code i: x,y,z–1) is 3.937(3) Å, and the dihedral angle between the ring planes is 1.1(2)°.

Table 1. Data collection and handling.

Crystal:	yellow block, size 0.06 × 0.25 × 0.28 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	3.19 cm^{-1}
Diffractometer, scan mode:	Bruker SMART 1000 CCD, φ/ω
$2\theta_{max}$:	56.58°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	4131, 2719
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 1755
$N(param)_{refined}$:	157
Programs:	SHELXS-97, SHELXL-97 [1], ORTEP-3 [2], PLATON [3]

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

Atom	Site	x	y	z	U_{iso}
H(1)	2*a*	1.07(1)	0.261(3)	0.945(7)	0.07(2)
H(2)	2*a*	1.1718	0.3426	0.6715	0.038
H(3)	2*a*	1.0623	0.4593	0.4549	0.045
H(4)	2*a*	0.7275	0.5542	0.4878	0.048
H(5)	2*a*	0.5094	0.5367	0.7439	0.044
H(7)	2*a*	0.4421	0.4491	1.0412	0.034
H(9)	2*a*	0.3717	0.3575	1.3311	0.043
H(10)	2*a*	0.4891	0.2363	1.5336	0.046
H(11)	2*a*	0.8240	0.1462	1.4842	0.045
H(12)	2*a*	1.0397	0.1721	1.2303	0.037
H(1A)	2*a*	0.697(9)	0.077(3)	0.850(6)	0.05(1)
H(1B)	2*a*	0.99(1)	0.074(4)	0.842(7)	0.08(2)

* e-mail: hakwang@chonnam.ac.kr

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*a*	0.3383(2)	0.15989(8)	0.8646(1)	0.0360(5)	0.0374(5)	0.0391(5)	0.0025(6)	0.0098(4)	–0.0031(6)
N(1)	2*a*	0.9580(7)	0.2989(2)	0.9686(5)	0.027(2)	0.030(2)	0.029(2)	0.003(2)	0.005(2)	–0.002(2)
C(1)	2*a*	0.8988(7)	0.3672(3)	0.8407(5)	0.023(2)	0.023(2)	0.025(2)	–0.004(2)	–0.000(2)	–0.001(2)
C(2)	2*a*	1.0365(8)	0.3808(3)	0.6865(6)	0.030(2)	0.036(2)	0.029(2)	–0.003(2)	0.005(2)	–0.003(2)
C(3)	2*a*	0.9711(9)	0.4499(3)	0.5593(6)	0.040(3)	0.040(3)	0.033(3)	–0.009(2)	0.006(2)	0.004(2)
C(4)	2*a*	0.7713(9)	0.5075(3)	0.5798(6)	0.049(3)	0.031(3)	0.035(3)	–0.009(2)	–0.005(2)	0.008(2)
C(5)	2*a*	0.6413(9)	0.4967(3)	0.7300(7)	0.040(3)	0.026(2)	0.042(3)	0.003(2)	0.000(2)	–0.001(2)
C(6)	2*a*	0.7013(8)	0.4257(3)	0.8674(6)	0.032(2)	0.024(2)	0.028(2)	–0.005(2)	0.003(2)	–0.002(2)
C(7)	2*a*	0.5744(7)	0.4102(3)	1.0224(6)	0.025(2)	0.025(2)	0.033(2)	–0.004(2)	–0.001(2)	–0.010(2)
C(8)	2*a*	0.6351(8)	0.3396(3)	1.1513(5)	0.027(2)	0.031(2)	0.025(2)	–0.003(2)	0.002(2)	–0.007(2)
C(9)	2*a*	0.5067(9)	0.3207(3)	1.3085(7)	0.035(3)	0.038(3)	0.035(3)	–0.004(2)	0.010(2)	–0.009(2)
C(10)	2*a*	0.5769(9)	0.2492(3)	1.4287(6)	0.047(3)	0.041(3)	0.030(2)	–0.018(2)	0.014(2)	–0.005(2)
C(11)	2*a*	0.7769(8)	0.1948(3)	1.3980(6)	0.041(3)	0.035(3)	0.034(3)	–0.004(2)	0.002(2)	0.001(2)
C(12)	2*a*	0.9049(8)	0.2098(3)	1.2488(6)	0.030(2)	0.029(2)	0.032(2)	–0.003(2)	0.003(2)	0.003(2)
C(13)	2*a*	0.8358(7)	0.2822(3)	1.1212(5)	0.025(2)	0.027(2)	0.023(2)	–0.002(2)	0.002(2)	–0.004(2)
O(1)	2*a*	0.8319(8)	0.0439(2)	0.8322(5)	0.037(2)	0.044(2)	0.072(3)	–0.003(2)	0.019(2)	–0.007(2)

Acknowledgment. This work was supported by Priority Research Centers Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (grant no. 2010-0029626).

References

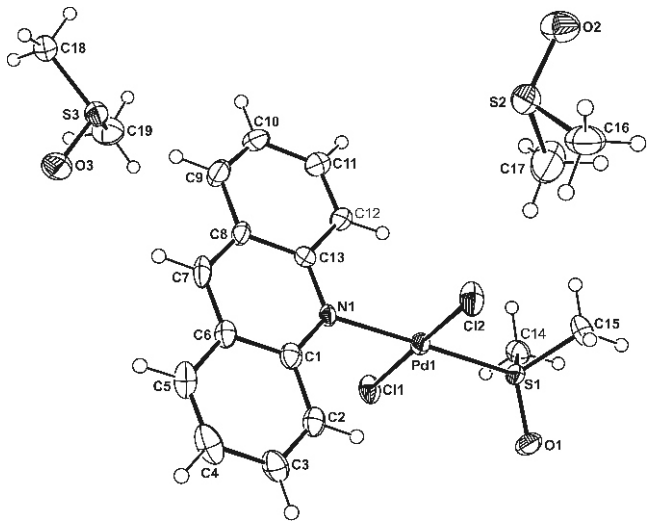
1. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. **A64** (2008) 112-122.
2. Farrugia, L. J.: ORTEP-3 for Windows - a version of ORTEP-III with a Graphical User Interface (GUI) J. Appl. Crystallogr. **30** (1997) 565.
3. Spek, A. L.: Single-crystal structure validation with the program PLATON. J. Appl. Crystallogr. **36** (2003) 7-13.

Crystal structure of (acridine)dichloro(dimethyl sulfoxide-κS)-palladium(II) — dimethyl sulfoxide (1:2), $PdCl_2(C_{13}H_9N)(C_2H_6SO) \cdot 2C_2H_6SO$

Kwang Ha*

Chonnam National University, School of Applied Chemical Engineering, Research Institute of Catalysis, Gwangju 500-757, Republic of Korea

Received March 11, 2011, accepted and available on-line June 17, 2011; CCDC no. 1267/3440



Abstract

$C_{19}H_{27}Cl_2NO_3PdS_3$, triclinic, $P\bar{1}$ (no. 2), a = 9.6245(6) Å, b = 10.9445(6) Å, c = 12.7679(7) Å, α = 101.015(1)°, β = 111.510(1)°, γ = 93.545(1)°, V = 1215.3 Å^3, Z = 2, $R_{gt}(F)$ = 0.046, $wR_{ref}(F^2)$ = 0.107, T = 200 K.

Source of material

To a solution of Na_2PdCl_4 (0.2014 g, 0.685 mmol) in H_2O (20 ml) was added acridine (acr, 0.2561 g, 1.429 mmol), and the mixture was refluxed for 7 h. The precipitate was then separated by filtration, washed with acetone and pentane, and dried at 50 °C, to give a yellow powder (0.3369 g). Crystals suitable for X-ray diffraction analysis were obtained by slow evaporation from a dimethyl sulfoxide (DMSO) solution at 90 °C.

Experimental details

Hydrogen atoms were positioned geometrically and allowed to ride on their parent atoms with d(C—H) = 0.95 Å (CH) or 0.98 Å (CH_3) and U_{iso}(H) = 1.2 U_{eq}(C) or 1.5 $U_{eq}(C_{methyl})$. The highest peak (0.87 e Å^{-3}) and the deepest hole (–0.83 e Å^{-3}) in the difference Fourier map are located 1.11 Å and 0.83 Å from the Pd1 atom, respectively.

Discussion

Single crystals of the title compound were obtained from a dimethyl sulfoxide solution of $[PdCl_2(acr)_2]$. It seems that an acridine ligand of the complex $[PdCl_2(acr)_2]$ was replaced by a DMSO molecule during crystallization, whereas the analogous Pt complex $[PtCl_2(acr)_2]$ crystallized without substitution from a DMSO solution at 80 °C [1]. It was previously reported that single crystals of the complex $[PdCl_2(acr)(CH_3)_2NH]$ were acquired from an *N*,*N*-dimethylformamide solution of the Pd complex $[PdCl_2(acr)_2]$ at 50 °C [2].

The title compound consists of a neutral Pd(II) complex and two DMSO solvent molecules. In the complex, the Pd(II) ion is four-coordinated in a slightly distorted square-planar environment by one N atom from an acridine ligand, one S atom of the DMSO molecule and two chloride ions. The Cl atoms are in *trans* conformation with respect to each other (∠Cl1–Pd1–Cl2 = 176.46(6)°) and almost perpendicular to the nearly planar acridine ligand, with the bond angles ∠N1–Pd1–Cl1 = 88.6(1)° and ∠N1–Pd1–Cl2 = 89.7(1)°. In the crystal structure, the complex and the solvent molecules are linked by C–H···O and C–H···Cl hydrogen bonds with d(C···O) = 3.114(7) - 3.504(8) Å and d(C···Cl) = 3.170(6) - 3.666(6) Å, forming a three-dimensional network structure. In addition, several intermolecular π-π interactions between adjacent six-membered rings are present. The shortest distance between Cg1 (the centroid of ring N1-C13) and $Cg1^{i}$ (symmetry code i: 1–x,1–y,1–z) is 3.769(3) Å; the ring planes are parallel and shifted by 1.400 Å.

Table 1. Data collection and handling.

Crystal:	yellow block, size 0.06 × 0.12 × 0.24 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	12.61 cm^{-1}
Diffractometer, scan mode:	Bruker SMART 1000 CCD, φ/ω
$2\theta_{max}$:	51.96°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	7673, 4694
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 3402
$N(param)_{refined}$:	268
Programs:	SHELXS-97, SHELXL-97 [3], ORTEP-3 [4], PLATON [5]

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

Atom	Site	x	y	z	U_{iso}
H(2)	2*i*	0.0067	0.4407	0.3680	0.041
H(3)	2*i*	–0.0336	0.6336	0.4519	0.049
H(4)	2*i*	0.1565	0.8100	0.5198	0.058
H(5)	2*i*	0.3744	0.7949	0.4883	0.051
H(7)	2*i*	0.5326	0.6643	0.4087	0.043
H(9)	2*i*	0.6816	0.5325	0.3191	0.050
H(10)	2*i*	0.7087	0.3399	0.2270	0.054
H(11)	2*i*	0.5189	0.1651	0.1749	0.053
H(12)	2*i*	0.3143	0.1838	0.2246	0.044

* e-mail: hakwang@chonnam.ac.kr

Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
H(14A)	2*i*	–0.1824	–0.1167	0.0668	0.052
H(14B)	2*i*	–0.0132	–0.0629	0.0886	0.052
H(14C)	2*i*	–0.1499	0.0084	0.0270	0.052
H(15A)	2*i*	–0.0135	–0.0200	0.3882	0.062
H(15B)	2*i*	0.0667	–0.0819	0.3054	0.062
H(15C)	2*i*	–0.1053	–0.1327	0.2785	0.062
H(16A)	2*i*	0.5147	0.0638	0.9100	0.083
H(16B)	2*i*	0.4917	0.2080	0.9150	0.083
H(16C)	2*i*	0.6459	0.1731	0.9993	0.083

Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
H(17A)	2*i*	0.4961	0.0758	0.6227	0.122
H(17B)	2*i*	0.4014	0.1495	0.6878	0.122
H(17C)	2*i*	0.4310	0.0096	0.7000	0.122
H(18A)	2*i*	0.9703	0.6653	0.0754	0.059
H(18B)	2*i*	1.0249	0.5442	0.1231	0.059
H(18C)	2*i*	1.0354	0.6729	0.2116	0.059
H(19A)	2*i*	0.5999	0.4794	–0.0505	0.084
H(19B)	2*i*	0.7574	0.4373	–0.0476	0.084
H(19C)	2*i*	0.7198	0.5736	–0.0673	0.084

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}
Pd(1)	2*i*	0.08368(5)	0.22413(4)	0.27753(4)	0.0232(2)	0.0232(2)	0.0285(2)	0.0003(2)	0.0079(2)	0.0075(2)
Cl(1)	2*i*	–0.0355(2)	0.2701(1)	0.1008(1)	0.0394(9)	0.0332(8)	0.0284(8)	–0.0013(6)	0.0034(7)	0.0133(7)
Cl(2)	2*i*	0.1996(2)	0.1897(1)	0.4595(1)	0.043(1)	0.0408(9)	0.0322(9)	–0.0092(7)	–0.0018(7)	0.0159(7)
S(1)	2*i*	–0.0891(2)	0.0516(1)	0.2224(1)	0.0227(7)	0.0203(7)	0.0341(8)	0.0015(5)	0.0125(6)	0.0056(6)
O(1)	2*i*	–0.2373(4)	0.0796(3)	0.2205(4)	0.030(2)	0.031(2)	0.066(3)	0.001(2)	0.027(2)	0.001(2)
N(1)	2*i*	0.2408(5)	0.3849(4)	0.3231(4)	0.024(2)	0.014(2)	0.026(2)	–0.001(2)	0.009(2)	0.005(2)
C(1)	2*i*	0.2172(6)	0.4975(5)	0.3739(5)	0.033(3)	0.030(3)	0.027(3)	0.003(3)	0.009(3)	0.012(3)
C(2)	2*i*	0.0823(7)	0.5116(5)	0.3917(5)	0.039(4)	0.033(3)	0.030(3)	–0.001(3)	0.012(3)	0.013(3)
C(3)	2*i*	0.0590(8)	0.6254(5)	0.4424(5)	0.056(4)	0.025(3)	0.040(4)	0.006(3)	0.021(3)	0.000(3)
C(4)	2*i*	0.1719(9)	0.7319(6)	0.4812(5)	0.092(6)	0.027(3)	0.032(4)	0.012(4)	0.033(4)	0.001(3)
C(5)	2*i*	0.3006(8)	0.7225(5)	0.4635(5)	0.060(5)	0.029(3)	0.038(4)	–0.007(3)	0.020(4)	0.006(3)
C(6)	2*i*	0.3287(6)	0.6055(5)	0.4080(5)	0.031(3)	0.026(3)	0.023(3)	–0.003(2)	0.004(3)	0.006(2)
C(7)	2*i*	0.4572(7)	0.5932(5)	0.3855(5)	0.039(4)	0.029(3)	0.030(3)	–0.010(3)	0.002(3)	0.016(3)
C(8)	2*i*	0.4781(6)	0.4790(5)	0.3297(5)	0.021(3)	0.029(3)	0.034(3)	–0.005(2)	0.002(3)	0.014(3)
C(9)	2*i*	0.6063(7)	0.4625(6)	0.2999(6)	0.031(4)	0.045(4)	0.050(4)	–0.003(3)	0.015(3)	0.020(3)
C(10)	2*i*	0.6223(7)	0.3495(6)	0.2453(6)	0.028(4)	0.055(4)	0.065(5)	0.011(3)	0.024(3)	0.028(4)
C(11)	2*i*	0.5087(7)	0.2443(6)	0.2151(6)	0.033(4)	0.038(4)	0.062(5)	0.006(3)	0.019(3)	0.012(3)
C(12)	2*i*	0.3866(6)	0.2559(5)	0.2431(5)	0.026(3)	0.027(3)	0.056(4)	0.000(3)	0.014(3)	0.008(3)
C(13)	2*i*	0.3650(6)	0.3718(5)	0.2987(5)	0.025(3)	0.027(3)	0.034(3)	0.007(2)	0.009(3)	0.013(3)
C(14)	2*i*	–0.1111(7)	–0.0401(5)	0.0860(5)	0.037(4)	0.026(3)	0.036(4)	0.004(3)	0.011(3)	0.002(3)
C(15)	2*i*	–0.0286(8)	–0.0579(5)	0.3081(5)	0.056(4)	0.029(3)	0.033(4)	0.007(3)	0.008(3)	0.014(3)
S(2)	2*i*	0.6435(2)	0.1514(2)	0.8159(2)	0.035(1)	0.0388(9)	0.073(1)	0.0015(8)	0.0121(9)	0.0190(9)
O(2)	2*i*	0.7437(5)	0.0518(4)	0.8228(4)	0.044(3)	0.047(3)	0.057(3)	0.010(2)	0.013(2)	–0.002(2)
C(16)	2*i*	0.5652(8)	0.1488(6)	0.9220(6)	0.035(4)	0.049(4)	0.070(5)	0.010(3)	0.010(4)	0.006(4)
C(17)	2*i*	0.4740(9)	0.0897(8)	0.6928(7)	0.053(5)	0.110(7)	0.072(6)	–0.009(5)	0.000(4)	0.057(6)
S(3)	2*i*	0.7909(2)	0.5714(1)	0.1256(2)	0.0387(9)	0.0323(8)	0.046(1)	0.0063(7)	0.0206(8)	0.0101(7)
O(3)	2*i*	0.7243(5)	0.6884(4)	0.1475(4)	0.051(3)	0.042(3)	0.074(4)	0.014(2)	0.030(3)	0.003(3)
C(18)	2*i*	0.9762(7)	0.6188(5)	0.1350(5)	0.040(4)	0.034(3)	0.044(4)	0.004(3)	0.015(3)	0.012(3)
C(19)	2*i*	0.7076(8)	0.5083(7)	–0.0272(6)	0.047(4)	0.061(5)	0.046(4)	0.008(4)	0.008(4)	0.003(4)

Acknowledgment. This work was supported by Priority Research Centers Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (grant no. 2010-0029626).

References

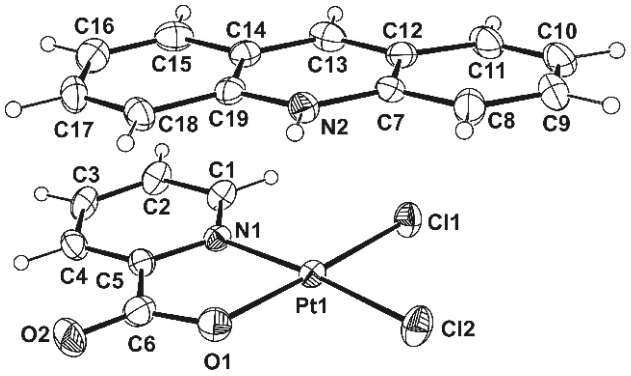
1. Ha, K.: Crystal structure of dichlorobis(acridine)platinum(II), $PtCl_2(C_{13}H_9N)_2$. Z. Kristallogr. NCS **225** (2010) 323-324.
2. Ha, K.: Crystal structure of dichloroacridinedimethylaminepalladium(II), $PdCl_2(C_{13}H_9N)(C_2H_7N)$. Z. Kristallogr. NCS **225** (2010) 655-656.
3. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. **A64** (2008) 112-122.
4. Farrugia, L. J.: ORTEP-3 for Windows - a version of ORTEP-III with a Graphical User Interface (GUI) J. Appl. Crystallogr. **30** (1997) 565.
5. Spek, A. L.: Single-crystal structure validation with the program PLATON. J. Appl. Crystallogr. **36** (2003) 7-13.

Crystal structure of acridinium dichloro(pyridine-2-carboxylato-k^2*N*,*O*)platinate(II), $[C_{13}H_{10}N][PtCl_2(C_6H_4NO_2)]$

Kwang Ha*

Chonnam National University, School of Applied Chemical Engineering, Research Institute of Catalysis, Gwangju 500-757, Republic of Korea

Received February 28, 2011, accepted and available on-line May 20, 2011; CCDC no. 1267/3419



Abstract

$C_{19}H_{14}Cl_2N_2O_2Pt$, monoclinic, *C*12/*c*1 (no. 15), *a* = 26.276(5) Å, *b* = 8.056(1) Å, *c* = 19.944(3) Å, β = 121.309(3)°, *V* = 3606.8 Å^3, *Z* = 8, $R_{gt}(F)$ = 0.037, $wR_{ref}(F^2)$ = 0.086, *T* = 200 K.

Source of material

To a suspension of acridine (0.1792 g, 1.000 mmol) and pyridine-2-carboxylic acid (0.1231 g, 1.000 mmol) in H_2O (20 ml) was added K_2PtCl_4 (0.4156 g, 1.001 mmol), and the mixture was stirred at room temperature for 3 h. The formed precipitate was separated by filtration, washed with H_2O, EtOH and ether, and dried at 50 °C, to give a yellow powder (0.4513 g). Crystals suitable for X-ray diffraction analysis were obtained by slow evaporation from a CH_3CN solution.

Experimental details

Hydrogen atoms were positioned geometrically and allowed to ride on their parent atoms with *d*(C—H) = 0.95 Å, *d*(N—H) = 0.88 Å and U_{iso}(H) = 1.2U_{eq}(C, N). The highest peak (1.46 e·Å^{-3}) and the deepest hole (–2.10 e·Å^{-3}) in the difference Fourier map are located 0.96 Å and 0.95 Å from the atoms N1 and Pt1, respectively.

Discussion

The crystal structure of the title compound consists of an acridinium cation and an anionic Pt(II) complex. In the complex, the Pt(II) ion has a distorted square-planar environment defined by the N and O atoms from the chelating pyridine-2-carboxylate anionic ligand and two Cl^- anions. The tight N1–Pt1–O1 chelate angle of 81.6(2)° results in non-linear *trans* arrangements (∠Cl1–Pt1–O1 = 176.6(2)° and ∠Cl2–Pt1–N1 = 172.4(2)°). Because the two Pt—Cl bond lengths are almost equal (2.286(2) Å and 2.292(2) Å), the different *trans* effects of the O and N atoms cannot be observed reliably. The Pt—O bond (2.035(5) Å) is slightly longer than the Pt—N bond (2.002(6) Å). In the crystal structure, the ions are linked by intermolecular N–H···O hydrogen bonding with *d*(N···O) = 2.792(9) Å. The acridinium and the complex are located approximately parallel: the dihedral angle between the cation and pyridyl ring planes is 5.2(4)°. There are also numerous intermolecular π-π interactions between adjacent six-membered rings. For Cg1 (the centroid of ring N2-C19) and Cg2^i (ring C14-C19; symmetry code i: –*x*,1–*y*,–*z*), the centroid-centroid distance is 3.811(5) Å and the dihedral angle between the ring planes is 1.9(4)°.

Table 1. Data collection and handling.

Crystal:	yellow block, size 0.09 × 0.15 × 0.16 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	80.93 cm^{-1}
Diffractometer, scan mode:	Bruker SMART 1000 CCD, φ/ω
$2\theta_{max}$:	56.58°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	12849, 4428
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2827
$N(param)_{refined}$:	235
Programs:	SHELXS-97, SHELXL-97 [1], ORTEP-3 [2], PLATON [3]

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

Atom	Site	*x*	*y*	*z*	U_{iso}
H(1)	8*f*	0.2304	0.7466	0.2921	0.048
H(2)	8*f*	0.2145	0.6672	0.3922	0.053
H(3)	8*f*	0.1334	0.7755	0.3950	0.054
H(4)	8*f*	0.0659	0.9466	0.2929	0.051
H(2A)	8*f*	0.0250	0.7751	–0.0593	0.047
H(8)	8*f*	0.0699	0.7830	–0.1378	0.059
H(9)	8*f*	0.1533	0.7245	–0.1428	0.067
H(10)	8*f*	0.2325	0.5770	–0.0441	0.069
H(11)	8*f*	0.2320	0.4884	0.0659	0.061
H(13)	8*f*	0.1740	0.4590	0.1349	0.052
H(15)	8*f*	0.1170	0.4465	0.2031	0.058
H(16)	8*f*	0.0344	0.5287	0.2079	0.058
H(17)	8*f*	–0.0377	0.7001	0.1111	0.054
H(18)	8*f*	–0.0324	0.7881	0.0045	0.049

* e-mail: hakwang@chonnam.ac.kr

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}
Pt(1)	8*f*	0.16636(1)	0.97934(3)	0.14687(2)	0.0332(2)	0.0331(2)	0.0323(2)	–0.0021(1)	0.0176(1)	0.0013(1)
Cl(1)	8*f*	0.25548(9)	0.8535(2)	0.1856(1)	0.038(1)	0.058(1)	0.049(1)	0.0054(9)	0.026(1)	0.007(1)
Cl(2)	8*f*	0.16119(9)	1.0930(3)	0.0382(1)	0.052(1)	0.064(1)	0.044(1)	0.003(1)	0.029(1)	0.015(1)
O(1)	8*f*	0.0876(2)	1.0874(6)	0.1185(3)	0.046(4)	0.045(3)	0.049(4)	0.013(3)	0.026(3)	0.015(3)
O(2)	8*f*	0.0239(3)	1.1127(6)	0.1594(4)	0.051(4)	0.057(3)	0.090(5)	0.028(3)	0.045(4)	0.021(3)
N(1)	8*f*	0.1604(3)	0.8941(6)	0.2369(3)	0.031(4)	0.033(3)	0.029(4)	–0.006(3)	0.013(3)	–0.003(3)
C(1)	8*f*	0.1970(3)	0.7896(9)	0.2930(4)	0.034(5)	0.045(4)	0.034(5)	–0.001(4)	0.014(4)	0.008(4)
C(2)	8*f*	0.1878(4)	0.7417(9)	0.3526(5)	0.044(5)	0.058(5)	0.027(5)	–0.001(4)	0.015(4)	0.012(4)
C(3)	8*f*	0.1396(4)	0.804(1)	0.3535(5)	0.053(6)	0.061(5)	0.028(5)	–0.014(4)	0.026(5)	–0.003(4)
C(4)	8*f*	0.1003(4)	0.9062(9)	0.2941(5)	0.043(5)	0.045(4)	0.046(6)	–0.002(4)	0.027(5)	–0.012(4)
C(5)	8*f*	0.1113(3)	0.9499(8)	0.2365(5)	0.046(5)	0.035(4)	0.035(5)	–0.002(3)	0.026(4)	–0.004(3)
C(6)	8*f*	0.0707(4)	1.0579(9)	0.1684(5)	0.046(6)	0.040(4)	0.054(6)	–0.001(4)	0.028(5)	0.005(4)
N(2)	8*f*	0.0536(3)	0.7148(6)	–0.0220(4)	0.034(4)	0.034(3)	0.053(5)	0.003(3)	0.025(4)	–0.001(3)
C(7)	8*f*	0.1006(3)	0.6742(8)	–0.0292(5)	0.042(5)	0.025(3)	0.059(6)	0.000(3)	0.034(5)	–0.005(4)
C(8)	8*f*	0.1024(4)	0.7249(9)	–0.0960(5)	0.060(6)	0.045(4)	0.062(6)	0.011(4)	0.045(6)	0.012(4)
C(9)	8*f*	0.1513(4)	0.689(1)	–0.0988(6)	0.076(7)	0.048(5)	0.071(7)	0.006(5)	0.057(7)	–0.003(5)
C(10)	8*f*	0.1991(4)	0.601(1)	–0.0394(6)	0.052(6)	0.048(5)	0.091(8)	0.002(4)	0.050(6)	–0.015(5)
C(11)	8*f*	0.1989(4)	0.5471(9)	0.0254(6)	0.038(5)	0.046(5)	0.071(7)	0.004(4)	0.030(5)	–0.011(4)
C(12)	8*f*	0.1482(3)	0.5808(8)	0.0312(5)	0.035(5)	0.028(4)	0.063(6)	–0.003(3)	0.028(5)	–0.006(4)
C(13)	8*f*	0.1435(3)	0.5258(8)	0.0951(5)	0.032(5)	0.038(4)	0.045(5)	0.005(3)	0.010(4)	–0.005(4)
C(14)	8*f*	0.0941(3)	0.5694(8)	0.0996(5)	0.038(5)	0.031(4)	0.037(5)	–0.006(3)	0.017(4)	–0.005(3)
C(15)	8*f*	0.0876(4)	0.5156(9)	0.1631(5)	0.056(6)	0.040(4)	0.037(5)	–0.004(4)	0.016(4)	–0.003(4)
C(16)	8*f*	0.0388(4)	0.564(1)	0.1658(5)	0.054(6)	0.056(5)	0.039(5)	–0.013(4)	0.026(5)	–0.009(4)
C(17)	8*f*	–0.0048(4)	0.6665(9)	0.1069(5)	0.034(5)	0.057(5)	0.050(6)	–0.001(4)	0.026(5)	–0.005(4)
C(18)	8*f*	–0.0022(3)	0.7197(9)	0.0438(5)	0.031(5)	0.044(4)	0.048(6)	0.000(3)	0.020(4)	–0.011(4)
C(19)	8*f*	0.0482(3)	0.6679(8)	0.0393(5)	0.033(5)	0.033(4)	0.033(5)	–0.009(3)	0.015(4)	–0.007(3)

Acknowledgment. This work was supported by Priority Research Centers Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (grant no. 2010-0029626).

References

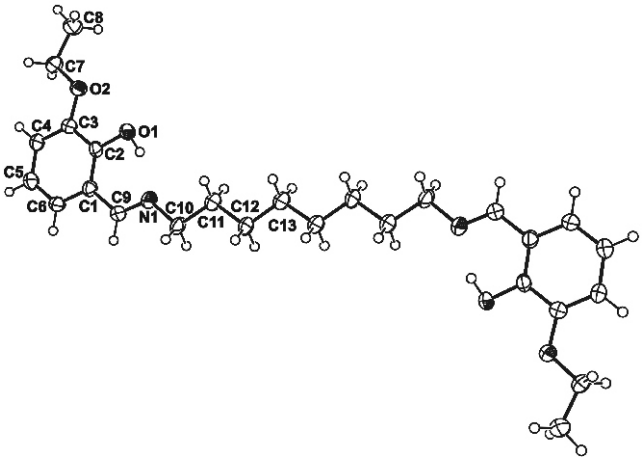
1. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. **A64** (2008) 112-122.
2. Farrugia, L. J.: ORTEP-3 for Windows - a version of ORTEP-III with a Graphical User Interface (GUI) J. Appl. Crystallogr. **30** (1997) 565.
3. Spek, A. L.: Single-crystal structure validation with the program PLATON. J. Appl. Crystallogr. **36** (2003) 7-13.

Crystal structure of *N*,*N*′-bis(3-ethoxy-2-hydroxybenzylidene)-octane-1,8-diamine, $C_{26}H_{36}N_2O_4$

Kwang Ha*

Chonnam National University, School of Applied Chemical Engineering, Research Institute of Catalysis, Gwangju 500-757, Republic of Korea

Received March 3, 2011, accepted and available on-line May 20, 2011; CCDC no. 1267/3422



Abstract

$C_{26}H_{36}N_2O_4$, triclinic, $P\bar{1}$ (no. 2), a = 6.905(1) Å, b = 6.910(1) Å, c = 12.981(2) Å, α = 90.123(4)°, β = 101.625(4)°, γ = 101.530(4)°, V = 593.8 Å^3, Z = 1, $R_{gt}(F)$ = 0.059, $wR_{ref}(F^2)$ = 0.176, T = 200 K.

Source of material

1,8-Diaminooctane (1.0098 g, 7.000 mmol) and 3-ethoxy-salicylaldehyde (2.3266 g, 14.001 mmol) in EtOH (20 ml) were stirred for 5 h at room temperature. After addition of pentane (30 ml) to the reaction mixture, the formed precipitate was separated by filtration, washed with ether, and dried at 50 °C, to give a yellow powder (2.7674 g). Crystals suitable for X-ray diffraction analysis were obtained by slow evaporation from a CH_3CN solution.

Experimental details

Hydrogen atoms were positioned geometrically and allowed to ride on their parent atoms with d(C—H) = 0.95 Å (CH), 0.99 Å (CH_2) or 0.98 Å (CH_3) and U_{iso}(H) = 1.2U_{eq}(C) or 1.5U_{eq}(C_{methyl}). The hydroxy H atom was located from Fourier difference maps and refined isotropically: d(O—H) = 0.89(3) Å. The highest peak (0.38 e·Å^{-3}) and the deepest hole (–0.23 e·Å^{-3}) in the difference Fourier map are located 1.29 Å and 0.91 Å from the atoms O1 and C1, respectively.

Discussion

The title compound is a tetradentate Schiff-base, which can act as a dibasic ligand, i.e. the N and O donor atoms can coordinate one or two metal ions. The compound crystallizes in the same space group as the analogous compounds with propylene chain ($C_{21}H_{26}N_2O_4$) [1] and butylene chain ($C_{22}H_{28}N_2O_4$) [2], whereas the analogous Schiff-base with ethylene group ($C_{20}H_{24}N_2O_4$) crystallizes in the monoclinic space group $C2/c$ [3]. A center of inversion is located at the centroid of the title molecule, and therefore the asymmetric unit contains one half of the molecule, and the two benzene rings are exactly parallel. In the crystal structure, the ethoxy group is located approximately parallel to the carrier benzene ring. The N—C bond lengths and the C–N–C bond angle indicate that the imino N1 atom is sp^2-hybridized with d(N1=C9) = 1.270(3) Å, d(N1—C10) = 1.468(3) Å and ∠C9–N1–C10 = 121.1(2)°. The Schiff-base displays strong intramolecular O–H···N hydrogen bonding between the hydroxy O atom and the imino N atom with d(O1···N1) = 2.575(3) Å thus forming a nearly planar six-membered ring. There are also weak intermolecular C–H···O hydrogen bonds with d(C···O) = 3.235(3) Å. The torsion angles for the four atoms within the diiminooctylene chain indicate that the chain is almost perfectly in the anti conformation with ∠N1–C10–C11–C12 = 179.6(2)°, ∠C10–C11–C12–C13 = –179.8(2)° and ∠C11–C12–C13–C13^{i} = 178.5(3)° (symmetry code i: 1–x,2–y,–z).

Table 1. Data collection and handling.

Crystal:	yellow block, size 0.14 × 0.24 × 0.40 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	0.83 cm^{-1}
Diffractometer, scan mode:	Bruker SMART 1000 CCD, φ/ω
$2\theta_{max}$:	52°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	3645, 2303
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 1514
$N(param)_{refined}$:	150
Programs:	SHELXS-97, SHELXL-97 [4], ORTEP-3 [5], PLATON [6]

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

Atom	Site	x	y	z	U_{iso}
H(1)	2*i*	0.891(5)	0.315(5)	0.239(3)	0.07(1)
H(4)	2*i*	1.2818	–0.1797	0.4069	0.041
H(5)	2*i*	1.5514	0.0040	0.3413	0.045
H(6)	2*i*	1.5075	0.2784	0.2437	0.041
H(7A)	2*i*	1.0172	–0.2662	0.5007	0.043
H(7B)	2*i*	0.9641	–0.3849	0.3886	0.043
H(8A)	2*i*	0.6702	–0.2843	0.4945	0.068
H(8B)	2*i*	0.7100	–0.5031	0.4836	0.068
H(8C)	2*i*	0.6153	–0.3977	0.3815	0.068
H(9)	2*i*	1.2966	0.5151	0.1666	0.039

* e-mail: hakwang@chonnam.ac.kr

Table 2. Continued.

Atom	Site	*x*	*y*	*z*	U_{iso}
H(10A)	2*i*	1.0304	0.6627	0.0446	0.043
H(10B)	2*i*	1.0894	0.7933	0.1529	0.043
H(11A)	2*i*	0.7477	0.7134	0.1709	0.045
H(11B)	2*i*	0.6893	0.5848	0.0625	0.045

Table 2. Continued.

Atom	Site	*x*	*y*	*z*	U_{iso}
H(12A)	2*i*	0.8302	1.0046	0.0785	0.042
H(12B)	2*i*	0.7711	0.8757	–0.0300	0.042
H(13A)	2*i*	0.4909	0.9135	0.0994	0.045
H(13B)	2*i*	0.4331	0.7898	–0.0105	0.045

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*i*	0.8686(2)	0.2066(3)	0.2756(1)	0.0283(9)	0.042(1)	0.051(1)	0.0161(7)	0.0116(7)	0.0183(8)
O(2)	2*i*	0.9083(2)	–0.1104(2)	0.3800(1)	0.0320(9)	0.0354(9)	0.049(1)	0.0115(7)	0.0129(7)	0.0171(7)
N(1)	2*i*	1.0187(3)	0.4985(3)	0.1734(2)	0.036(1)	0.034(1)	0.039(1)	0.0141(9)	0.0084(9)	0.0111(9)
C(1)	2*i*	1.2130(3)	0.2659(3)	0.2522(2)	0.031(1)	0.035(1)	0.030(1)	0.013(1)	0.0068(9)	0.0050(9)
C(2)	2*i*	1.0519(3)	0.1573(3)	0.2907(2)	0.025(1)	0.034(1)	0.031(1)	0.0115(9)	0.0038(9)	0.0039(9)
C(3)	2*i*	1.0779(3)	–0.0123(3)	0.3479(2)	0.028(1)	0.032(1)	0.032(1)	0.0058(9)	0.008(1)	0.0037(9)
C(4)	2*i*	1.2636(3)	–0.0671(3)	0.3671(2)	0.032(1)	0.034(1)	0.038(1)	0.012(1)	0.005(1)	0.009(1)
C(5)	2*i*	1.4243(4)	0.0423(3)	0.3282(2)	0.031(1)	0.040(1)	0.044(2)	0.013(1)	0.006(1)	0.009(1)
C(6)	2*i*	1.3983(4)	0.2056(3)	0.2709(2)	0.030(1)	0.036(1)	0.038(1)	0.009(1)	0.012(1)	0.009(1)
C(7)	2*i*	0.9198(4)	–0.2918(3)	0.4325(2)	0.040(1)	0.027(1)	0.043(1)	0.009(1)	0.010(1)	0.010(1)
C(8)	2*i*	0.7105(4)	–0.3766(4)	0.4495(2)	0.041(2)	0.036(1)	0.060(2)	0.006(1)	0.014(1)	0.015(1)
C(9)	2*i*	1.1857(3)	0.4415(3)	0.1922(2)	0.030(1)	0.036(1)	0.034(1)	0.008(1)	0.008(1)	0.008(1)
C(10)	2*i*	0.9961(4)	0.6763(3)	0.1143(2)	0.042(1)	0.030(1)	0.037(1)	0.015(1)	0.007(1)	0.012(1)
C(11)	2*i*	0.7806(4)	0.7036(3)	0.1005(2)	0.039(1)	0.033(1)	0.044(2)	0.013(1)	0.007(1)	0.012(1)
C(12)	2*i*	0.7395(3)	0.8853(3)	0.0407(2)	0.038(1)	0.030(1)	0.037(1)	0.014(1)	0.005(1)	0.009(1)
C(13)	2*i*	0.5229(4)	0.9082(3)	0.0286(2)	0.040(1)	0.032(1)	0.044(1)	0.013(1)	0.009(1)	0.012(1)

Acknowledgment. This work was supported by Priority Research Centers Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (grant no. 2010-0029626)

References

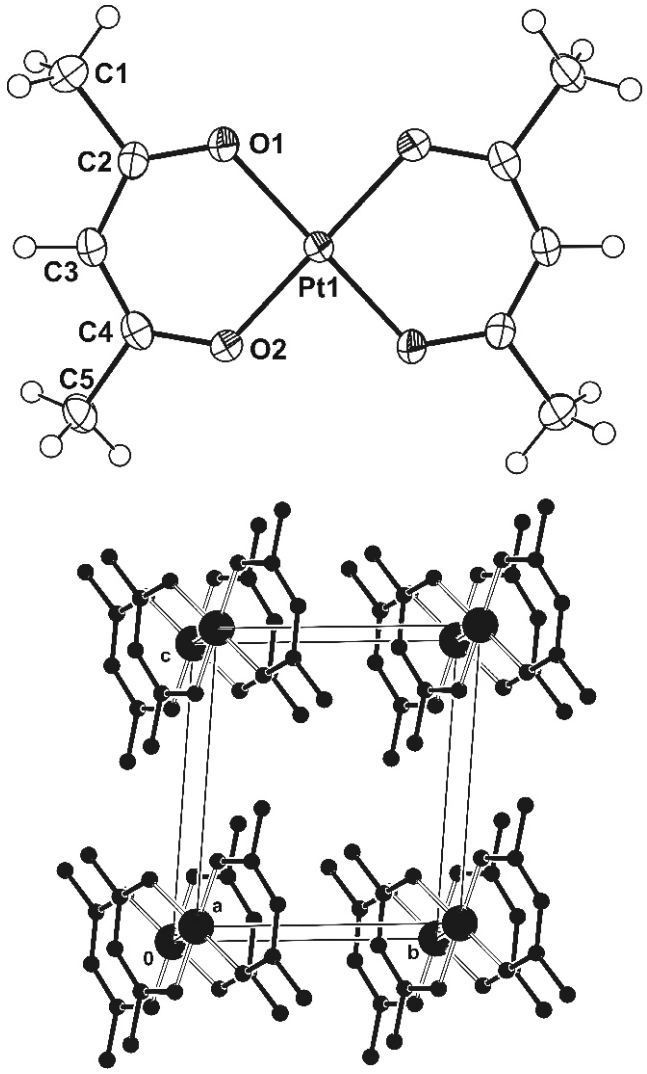
1. Ha, K.: Crystal structure of *N*,*N*′-bis(3-ethoxy-2-hydroxybenzylidene)-propane-1,3-diamine, $C_{21}H_{26}N_2O_4$. Z. Kristallogr. NCS **225** (2010) 737-738.
2. Fun, H.-K.; Kia, R.; Kargar, H.; Jamshidvand, A.: *N*,*N*′-Bis(2-hydroxy-3-ethoxybenzylidene)butane-1,4-diamine. Acta Crystallogr. **E65** (2009) 706.
3. Bermejo, M. R.; Fernández, M. I.; Gómez-Fórneas, E.; González-Noya, A.; Maneiro, M.; Pedrido, R.; Rodríguez, M. J.: Self-assmebly of dimeric Mn^{III}-Schiff-base complexes tuned by perchlorate anions. Eur. J. Inorg. Chem. (2007) 3789-3797.
4. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. **A64** (2008) 112-122.
5. Farrugia, L. J.: ORTEP-3 for Windows - a version of ORTEP-III with a Graphical User Interface (GUI) J. Appl. Crystallogr. **30** (1997) 565.
6. Spek, A. L.: Single-crystal structure validation with the program PLATON. J. Appl. Crystallogr. **36** (2003) 7-13.

Crystal structure of bis(pentane-2,4-dionato-κ^2O,O')platinum(II), $Pt(C_5H_7O_2)_2$

Kwang Ha*

Chonnam National University, School of Applied Chemical Engineering, Research Institute of Catalysis, Gwangju 500-757, Republic of Korea

Received March 5, 2011, accepted and available on-line May 20, 2011; CCDC no. 1267/3425



Abstract

$C_{10}H_{14}O_4Pt$, triclinic, $P\bar{1}$ (no. 2), a = 5.7236(7) Å, b = 7.0751(9) Å, c = 7.942(1) Å, α = 81.001(2)°, β = 70.010(2)°, γ = 66.231(2)°, V = 276.5 Å^3, Z = 1, $R_{gt}(F)$ = 0.029, $wR_{ref}(F^2)$ = 0.070, T = 200 K.

Source of material

The title compound bis(pentane-2,4-dionato-κ^2O,O')platinum(II) was purchased from Aldrich chemicals and used as received. Crystals suitable for X-ray diffraction analysis were obtained by slow evaporation from a mixture of MeOH and CH_3CN solution.

Experimental details

Hydrogen atoms were positioned geometrically and allowed to ride on their parent atoms with d(C—H) = 0.95 Å (CH) or 0.98 Å (CH_3) and U_{iso}(H) = 1.2U_{eq}(C) or 1.5U_{eq}(C_{methyl}). The highest peak (1.79 e·Å^{-3}) and the deepest hole (-1.71 e·Å^{-3}) in the difference Fourier map are located 1.04 Å and 0.99 Å from the Pt1 atom, respectively.

Discussion

In the title complex, the Pt(II) ion is four-coordinated by O atoms from two chelating pentane-2,4-dionate (acetylacetonate, acac) anionic ligands in a slightly distorted square-planar manner (figure, top). The Pt atom is located on an inversion center, and therefore the asymmetric unit contains one half of the complex and the PtO_4 moiety is exactly planar. The O1–Pt1–O2 chelate angle of 96.0(2)° contributes the distortion of square. The Pt—O and O—C bond lengths are almost equivalent (d(Pt—O) = 1.981(5) Å and 1.982(5) Å; d(O—C) = 1.291(9) Å and 1.290(9) Å. On the basis of the bond lengths d(C2—C3) = 1.39(1)Å and d(C3—C4) = 1.38(1) Å, the negative charge of the anionic ligand appears to be delocalized over the five atoms O1, C2, C3, C4 and O2. In the crystal structure, the acac ligand is coordinated to the Pt atom nearly symmetrical, to form a practically planar six-membered ring (Pt1-O2) with a maximum deviation of 0.006(3) Å from least-squares plane. The planar complexes are stacked in columns parallel to the (110) plane (figure, bottom).

Table 1. Data collection and handling.

Crystal:	yellow plate, size 0.07 × 0.13 × 0.30 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	126.76 cm^{-1}
Diffractometer, scan mode:	Bruker SMART 1000 CCD, φ/ω
$2\theta_{max}$:	52.02°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	1691, 1036
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 1035
$N(param)_{refined}$:	72
Programs:	SHELXS-97, SHELXL-97[1], ORTEP-3 [2], PLATON [3]

* e-mail: hakwang@chonnam.ac.kr

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

Atom	Site	*x*	*y*	*z*	U_{iso}
H(1A)	2*i*	0.4226	0.3589	–0.3804	0.055
H(1B)	2*i*	0.6108	0.3484	–0.2667	0.055
H(1C)	2*i*	0.3305	0.5389	–0.2448	0.055
H(3)	2*i*	0.3793	0.3589	0.0726	0.033
H(5A)	2*i*	0.0773	0.1656	0.4815	0.051
H(5B)	2*i*	0.1934	0.3418	0.3940	0.051
H(5C)	2*i*	0.3931	0.1049	0.3875	0.051

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}
Pt(1)	1*a*	0	0	0	0.0293(2)	0.0292(3)	0.0190(2)	–0.0176(2)	–0.0094(1)	0.0023(2)
O(1)	2*i*	0.180(1)	0.1735(8)	–0.1687(6)	0.040(3)	0.025(3)	0.023(2)	–0.019(2)	–0.012(2)	0.000(2)
O(2)	2*i*	0.058(1)	0.0591(8)	0.2152(6)	0.036(2)	0.032(3)	0.023(2)	–0.021(2)	–0.013(2)	0.006(2)
C(1)	2*i*	0.425(2)	0.390(1)	–0.265(1)	0.045(4)	0.045(5)	0.028(4)	–0.029(4)	–0.011(3)	0.007(3)
C(2)	2*i*	0.287(1)	0.275(1)	–0.117(1)	0.030(3)	0.024(4)	0.033(4)	–0.015(3)	–0.013(3)	0.003(3)
C(3)	2*i*	0.291(1)	0.278(1)	0.056(1)	0.035(3)	0.027(4)	0.031(4)	–0.018(3)	–0.014(3)	–0.002(3)
C(4)	2*i*	0.184(1)	0.178(1)	0.207(1)	0.028(3)	0.034(5)	0.027(4)	–0.013(3)	–0.010(3)	–0.007(3)
C(5)	2*i*	0.215(2)	0.199(1)	0.383(1)	0.044(4)	0.046(5)	0.027(4)	–0.028(4)	–0.013(3)	–0.003(3)

Acknowledgment. This work was supported by Priority Research Centers Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (grant no. 2010-0029626).

References

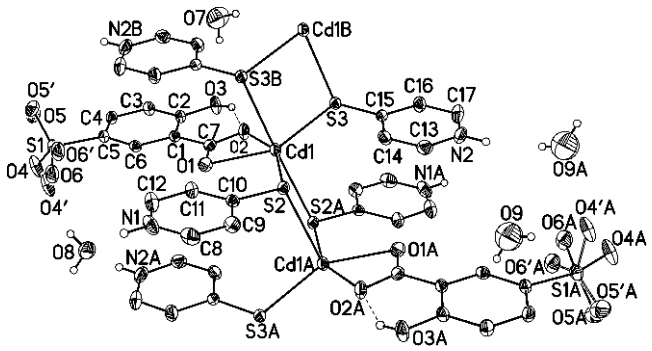
1. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. **A64** (2008) 112-122.
2. Farrugia, L. J.: ORTEP-3 for Windows - a version of ORTEP-III with a Graphical User Interface (GUI) J. Appl. Crystallogr. **30** (1997) 565.
3. Spek, A. L.: Single-crystal structure validation with the program PLATON. J. Appl. Crystallogr. **36** (2003) 7-13.

Crystal structure of *catena*-[(5-sulfosalicylato-κ^2O,O')-bis(μ_2-4-thiolatopyridinium-κ^2S:S)cadmium(II)] hydrate, $Cd(C_7H_4O_6S)(C_5H_5NS)_2 \cdot 2.5H_2O$

Jun-Xia Li* and Zhong-Xiang Du

Luoyang Normal University, College of Chemistry and Chemical Engineering, Luoyang 471022, Henan, P. R. China

Received October 13, 2010, in revised form November 22, 2010, accepted and available on-line May 21, 2011; CCDC no. 1267/3240



Abstract

$C_{17}H_{19}CdN_2O_{8.5}S_3$, triclinic, $P\bar{1}$ (no. 2), a = 7.3730(7) Å, b = 9.920(1) Å, c = 15.228(2) Å, α = 79.474(1)°, β = 89.189(1)°, γ = 81.344(1)°, V = 1082.4 Å^3, Z = 2, $R_{gt}(F)$ = 0.027, $wR_{ref}(F^2)$ = 0.077, T = 294 K.

Source of material

$Cd(CH_3COO)_2 \cdot 2H_2O$ (0.5 mmol, 0.133 g), 5-sulfosalicylic acid (H_3ssa, 0.5 mmol, 0.109 g) and pyridine-4-thiol (HSpy, 1.0 mmol, 0.111 g) were dissolved in 20 mL H_2O. Then the mixed solution was sealed in a 25 mL Teflon-lined reactor and kept under autogeneous pressure at 403 K for 5 days. After cooling to room temperature at a rate of 279 K/h, colourless needle-like crystals of the title compound suitable for X-ray diffraction were obtained and collected (yield 108 mg, 36 %, based on Cd).

Experimental details

We refined the O9 atom, but the residual values were not reduced by splitting it into two positions.

Discussion

In recent years, pyridine-4-thiol has aroused more and more attention in coordination chemistry, not only because it is a better bridging ligand in preparing structurally novel coordination compounds, but also because its compounds display potential application as anticancer [1], chemical switches [2], non-linear optical [3], or luminescence material [4,5].

The crystal structure of the title compound is comprised of $Cd(C_7H_4O_6S)(C_5H_5NS)_2$ complex and lattice water in a ratio 1 : 3. The Cd(II) center is six-coordinated in an elongated CdO_2S_4 octahedral configuration formed by two carboxylate O atoms (O1, O2) of one bidentate chelate 5-sulfosalicylate dianion (Hssa) and four S atoms (S2, S3, S2A, S3B) of four different 4-thiolatopyridinium (SpyH) (symmetry codes A: 1–x,–y,1–z; B: 2–x,–y, 1–z). The S2A, S3B atoms occupy the axial positions, while the O1, O2, S2, S3 atoms define the equatorial plane. The Cd(II) ion deviates from the equatorial least-squares plane O1/O2/S2/S3 by about 0.090 Å towards S2A. The N atoms of HSpy are protonated and thus forms SpyH ligands. Each SpyH ligand acts as a μ_2-bridging one, interlinking two adjacent Cd(II) ions. Thus a Cd_2S_2 parallelogram is formed between face-to-face arranged Cd(II) ions and SpyH ligands. The dihedral angle between the neighbouring parallelograms is 62.5°. Through the μ_2-bridging function of SpyH ligands a zigzag chain of the title complexes forms along [100]. The neighbouring Cd···Cd distances are 4.097 Å (Cd1···Cd1A) and 3.916 Å (Cd1A···Cd1B), respectively. The central Cd(II) ion is octahedrally coordinated. This is quite different from the two other Cd(II) compounds of SpyH [6], because the Cd(II) center ions of the latter adopt distorted tetrahedral coordination. In addition, the sulfo group of Hssa ligand displays positional disorder [occupancy 0.834(4):0.166(4)]. The partly deprotonated Hssa ligand forms intramolecular O–H···O hydrogen bonds. Together with the intermolecular O–H···O, O–H···S, N–H···O and N–H···S hydrogen bonding interactions among lattice water, Hssa dianion and SpyH ligands, the zigzag chain structure is stabilized and further interconnected to a three-dimensional supramolecular framework.

Table 1. Data collection and handling.

Crystal:	colorless needle, size 0.19 × 0.21 × 0.25 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	13.52 cm^{-1}
Diffractometer, scan mode:	Bruker APEX II CCD, φ/ω
$2\theta_{max}$:	51°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	8292, 3988
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 3674
$N(param)_{refined}$:	288
Programs:	SHELXS-97, SHELXL-97, SHELXTL [7]

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

Atom	Site	Occ.	x	y	z	U_{iso}
H(3)	2*i*		0.9459	0.4194	0.5612	0.077
H(1)	2*i*		0.4644	–0.3767	0.8963	0.065
H(2)	2*i*		0.7332	–0.1685	0.1406	0.062
H(3A)	2*i*		1.0185	0.6010	0.7150	0.046
H(4)	2*i*		0.9629	0.5387	0.8651	0.043
H(6)	2*i*		0.7306	0.2184	0.8159	0.037
H(8)	2*i*		0.3845	–0.4840	0.7906	0.062
H(9)	2*i*		0.4363	–0.3942	0.6444	0.051

* Correspondence author (e-mail: ljx6281@126.com)

Table 2. Continued.

Atom	Site	Occ.	*x*	*y*	*z*	U_{iso}
H(11)	2*i*		0.6606	–0.0923	0.7273	0.048
H(12)	2*i*		0.6015	–0.1886	0.8719	0.064
H(13)	2*i*		0.6612	–0.2428	0.2814	0.057
H(14)	2*i*		0.7441	–0.1309	0.3898	0.048
H(16)	2*i*		0.9701	0.1282	0.1996	0.053
H(17)	2*i*		0.8861	0.0080	0.0961	0.064

Table 2. Continued.

Atom	Site	Occ.	*x*	*y*	*z*	U_{iso}
H(1W)	2*i*		1.3835	0.3622	0.5444	0.173
H(2W)	2*i*		1.2716	0.4714	0.5698	0.173
H(3W)	2*i*		0.4158	0.2656	0.9495	0.107
H(4W)	2*i*		0.2447	0.3416	0.9418	0.107
H(6W)	2*i*	0.50	0.3081	–0.0161	0.0263	0.246
H(5W)	2*i*	0.50	0.2133	0.0573	0.0838	0.246

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}
Cd(1)	2*i*		0.74405(3)	0.05794(2)	0.52931(1)	0.0367(1)	0.0411(1)	0.0281(1)	–0.0157(1)	0.00562(9)	–0.01231(9)
S(1)	2*i*		0.8097(1)	0.3219(1)	0.97161(5)	0.0442(5)	0.0574(5)	0.0241(4)	–0.0094(4)	0.0037(3)	–0.0027(3)
S(2)	2*i*		0.5910(1)	–0.16612(8)	0.55617(5)	0.0344(4)	0.0383(4)	0.0241(3)	–0.0139(3)	0.0003(3)	–0.0013(3)
S(3)	2*i*		0.9342(1)	0.10583(8)	0.38601(5)	0.0322(4)	0.0363(4)	0.0270(4)	–0.0091(3)	0.0024(3)	–0.0058(3)
O(1)	2*i*		0.6945(3)	0.1409(2)	0.6667(2)	0.044(1)	0.039(1)	0.046(1)	–0.013(1)	0.001(1)	–0.016(1)
O(2)	2*i*		0.8299(3)	0.2690(3)	0.5601(2)	0.061(2)	0.053(1)	0.030(1)	–0.016(1)	0.002(1)	–0.017(1)
O(3)	2*i*		0.9610(4)	0.4809(3)	0.5886(2)	0.083(2)	0.051(1)	0.027(1)	–0.030(1)	0.013(1)	–0.007(1)
O(4)	2*i*	0.834(4)	0.7194(5)	0.4489(3)	1.0024(2)	0.113(3)	0.060(2)	0.039(2)	–0.009(2)	0.031(2)	–0.017(2)
O(5)	2*i*	0.834	0.9870(4)	0.2739(4)	1.0142(2)	0.054(2)	0.128(4)	0.038(2)	–0.010(2)	–0.012(1)	0.017(2)
O(6)	2*i*	0.834	0.6891(4)	0.2196(3)	0.9839(2)	0.076(3)	0.075(2)	0.036(2)	–0.032(2)	0.005(2)	–0.000(2)
O(4')	2*i*	0.166	0.6324(4)	0.3848(3)	0.9838(2)	0.113(3)	0.060(2)	0.039(2)	–0.009(2)	0.031(2)	–0.017(2)
O(6')	2*i*	0.166	0.7898(5)	0.1587(3)	0.9723(2)	0.076(3)	0.075(2)	0.036(2)	–0.032(2)	0.005(2)	–0.000(2)
O(5')	2*i*	0.166	0.9590(4)	0.3302(4)	1.0085(2)	0.054(2)	0.128(4)	0.038(2)	–0.010(2)	–0.012(1)	0.017(2)
N(1)	2*i*		0.4868(5)	–0.3426(3)	0.8418(2)	0.066(2)	0.054(2)	0.034(2)	–0.001(2)	0.017(1)	0.008(1)
N(2)	2*i*		0.7659(4)	–0.1255(3)	0.1805(2)	0.050(2)	0.064(2)	0.044(2)	–0.002(2)	–0.014(1)	–0.025(2)
C(1)	2*i*		0.8254(4)	0.3289(3)	0.7043(2)	0.030(1)	0.030(1)	0.028(1)	–0.003(1)	0.001(1)	–0.007(1)
C(2)	2*i*		0.9160(4)	0.4441(3)	0.6747(2)	0.039(2)	0.034(2)	0.025(1)	–0.007(1)	0.003(1)	–0.004(1)
C(3)	2*i*		0.9632(5)	0.5229(3)	0.7352(2)	0.049(2)	0.035(2)	0.034(2)	–0.017(1)	0.005(1)	–0.008(1)
C(4)	2*i*		0.9288(4)	0.4865(3)	0.8249(2)	0.042(2)	0.039(2)	0.031(2)	–0.010(1)	–0.000(1)	–0.012(1)
C(5)	2*i*		0.8425(4)	0.3708(3)	0.8553(2)	0.035(2)	0.039(2)	0.025(1)	–0.005(1)	0.002(1)	–0.007(1)
C(6)	2*i*		0.7901(4)	0.2942(3)	0.7954(2)	0.029(1)	0.030(1)	0.031(2)	–0.006(1)	0.003(1)	–0.002(1)
C(7)	2*i*		0.7777(4)	0.2411(3)	0.6408(2)	0.031(2)	0.034(2)	0.036(2)	–0.001(1)	–0.003(1)	–0.011(1)
C(8)	2*i*		0.4393(5)	–0.4043(4)	0.7767(3)	0.051(2)	0.044(2)	0.053(2)	–0.011(2)	0.011(2)	0.010(2)
C(9)	2*i*		0.4707(5)	–0.3512(3)	0.6896(2)	0.047(2)	0.037(2)	0.042(2)	–0.014(1)	0.002(2)	0.001(1)
C(10)	2*i*		0.5549(4)	–0.2316(3)	0.6683(2)	0.027(1)	0.031(1)	0.028(1)	–0.002(1)	0.003(1)	0.001(1)
C(11)	2*i*		0.6040(5)	–0.1713(3)	0.7388(2)	0.051(2)	0.038(2)	0.030(2)	–0.006(1)	0.003(1)	–0.004(1)
C(12)	2*i*		0.5687(6)	–0.2286(4)	0.8249(2)	0.073(3)	0.053(2)	0.031(2)	–0.002(2)	0.005(2)	–0.008(2)
C(13)	2*i*		0.7241(5)	–0.1675(4)	0.2659(3)	0.040(2)	0.053(2)	0.056(2)	–0.011(2)	0.004(2)	–0.021(2)
C(14)	2*i*		0.7733(4)	–0.1006(3)	0.3306(2)	0.042(2)	0.046(2)	0.036(2)	–0.014(2)	0.011(1)	–0.013(1)
C(15)	2*i*		0.8680(4)	0.0139(3)	0.3083(2)	0.027(1)	0.038(2)	0.027(1)	–0.001(1)	–0.000(1)	–0.005(1)
C(16)	2*i*		0.9081(5)	0.0530(4)	0.2177(2)	0.052(2)	0.051(2)	0.029(2)	–0.011(2)	0.001(1)	–0.004(1)
C(17)	2*i*		0.8572(6)	–0.0182(4)	0.1558(2)	0.068(2)	0.063(2)	0.029(2)	–0.008(2)	–0.006(2)	–0.009(2)
O(7)	2*i*		1.3750(6)	0.4244(5)	0.5767(3)	0.114(3)	0.098(3)	0.140(4)	–0.003(2)	–0.021(3)	–0.048(3)
O(8)	2*i*		0.3336(4)	0.3092(3)	0.9131(2)	0.066(2)	0.087(2)	0.071(2)	–0.014(2)	–0.003(2)	–0.037(2)
O(9)	2*i*	0.50	0.307(2)	0.046(1)	0.0563(8)	0.165(4)	0.163(4)	0.164(4)	–0.026(1)	0.001(1)	–0.030(1)

Acknowledgments. This work was supported by the National Natural Science Foundation of China (grant no. 20471026) and the Natural Science Foundation of Henan province (grant no. 0311021200).

References

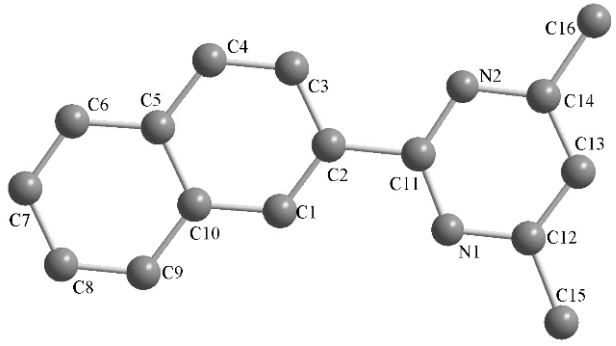
1. Gras, M.; Therrien, B.; Süss-Fink, G; Stepnicka, P.; Renfrew, A. K.; Dyson, P. J.: Water-soluble arene ruthenium complexes containing pyridinethiolato ligands:Synthesis, molecular structure, redox properties and anticancer activity of the cations $[(\eta_6\text{-arene})Ru(p\text{-}SC_5H_4NH)_3]^{2+}$. J. Organomet. Chem. **693** (2008) 3419-3424.
2. Chuchuryukin, A. V.; Chase, P. A.; Mills, A. M.; Lutz, M.; Spek, A. L.; van Klink, G. P. M.; van Koten, G.: Hydroxy- and Mercaptopyridine Pincer Platinum and Palladium Complexes Generated by Silver-Free Halide Abstraction. Inorg. Chem. **45** (2006) 2045-2054.
3. Hao, Z.-M.; Zhang, X.-M.: Phosphorescent Acentric Cuprous Halide Coordination Polymers for Nonlinear Optical Materials. Cryst. Growth Des. **8** (2008) 2359-2363.
4. Wang, J.; Zhang, Y.-H.; Li, H.-X.; Lin, Z.-J.; Tong, M.-L.: Construction of Pyridinethiolate-Bridged 2D and 3D Coordination Networks of d^{10} Metal Halides via Solvothermal *in Situ* Disulfide Cleavage Reactions. Cryst. Growth Des. **7** (2007) 2352-2360.
5. He, Y.-K.; Han, Z.-B.; Ma, Y.; Zhang, X.-D.: Syntheses, crystal structures and luminescence properties of lanthanide coordination polymers involving *in situ* C–S bond cleavage of (4-pyridylthio)acetic acid. Inorg. Chem. Commun. **10** (2007) 829-832.
6. Anjali, K. S.; Vittal, J. J.; Dean, P. A. W.: Syntheses, characterization and thermal properties of $[M(Spy)_2(SpyH)_2]$ (M = Cd and Hg; Spy = pyridine-4-thiolate; SpyH = pyridinium-4-thiolate)) and $[M(SpyH)_4](ClO_4)_2$ (M = Zn, Cd and Hg). Inorg. Chim. Acta **351** (2003) 79-88.
7. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. **A64** (2008) 112-122.

Crystal structure of 2-(2-naphthyl)-4,6-dimethylpyrimidine, $C_{16}H_{14}N_2$

Li-Ming Qiang[I], Jun-Ling Si[II], Xin-Ming Dong[III], Xin-Qi Hao[III], Kui Lu[*,I] and Yu-Fen Zhao[IV]

[I] Henan Institute of Engineering, Department of Material and Chemical Engineering, Zhengzhou 470007, P. R. China
[II] Zhengzhou University of Light Industry, School of Food and Biological Engineering, Zhengzhou 450002, P. R. China
[III] Zhengzhou University, Department of Chemistry, Zhengzhou 450052, P. R. China
[IV] Xiamen University, College of Chemistry and Chemical Engineering, Xiamen 361005, P. R. China

Received January 8, 2011, accepted and available on-line May 20, 2011; CCDC no. 1267/3361



Abstract

$C_{16}H_{14}N_2$, monoclinic, $P12_1/c1$ (no. 14), a = 8.387(1) Å, b = 17.453(3) Å, c = 8.694(1) Å, β = 93.092(2)°, V = 1270.8 Å^3, Z = 4, $R_{gt}(F)$ = 0.046, $wR_{ref}(F^2)$ = 0.129, T = 294 K.

Source of material

The title compound was obtained from the coupling reaction of 2-naphthaleneboronic acid and 2-iodo-4,6-dimethylpyrimidine as described in literature [1] and recrystallized from dichloromethane/petroleum ether solution at room temperature to give the desired crystals suitable for single crystal X-ray diffraction.

Experimental details

All the hydrogen atoms were positioned geometrically with d(C—H) = 0.93 Å, U_{iso}(H) = 1.2 U_{eq}(C) for the aromatic groups and d(C—H) = 0.96 Å, U_{iso}(H) = 1.5 U_{eq}(C) for the methyl groups. The H atoms of the methyl groups in the pyrimidine ring are disordered over two positions with occupation factors fixed at 0.5.

Discussion

Cyclometalated iridium complexes have attracted considerable attention in material research because of their outstanding performance in organic light-emitting diodes (OLED) [2,3]. In recent years, various types of cyclometalated Ir(III) complexes have been developed, such as homoleptic complexes, heteroleptic neutral complexes and cationic complexes [4-6]. In contrast to the most famous substituted phenylpyridine ligands, few examples of naphthalenylpyridine iridium complexes have been reported [7,8].

The pyrimidine ring and naphthalene ring in the crystal structure of the title compound are approximately coplanar with a dihedral angle of 2.4°. There exist two types of intermolecular π-π stacking interactions. One π-π stacking interaction is between the pyrimidine rings (the inter-plane distance is 3.400 Å). The other π-π stacking interaction is between pyrimidine ring and naphthalene ring (the inter-plane distance is 3.748 Å). Both are attributed to construct the layer structure.

Table 1. Data collection and handling.

Crystal:	colorless block, size 0.03 × 0.31 × 0.42 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	0.73 cm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD, φ/ω
$2\theta_{max}$:	51°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	7463, 2367
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 1465
$N(param)_{refined}$:	164
Programs:	SHELXS-97, SHELXL-97, SHELXTL [9]

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

Atom	Site	Occ.	x	y	z	U_{iso}
H(1)	4*e*		0.3477	0.5292	0.6776	0.058
H(3)	4*e*		–0.0869	0.6172	0.5798	0.066
H(4)	4*e*		0.0189	0.7064	0.4241	0.069
H(6)	4*e*		0.2569	0.7642	0.3034	0.074
H(7)	4*e*		0.5251	0.7632	0.2707	0.081
H(8)	4*e*		0.6882	0.6728	0.3957	0.076
H(9)	4*e*		0.5846	0.5857	0.5581	0.066
H(13)	4*e*		–0.1134	0.3600	0.9823	0.070
H(15A)	4*e*	0.50	0.3113	0.3528	0.9412	0.120
H(15B)	4*e*	0.50	0.1751	0.2913	0.9411	0.120
H(15C)	4*e*	0.50	0.2029	0.3466	1.0820	0.120
H(15D)	4*e*	0.50	0.1482	0.3076	1.0350	0.120
H(15E)	4*e*	0.50	0.2844	0.3692	1.0351	0.120
H(15F)	4*e*	0.50	0.2566	0.3138	0.8942	0.120
H(16A)	4*e*	0.50	–0.3891	0.4981	0.8181	0.109
H(16B)	4*e*	0.50	–0.3589	0.4632	0.9832	0.109
H(16C)	4*e*	0.50	–0.3923	0.4091	0.8411	0.109
H(16D)	4*e*	0.50	–0.3711	0.4154	0.9435	0.109
H(16E)	4*e*	0.50	–0.4013	0.4504	0.7784	0.109
H(16F)	4*e*	0.50	–0.3679	0.5045	0.9204	0.109

* Correspondence author (e-mail: lmq06@126.com)

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*	0.2820(2)	0.5648(1)	0.6258(2)	0.045(1)	0.051(1)	0.049(1)	0.0058(8)	–0.0011(9)	–0.0031(9)
C(2)	4*e*	0.1210(2)	0.5624(1)	0.6445(2)	0.042(1)	0.051(1)	0.045(1)	0.0045(8)	0.0020(8)	–0.0076(9)
C(3)	4*e*	0.0225(2)	0.6175(1)	0.5672(2)	0.042(1)	0.061(1)	0.062(1)	0.0081(9)	0.0025(9)	–0.004(1)
C(4)	4*e*	0.0861(2)	0.6710(1)	0.4744(2)	0.052(1)	0.057(1)	0.063(1)	0.0140(9)	–0.002(1)	0.001(1)
C(5)	4*e*	0.2516(2)	0.6742(1)	0.4527(2)	0.054(1)	0.046(1)	0.050(1)	0.0043(9)	0.0003(9)	–0.0070(9)
C(6)	4*e*	0.3211(3)	0.7280(1)	0.3549(2)	0.070(1)	0.052(1)	0.062(1)	0.004(1)	0.003(1)	0.005(1)
C(7)	4*e*	0.4810(3)	0.7274(1)	0.3351(3)	0.073(2)	0.062(1)	0.068(2)	–0.009(1)	0.010(1)	0.007(1)
C(8)	4*e*	0.5793(2)	0.6732(1)	0.4111(2)	0.052(1)	0.069(1)	0.070(1)	–0.009(1)	0.009(1)	–0.003(1)
C(9)	4*e*	0.5174(2)	0.6209(1)	0.5071(2)	0.047(1)	0.059(1)	0.059(1)	–0.0001(9)	0.0013(9)	–0.002(1)
C(10)	4*e*	0.3515(2)	0.6195(1)	0.5306(2)	0.047(1)	0.048(1)	0.046(1)	0.0014(8)	0.0020(9)	–0.0068(9)
C(11)	4*e*	0.0512(2)	0.5032(1)	0.7431(2)	0.043(1)	0.054(1)	0.044(1)	0.0009(9)	0.0017(8)	–0.0110(9)
C(12)	4*e*	0.0910(2)	0.3986(1)	0.8973(2)	0.054(1)	0.056(1)	0.056(1)	–0.0023(9)	0.007(1)	–0.003(1)
C(13)	4*e*	–0.0706(2)	0.3975(1)	0.9207(2)	0.057(1)	0.061(1)	0.058(1)	–0.010(1)	0.009(1)	–0.003(1)
C(14)	4*e*	–0.1669(2)	0.4524(1)	0.8516(2)	0.045(1)	0.069(1)	0.051(1)	–0.008(1)	0.0056(9)	–0.014(1)
C(15)	4*e*	0.2053(3)	0.3423(1)	0.9721(3)	0.070(2)	0.071(1)	0.100(2)	0.008(1)	0.011(1)	0.024(1)
C(16)	4*e*	–0.3426(2)	0.4560(1)	0.8756(3)	0.045(1)	0.095(2)	0.078(2)	–0.007(1)	0.010(1)	–0.007(1)
N(1)	4*e*	0.1527(2)	0.45174(8)	0.8067(2)	0.0465(9)	0.0518(9)	0.056(1)	0.0018(7)	0.0069(8)	–0.0002(8)
N(2)	4*e*	–0.1066(2)	0.50631(9)	0.7609(2)	0.0422(9)	0.065(1)	0.051(1)	–0.0008(7)	0.0038(7)	–0.0089(8)

Acknowledgments. We thank the program for innovation of science and technology talents of Henan Province (grant no. 104200510022), the program for science and technology leaders of Zhengzhou City (grant no. 10LJRC174), the Doctor Foundation (grant no. D09004) and the program for innovative research team of Henan Institute of Engineering (grant no. 2009IRTHNIE05) for financial support.

References

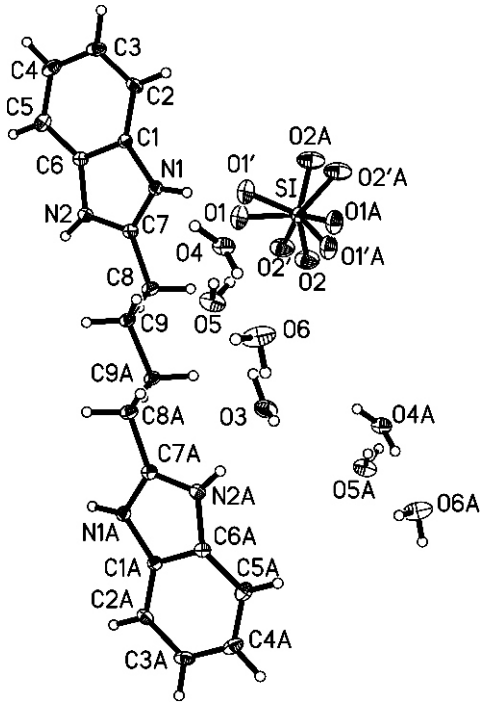
1. Wang, Z. Q.; Xu, C.; Dong, X. M.; Zhang, Y. P.; Hao, X. Q.; Gong, J. F.; Song, M. P.; Ji, B. M.: Synthesis, structure and properties of a novel iridium(III) pyrimidine complex. Inorg. Chem. Commun. **14** (2011) 316-319.
2. Hsu, N. M.; Li, W. R.: Accelerated discovery of red-phosphorescent emitters through combinatorial organometallic synthesis and screening. Angew. Chem., Int. Ed. **45** (2006) 4138-4143.
3. Chen, Z. Q.; Bian, Z. Q.; Huang, C. H.: Functional Ir(III) complexes and their applications. Adv. Mater. **22** (2010) 1534-1536.
4. You, Y.; Park, S. Y.: Inter-ligand energy transfer and related emission change in the cyclometalated heteroleptic iridium complex: facile and efficient color tuning over the whole visible range by the ancillary ligand structure. J. Am. Chem. Soc. **127** (2005) 12438-12439.
5. Huo, S. Q.; Deaton, J. C.; Rajeswaran, M.; Lenhart, W. C.: Highly efficient, selective, and general method for the preparation of meridional homo- and heteroleptic tris-cyclometalated iridium complexes. Inorg. Chem. **45** (2006) 3155-3157.
6. Talarico, A. M.; Aiello, I.; Bellusci, A.; Crispini, A.; Ghedini, M.; Godbert, N.; Pugliese, T.; Szerb, E.: Highly luminescent biscyclometalated iridium(III) ethylenediamine complex: synthesis and correlation between the solid state polymorphism and the photophysical properties. Dalton Trans. (2010) 1709-1712.
7. Yang, C. H.; Chen, C. H.; Sun, I. W.: Bathochromic effect of trifluoromethyl-substituted 2-naphthalen-1-yl-pyridine ligands in color tuning of iridium complexes. Polyhedron **25** (2006) 2407-2414.
8. Zhen, H. Y.; Luo, C.; Yang, W.; Song, W. Y.; Du, B.; Jiang, J. X.; Jiang, C. Y.; Zhang, Y.; Cao, Y.: Electrophosphorescent chelating copolymers based on linkage isomers of naphthylpyridine-iridium complexes with fluorene. Macromolecules **39** (2006) 1693-1700.
9. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. **A64** (2008) 112-122.

Crystal structure of 2,2′-(1,4-butanediyl)bis(3*H*-benzimidazolium) sulfate heptahydrate, $[C_{18}H_{20}N_4][SO_4] \cdot 7H_2O$

Wei-Xing Zhao* and Hong-Bo Jiang

Baoji University of Arts and Science, Department of Chemistry and Chemical Engineering, Baoji 721013, Shaanxi, P. R. China

Received December 26, 2010, accepted and available on-line May 21, 2011; CCDC no. 1267/3348



Abstract

$C_{18}H_{34}N_4O_{11}S$, monoclinic, *C*12/*c*1 (no. 15), a = 11.168(4) Å, b = 13.022(4) Å, c = 17.743(6) Å, β = 100.899(4)°, V = 2533.8 Å^3, Z = 4, $R_{gt}(F)$ = 0.068, $wR_{ref}(F^2)$ = 0.160, T = 143 K.

Source of material

2,2′-(1,4-butanediyl)bis(3*H*-benzimidazole) (87.0 mg, 0.3 mmol) was put in 14 mL (0.05 M) of sulfuric acid aqueous solution, and then was sealed in a 25 mL Teflon-lined stainless steel container, which was heated at 423 K for 72 h. Some colourless block-shaped crystals were obtained after cooled down to room temperature at a rate of 5 K/h and isolated for X-ray diffraction measurement.

Experimental details

All hydrogen atoms bound to carbon atoms were placed in calculated positions and refined in a riding model with d(C—H) = 0.95 Å (Csp^2) or 0.99 Å (Csp^3), and U_{iso}(H) = 1.2 U_{eq}(C). Hydrogen atoms bound to nitrogen and oxygen atoms were found in difference Fourier maps and refined freely. The oxygen atoms of sulfate are disordered over two sites with occupancies of 0.88(1):0.12(1). The disorder of spherical group SO_4^{2-} in the crystal structure is a primary reason for the relatively large R values. The H atoms bound to N1, N2 and O4 were obtained by difference Fourier syntheses. The other H atoms are set in theoretical positions. No additional solvent molecule was found.

Discussion

Organic ligands, especially the bridging ligands containing oxygen and nitrogen have attracted a considerable interest in recent years because of coordination polymers. Bis(2-benzimidazoles) and some substituted bis(2-benzimidazolyl)alkanes are alternative choices because of their multifunctional linking groups [1]. They are known to be strong chelating agents coordinating through both nitrogen atoms [2]. Many complexes based on them have been reported because of their wide-ranging antivirus activity [3], importance in selective ion-exchange resins [4] and mimicking biological systems [5].

The crystal structure of the title compound shows two protons from the one sulfuric acid molecule transferred to the N atoms of two benzimidazoles, respectively. There are six annular structures encircling the S atom in the crystal structure. These annular structures formed mostly by hydrogen bonds between sulfate anion and water molecules. Each sulfate anion is linked by these rings, and forms a reticular inorganic layer in (001). On the other hand, 2,2′-(1,4-butanediyl)bis(3*H*-benzimidazolium) is fixed in the inorganic layer by hydrogen bonds with d(N1–H1N···O1) = 2.67 Å, ∠N1–H1N···O1 = 165.8°; d(N2A–H2N···O3) = 2.75 Å, and ∠N2A–H2N···O3 = 168.3°, respectively. The dihedral angle of N1/C1/C6/N2/C7 ring with C1/C2/C3/C4/C5/C6 ring is 1.9(2)°, indicating such rings being almost coplanar. The π-π stacking interactions of the aromatic rings link the organic cations into an organic layer, which is also parallel (001). Organic and inorganic layers are interlacing in the crystal structure.

Table 1. Data collection and handling.

Crystal:	colorless block, size 0.17 × 0.19 × 0.21 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	1.89 cm^{-1}
Diffractometer, scan mode:	AFC10/Saturn724+, φ/ω
$2\theta_{max}$:	54.92°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	9790, 2884
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2184
$N(param)_{refined}$:	174
Programs:	SHELXS-97, SHELXL-97 [7]

* Correspondence author (e-mail: wenpuhong@gmail.com)

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

Atom	Site	*x*	*y*	*z*	U_{iso}
H(2)	8*f*	0.8365	0.6419	0.6267	0.031
H(3)	8*f*	0.9881	0.6141	0.5538	0.036
H(4)	8*f*	0.9380	0.5898	0.4219	0.038
H(5)	8*f*	0.7348	0.5882	0.3568	0.032
H(8A)	8*f*	0.3522	0.6120	0.5564	0.029
H(8B)	8*f*	0.3153	0.5929	0.4658	0.029
H(9A)	8*f*	0.3670	0.7931	0.5320	0.026
H(9B)	8*f*	0.3211	0.7714	0.4423	0.026
H(3A)	8*f*	–0.3788	0.4505	0.7180	0.042
H(3B)	8*f*	–0.2914	0.3928	0.6924	0.042
H(5A)	8*f*	–0.0897	0.4342	0.6898	0.049
H(5B)	8*f*	–0.1057	0.3298	0.6806	0.049
H(6A)	8*f*	0.2351	0.6545	0.7135	0.065
H(6B)	8*f*	0.1515	0.7327	0.7140	0.065
H(1N)	8*f*	0.572(3)	0.657(3)	0.608(2)	0.05(1)
H(2N)	8*f*	0.494(3)	0.607(3)	0.394(2)	0.031(9)
H(4A)	8*f*	0.050(2)	0.578(1)	0.732(2)	0.04(1)

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)	8*f*		0.5869(2)	0.6396(2)	0.5599(1)	0.021(1)	0.020(1)	0.022(1)	–0.0001(9)	0.0053(9)	0.0007(9)
N(2)	8*f*		0.5388(2)	0.6146(2)	0.4366(1)	0.022(1)	0.020(1)	0.022(1)	–0.0023(9)	0.001(1)	–0.0029(9)
C(1)	8*f*		0.6962(2)	0.6298(2)	0.5340(2)	0.020(1)	0.015(1)	0.025(1)	0.002(1)	0.006(1)	0.003(1)
C(2)	8*f*		0.8162(3)	0.6308(2)	0.5729(2)	0.024(1)	0.022(1)	0.027(1)	0.000(1)	–0.003(1)	0.006(1)
C(3)	8*f*		0.9048(3)	0.6148(2)	0.5293(2)	0.019(1)	0.021(1)	0.050(2)	0.003(1)	0.004(1)	0.007(1)
C(4)	8*f*		0.8744(3)	0.5997(2)	0.4499(2)	0.026(2)	0.024(1)	0.049(2)	0.003(1)	0.018(1)	–0.001(1)
C(5)	8*f*		0.7549(3)	0.5986(2)	0.4107(2)	0.032(2)	0.023(1)	0.029(2)	–0.002(1)	0.012(1)	–0.007(1)
C(6)	8*f*		0.6656(2)	0.6138(2)	0.4550(2)	0.020(1)	0.016(1)	0.025(1)	–0.000(1)	0.003(1)	–0.002(1)
C(7)	8*f*		0.4951(2)	0.6301(2)	0.5006(2)	0.021(1)	0.014(1)	0.028(1)	–0.001(1)	0.004(1)	0.001(1)
C(8)	8*f*		0.3635(2)	0.6374(2)	0.5056(2)	0.020(1)	0.020(1)	0.034(2)	–0.000(1)	0.006(1)	0.000(1)
C(9)	8*f*		0.3159(2)	0.7474(2)	0.4945(2)	0.018(1)	0.019(1)	0.029(1)	–0.003(1)	0.006(1)	0.001(1)
S(1)	4*e*		½	0.63841(8)	¾	0.0231(5)	0.0318(6)	0.0220(5)	0	0.0070(4)	0
O(1)	8*f*	0.88(1)	0.5141(5)	0.7080(2)	0.6861(2)	0.054(3)	0.035(1)	0.033(2)	–0.005(1)	0.017(2)	–0.002(1)
O(2)	8*f*	0.88	0.3910(3)	0.5757(2)	0.7259(3)	0.033(2)	0.041(2)	0.068(3)	–0.011(1)	0.001(2)	0.010(2)
O(1')	8*f*	0.12	0.567(2)	0.7051(4)	0.705(1)	0.054(3)	0.035(1)	0.033(2)	–0.005(1)	0.017(2)	–0.002(1)
O(2')	8*f*	0.12	0.421(2)	0.5702(4)	0.695(1)	0.033(2)	0.041(2)	0.068(3)	–0.011(1)	0.001(2)	0.010(2)
O(3)	8*f*		–0.3656(2)	0.3958(2)	0.6957(1)	0.030(1)	0.035(1)	0.037(1)	0.0022(9)	–0.0035(9)	–0.009(1)
O(4)	4*e*		0	0.5414(2)	¾	0.025(2)	0.027(2)	0.041(2)	0	0.002(1)	0
O(5)	8*f*		–0.1353(2)	0.3879(2)	0.6664(1)	0.036(1)	0.030(1)	0.051(1)	0.002(1)	–0.005(1)	–0.008(1)
O(6)	8*f*		0.1613(2)	0.6708(2)	0.7034(2)	0.030(1)	0.043(2)	0.089(2)	0.001(1)	0.013(1)	0.017(1)

Acknowledgments. This work was supported by Science and Technology Foundation of the Shaanxi Key Laboratory (grant no. 2003JS018), Scientific Research Project (no. 2011JM2009) from Science and Technology Department of Shaanxi Province and Key Research Project (grant no. ZK1051, ZK1035) from Baoji University of Arts and Sciences.

References

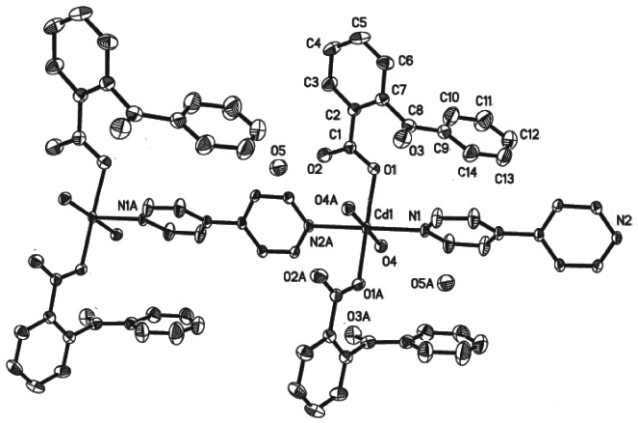
1. Koolhaas, G. J. A. A.; Berkel, P. M.; Slot, S. C.; Mendoza-Diaz, G.; Driessen, W. L.; Reedijk, J.: Copper(II) coordination Compounds with bis(imidazol-2-yl)methylamine and bis(imidazol-2-yl)methylaminomethane in relation to bis(imidazol-2-yl)methylamine-modified poly(glycidyl methacrylate)polymers and other bis(imidazol-2-yl)-containing ligands. Inorg. Chem. **35** (1996) 3525-3532.
2. Sun, T.; Ke, L.; Yulin, L.: Aqua[1,3-bis(benzimidazol-2-yl)-2-oxapropane]diethanolmanganese(II) dipicrate ethanol disolvate. Acta Crystallogr. **E66** (2010) m1058-1059.
3. Salunke, N. M.; Revankar, V. K.; Mahale, V. B.: Oxomolybdenum(V) complexes of bis-(2-benzimidazolyl)alkanes. Transit. Metal Chem. **19** (1994) 53-56.
4. Hoorn, H. J.; Joode, P.; Dijkstra, D. J.; Driessen, W. L.; Kooijman, H.; Veldman, N.; Spek, A. L.; Reedijk, J.: Metal-binding affinity of a series of bis-benzimidazoles immobilised on silica. J. Mater. Chem. **7** (1997) 1747-1754.
5. Bouwman, E.; Driessen, W. L.; Reedijk, J.: Model systems for type I copper proteins: structures of copper coordination compounds with thioether and azole-containing ligands. Coord. Chem. Rev. **104** (1990) 143-172.
6. Aghabozorg, H.; Manteghi, F.; Sheshmani, S.: A brief review on structural concepts of novel supramolecular proton transfer compounds and their metal complexes. J. Iran. Chem. Soc. **5** (2008) 184-227.
7. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. **A64** (2008) 112-122.

Crystal structure of diaqua(4,4′-bipyridine-*N*,*N*′)-bis(2-benzoylbenzoato)-cadmium(II) dihydrate, $Cd(C_{14}H_9O_3)_2(C_{10}H_8N_2)(H_2O)_2 \cdot 2H_2O$

Zhi-Min Chen*, Ying-Qun Yang, Jian-Ling Zou, Dai-Zhi Kuang, Fu-Xing Zhang, Jian-Qiu Wang and Man-Sheng Chen

Department of Chemistry and Materials Science, Hengyang Normal University, Hengyang 421008, P. R. China

Received March 22, 2011, accepted and available on-line June 16, 2011; CCDC no. 1267/3469



Abstract

$C_{38}H_{34}CdN_2O_{10}$, monoclinic, *P*12/*c*1 (no. 13), *a* = 12.923(3) Å, *b* = 11.651(2) Å, *c* = 13.133(3) Å, β = 115.88(3)°, *V* = 1779.1 Å^3, *Z* = 2, $R_{gt}(F)$ = 0.032, $wR_{ref}(F^2)$ = 0.079, *T* = 293 K.

Source of material

A mixture of 2-benzoylbenzoic acid (2.03 mmol), 4,4′-bipyridine (1.21 mmol) and cadmium acetate (1.00 mmol) was dissolved in the mixed solvent of ethanol (10 ml) and *N*,*N*-dimethylformamide (1 ml). The reaction was kept at 343 K for 6 h. Afterwards the system was filtrated, and the filtrate was allowed to stand at room temperature. Slow evaporation for three days afforded a few pale-yellow grain-shaped single crystals suitable for X-ray diffraction analysis.

Experimental details

Hydrogen atoms bound to carbon atoms were positioned geometrically with *d*(C—H) = 0.93 Å and refined as riding, with U_{iso}(H) = 1.2 U_{eq}(C).

Discussion

4,4′-bipyridine is an excellent bridging ligand, it coordinates most transitional metals via N atom to produce a series of complexes possessing novel structures [1-5]. 2-Benzoylbenzoic acid is a main raw material of anthraquinone dyes intermediates. It is used to manufacture anthraquinone and 1-aminoanthra- quinone. As ligand, 2-benzoylbenzoic acid can coordinate metal ions to generate complexes.

In the molecule of the title complex, two neighboring Cd(II) ions are linked by 4,4′-bipyridine, forming a chain structure. The Cd(II) ion is coordinated by two aqua oxygen atoms, two oxygen atoms from two 2-benzoylbenzoates and two nitrogen atoms of different 4,4′-bipyridine ligands to form a distorted CdN_2O_4 octahedron, where O1, N1, O1A and N2A are located at the equatorial plane, and O4 and O4A occupy the axial positions. The bond angles of the equatorial plane are ∠O1–Cd1–N1 = 89.30(3)°, ∠N1–Cd1–O1A = 89.30(3)°, ∠O1A–Cd1–N2A = 90.69(3)° and ∠N2A–Cd1–O1 = 90.70(3)°. The angles ∠O–Cd1–O and ∠O–Cd1–N are within the range of 85.14(5)° to 178.61(6)° and 89.16(3)° to 90.84(3)°, respectively. The average lengths are *d*(Cd1—N) = 2.3011 Å. *d*(Cd1—O1) = 2.2686 Å and *d*(Cd1—O4) = 2.3830 Å, which shows that the coordination ability of O4 in water is weaker than that of O1 from 2-benzoylbenzoate. Additionally, there exist O–H···O hydrogen bonding interaction involving the oxygen atoms of 2-benzoylbenzoate ligands and water molecules with the distances in the range of 2.681(2)-2.903(2) Å.

Table 1. Data collection and handling.

Crystal:	yellow grain, size 0.10 × 0.18 × 0.20 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	6.75 cm^{-1}
Diffractometer, scan mode:	Rigaku Saturn CCD area detector, ω/φ
$2\theta_{max}$:	50.04°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	13738, 3142
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2869
$N(param)_{refined}$:	234
Programs:	SHELXS-97, SHELXL-97, SHELXTL [6]

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

Atom	Site	*x*	*y*	*z*	U_{iso}
H(4A)	4*g*	0.5518	0.8176	0.0574	0.051
H(4B)	4*g*	0.4376	0.7904	0.0410	0.051
H(3)	4*g*	0.0817	0.8925	–0.1419	0.065
H(4)	4*g*	–0.1110	0.9210	–0.1937	0.072
H(5)	4*g*	–0.1880	0.8688	–0.0730	0.076
H(6)	4*g*	–0.0733	0.7910	0.1007	0.066
H(10)	4*g*	0.0854	0.5733	0.0778	0.098
H(11)	4*g*	0.1011	0.3802	0.1261	0.132
H(12)	4*g*	0.1813	0.3282	0.3134	0.120
H(13)	4*g*	0.2549	0.4636	0.4515	0.099
H(14)	4*g*	0.2425	0.6562	0.4055	0.082
H(15)	4*g*	0.4718	0.5548	0.3829	0.070
H(16)	4*g*	0.4679	0.3594	0.3853	0.071
H(19)	4*g*	0.6324	0.1841	0.2090	0.042
H(20)	4*g*	0.6310	–0.0112	0.2136	0.042
H(5A)	4*g*	0.7145	0.1077	0.5808	0.080
H(5B)	4*g*	0.6592	0.0114	0.5095	0.080

* Correspondence author (e-mail: czm5191@yahoo.com.cn)

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(1)	2*f*	½	0.77066(1)	¼	0.03489(8)	0.01611(8)	0.03602(8)	0	0.01423(6)	0
O(1)	4*g*	0.3065(1)	0.7683(1)	0.1448(1)	0.0325(6)	0.0483(8)	0.0465(7)	–0.0041(5)	0.0122(5)	0.0129(6)
O(2)	4*g*	0.2898(1)	0.8450(1)	–0.0172(1)	0.0480(6)	0.084(1)	0.0532(7)	0.0071(7)	0.0278(5)	0.0192(7)
O(3)	4*g*	0.1776(1)	0.8323(1)	0.2799(1)	0.082(1)	0.068(1)	0.0396(7)	–0.0041(8)	0.0171(7)	–0.0115(7)
O(4)	4*g*	0.5089(1)	0.7737(1)	0.0726(1)	0.0484(6)	0.0404(7)	0.0470(6)	–0.0004(5)	0.0291(5)	0.0015(5)
N(1)	2*f*	½	0.5742(2)	¼	0.047(1)	0.017(1)	0.047(1)	0	0.0235(8)	0
N(2)	2*f*	½	–0.0308(2)	¼	0.0352(9)	0.020(1)	0.037(1)	0	0.0125(8)	0
C(1)	4*g*	0.2492(1)	0.8121(2)	0.0480(1)	0.0394(8)	0.0336(9)	0.0400(8)	–0.0002(8)	0.0162(7)	0.0016(8)
C(2)	4*g*	0.1231(1)	0.8258(2)	0.0132(1)	0.0388(8)	0.037(1)	0.0332(8)	0.0024(8)	0.0141(7)	–0.0005(7)
C(3)	4*g*	0.0511(2)	0.8723(2)	–0.0921(2)	0.051(1)	0.071(1)	0.0405(9)	0.010(1)	0.0194(8)	0.0100(9)
C(4)	4*g*	–0.0644(2)	0.8890(2)	–0.1236(2)	0.049(1)	0.081(2)	0.040(1)	0.020(1)	0.0104(9)	0.008(1)
C(5)	4*g*	–0.1099(2)	0.8584(2)	–0.0516(2)	0.0363(9)	0.089(2)	0.055(1)	0.016(1)	0.0115(9)	–0.009(1)
C(6)	4*g*	–0.0411(2)	0.8121(2)	0.0525(2)	0.0427(9)	0.076(2)	0.049(1)	–0.001(1)	0.0236(8)	–0.005(1)
C(7)	4*g*	0.0756(1)	0.7967(2)	0.0863(1)	0.0389(8)	0.038(1)	0.0357(8)	–0.0012(8)	0.0135(7)	–0.0050(7)
C(8)	4*g*	0.1459(2)	0.7587(2)	0.2067(2)	0.0414(9)	0.055(1)	0.0369(9)	–0.0057(8)	0.0183(7)	–0.0028(8)
C(9)	4*g*	0.1598(2)	0.6346(2)	0.2357(2)	0.0429(9)	0.059(1)	0.047(1)	–0.0030(9)	0.0184(8)	0.0091(9)
C(10)	4*g*	0.1193(2)	0.5519(2)	0.1536(2)	0.098(2)	0.056(2)	0.061(1)	–0.010(1)	0.007(1)	0.006(1)
C(11)	4*g*	0.1282(3)	0.4360(2)	0.1823(3)	0.124(2)	0.054(2)	0.104(2)	–0.016(2)	0.007(2)	0.006(2)
C(12)	4*g*	0.1772(2)	0.4053(3)	0.2937(3)	0.087(2)	0.071(2)	0.124(2)	–0.003(2)	0.028(2)	0.043(2)
C(13)	4*g*	0.2201(2)	0.4860(2)	0.3759(2)	0.080(2)	0.093(2)	0.076(1)	0.017(1)	0.036(1)	0.041(1)
C(14)	4*g*	0.2125(2)	0.6012(2)	0.3487(2)	0.070(1)	0.083(2)	0.054(1)	0.010(1)	0.030(1)	0.017(1)
C(15)	4*g*	0.4831(2)	0.5147(2)	0.3274(2)	0.098(1)	0.028(1)	0.066(1)	–0.0003(9)	0.051(1)	–0.0049(8)
C(16)	4*g*	0.4815(2)	0.3971(2)	0.3299(2)	0.102(1)	0.029(1)	0.064(1)	–0.004(1)	0.051(1)	0.0006(8)
C(17)	2*f*	½	0.3348(2)	¼	0.040(1)	0.019(1)	0.038(1)	0	0.0155(9)	0
C(18)	2*f*	½	0.2079(2)	¼	0.035(1)	0.019(1)	0.030(1)	0	0.0094(9)	0
C(19)	4*g*	0.5787(1)	0.1460(1)	0.2261(1)	0.0397(8)	0.0231(8)	0.0470(9)	–0.0038(7)	0.0227(7)	0.0003(7)
C(20)	4*g*	0.5767(1)	0.0290(1)	0.2281(1)	0.0380(7)	0.0247(9)	0.0453(9)	0.0024(7)	0.0216(7)	–0.0026(7)
O(5)	4*g*	0.6572(1)	0.0866(1)	0.5208(1)	0.0564(8)	0.084(1)	0.0560(8)	–0.0001(8)	0.0208(6)	–0.0222(8)

Acknowledgments. This work was supported by Hengyang Bureau of Science & Technology (grant no. 2009KJ26) and the Construct Program of the Key Disciplines in Hunan Province.

References

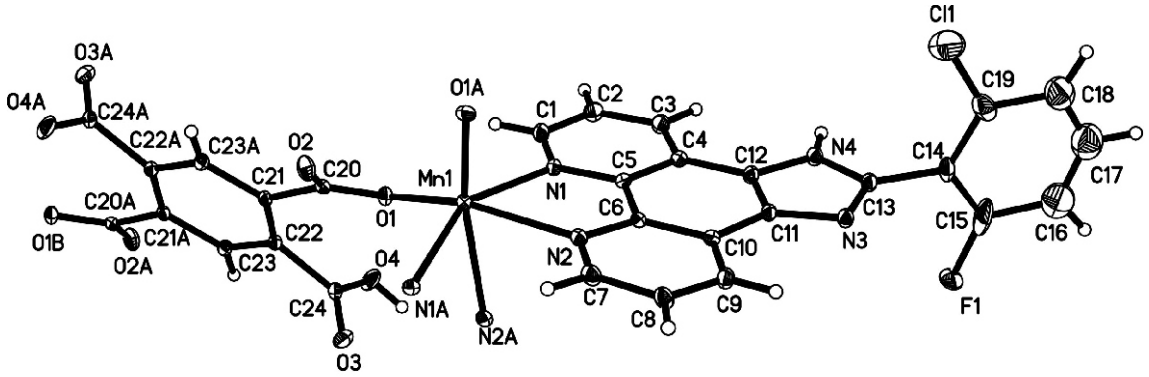
1. Li, X. L.: Crystal structure of triaqua-bis(4,4′-bipyridine)-(3-carboxybenzenesulfonylglycinato) cobalt(II) monohydrate, $[Co(H_2O)_3(C_{10}H_8N_2)_2(C_9H_7NO_6S)] \cdot H_2O$. Z. Kristallogr. NCS **224** (2009) 402-404.
2. Feng, X.; Shi, X. G.; Ruan, F.: Crystal structure of bis(*μ*-4,4′-bipyridyl-*N*,*N*′)-tetrakis(cyanoaceto)-dimanganese(II) tetrahydrate, $Mn_2(C_3H_2NO_2)_4(C_{10}H_8N_2)_2 \cdot 4H_2O$. Z. Kristallogr. NCS **224** (2009) 193-194.
3. Zheng, Y. Q.; Lin, J. L.; Jiang, J. Y.: Crystal structure of tetraaqua(*μ*-4,4′-bipyridine-*N*,*N*′)zinc(II) succinate tetrahydrate, $Zn(H_2O)_4(C_{10}H_8N_2)(C_4H_4O_4) \cdot 4H_2O$. Z. Kristallogr. NCS **218** (2003) 229-230.
4. Feng, X.; Wang, Y. F.; Wang, L.Y.: Crystal structure of (*μ*-4,4′-bipyridyl-*N*,*N*′)bis(*N*,*N*′-ethylene-bis(salicylaldiminato))dizinc(II) methanol disolvate, $Zn_2(C_{10}H_8N_2)(C_{16}H_{14}N_2O_2)_2 \cdot 2CH_3OH$. Z. Kristallogr. NCS **221** (2006) 460-462.
5. Feng, X.; Li, H.; Han, M. L.; Hu, S. Q.: Crystal structure of diaqua-((*μ*-4,4′-bipyridine)-bis(*N*-salicylideneaspartato)-dicopper(II), $Cu_2(H_2O)_2(C_{11}H_9NO_5)_2(C_{10}H_8N_2)$. Z. Kristallogr. NCS **222** (2007) 129-130.
6. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. **A64** (2008) 112-122.

Crystal structure of [bis[(2-(2-chloro-6-fluorophenyl)-1*H*-imidazo-[4,5-*f*][1,10]phenanthroline-κ^2N,N')]manganese(II) benzene-1,4-dicarboxylato-2,5-dicarboxylic acid], $[Mn(C_{19}H_{10}N_4FCl)_2(C_{10}H_4O_4)]$

Zhi-Guo Kong[*, I, II], Xiao-Yuan Ma[I, II] and Shuai Ma[I, II]

[I] Jilin Normal University, College of Chemistry, Siping 136000, P. R. China
[II] Key Laboratory of Preparation and Applications of Environmental Friendly Materials, Jilin Normal University, Siping 136000, P. R. China

Received February 3, 2011, accepted and available on-line June 16, 2011; CCDC no. 1267/3389



Abstract

$C_{48}H_{24}Cl_2F_2MnN_8O_8$, monoclinic, *C*12/*c*1 (no. 15), a = 18.878(5) Å, b = 13.481(5) Å, c = 19.633(5) Å, β = 121.659(5)°, V = 4253.0 Å^3, Z = 4, $R_{gt}(F)$ = 0.065, $wR_{ref}(F^2)$ = 0.183, T = 293 K.

Source of material

The pH value of a mixture of $MnCl_2 \cdot 4H_2O$ (0.5 mmol), benzene-1,2,4,5-tetracarboxylic acid (H_4btc, 0.5 mmol) and 2-(2-chloro-6-fluorophenyl)-1*H*-imidazo[4,5-*f*][1,10]phenanthroline (L, 0.5 mmol) in 12 mL distilled water was adjusted to between 5 and 6 by addition of triethylamine. The resultant solution was heated at 460 K in a Teflon-lined stainless steel autoclave for five days. The reaction system was then slowly cooled to room temperature. Pale yellow crystals suitable for single crystal X-ray diffraction analysis were collected from the final reaction system by filtration, washed several times with distilled water and dried in air at ambient temperature (yield 46 % based on Mn(II)).

Experimental details

All H atoms were positioned geometrically with d(C—H) = 0.93 Å and refined as riding, with U_{iso}(H) = 1.2 U_{eq}(carrier).

Discussion

2-(2-Chloro-6-fluorophenyl)-1*H*-imidazo[4,5-*f*][1,10]phenanthroline (L) as an important 1,10-phenanthroline derivative possesses aromatic systems and is a good candidate for the construction of metal-organic supramolecular architectures [1]. Here, we selected H_4btc as an organic linker and L as a N-chelating ligand, generating a new Mn(II) coordination polymer.

Each Mn(II) atom shows a distorted octahedral coordination sphere, formed by four nitrogen atoms from different ligands L, and two carboxylate oxygen atoms from different H_2btc dianions. The dianions link two neighboring Mn(II) atoms to a chain structure. The large conjugated ligands L are attached on opposite sides of the chains. The π-π stacking interactions as well as the N–H···O and O–H···N hydrogen bonds further stabilize the crystal structure.

* Correspondence author (e-mail: kongzhiguo1977@yahoo.com.cn)

Table 1. Data collection and handling.

Crystal:	pale yellow block size 0.20 × 0.22 × 0.28 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	5.14 cm^{-1}
Diffractometer, scan mode:	Oxford Diffraction Gemini R Ultra, ω
$2\theta_{max}$:	61.48°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	9548, 4945
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2568
$N(param)_{refined}$:	285
Programs:	SHELXS-97, SHELXL-97, SHELXTL [2]

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

Atom	Site	x	y	z	U_{iso}
H(1)	8*f*	0.3202	0.3223	0.1907	0.039
H(2)	8*f*	0.1871	0.2791	0.0967	0.045
H(3)	8*f*	0.1651	0.1514	0.0105	0.043
H(7)	8*f*	0.6207	0.1023	0.2178	0.042
H(8)	8*f*	0.6163	–0.0323	0.1445	0.043
H(9)	8*f*	0.4911	–0.0921	0.0463	0.040
H(16)	8*f*	0.0784	–0.3316	–0.2358	0.132
H(17)	8*f*	0.0596	–0.2677	–0.3469	0.130
H(18)	8*f*	0.1139	–0.1327	–0.3609	0.109
H(23)	8*f*	0.4395	0.4155	0.5617	0.031
H(4A)	8*f*	0.3699	0.2156	0.4320	0.071
H(4)	8*f*	0.1658	0.0110	–0.0837	0.038

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)	8*f*	0.3102(2)	0.2697(3)	0.1561(2)	0.035(2)	0.029(2)	0.029(2)	0.004(2)	0.013(2)	–0.006(2)
C(2)	8*f*	0.2319(3)	0.2451(3)	0.1006(3)	0.033(2)	0.035(2)	0.041(2)	0.011(2)	0.017(2)	–0.002(2)
C(3)	8*f*	0.2195(3)	0.1684(3)	0.0494(3)	0.028(2)	0.033(2)	0.036(2)	0.003(2)	0.009(2)	–0.003(2)
C(4)	8*f*	0.2848(1)	0.1145(2)	0.0531(1)	0.027(2)	0.025(2)	0.025(2)	0.001(2)	0.011(2)	–0.000(2)
C(5)	8*f*	0.3619(1)	0.1427(2)	0.1112(1)	0.028(2)	0.020(2)	0.023(2)	0.001(2)	0.011(2)	0.001(2)
C(6)	8*f*	0.4321(1)	0.0899(2)	0.1182(1)	0.023(2)	0.022(2)	0.020(2)	–0.001(2)	0.005(2)	0.000(2)
C(10)	8*f*	0.4250(1)	0.0092(2)	0.0687(1)	0.027(2)	0.024(2)	0.023(2)	0.002(2)	0.008(2)	0.002(2)
C(11)	8*f*	0.3469(1)	–0.0176(2)	0.0089(1)	0.024(2)	0.023(2)	0.024(2)	0.002(2)	0.007(2)	–0.003(2)
C(12)	8*f*	0.2809(1)	0.0338(2)	0.0019(1)	0.025(2)	0.026(2)	0.027(2)	0.000(2)	0.008(2)	–0.004(2)
C(7)	8*f*	0.5685(2)	0.0783(3)	0.1794(2)	0.024(2)	0.041(2)	0.031(2)	0.002(2)	0.007(2)	–0.002(2)
C(8)	8*f*	0.5669(3)	–0.0035(3)	0.1344(2)	0.027(2)	0.043(2)	0.029(2)	0.007(2)	0.009(2)	–0.005(2)
C(9)	8*f*	0.4952(2)	–0.0386(3)	0.0780(2)	0.029(2)	0.030(2)	0.033(2)	0.002(2)	0.011(2)	–0.008(2)
C(13)	8*f*	0.2462(2)	–0.0782(3)	–0.0919(2)	0.027(2)	0.027(2)	0.027(2)	0.004(2)	0.006(2)	–0.006(2)
C(14)	8*f*	0.1944(2)	–0.1346(2)	–0.1649(2)	0.027(2)	0.043(2)	0.036(2)	0.005(2)	0.005(2)	–0.019(2)
C(15)	8*f*	0.1575(2)	–0.2211(3)	–0.1598(2)	0.044(3)	0.066(4)	0.104(5)	–0.018(3)	0.017(3)	–0.055(4)
C(16)	8*f*	0.1046(3)	–0.2725(3)	–0.2342(3)	0.104(3)	0.103(3)	0.116(3)	–0.001(2)	0.053(2)	–0.010(2)
C(17)	8*f*	0.0947(2)	–0.2324(3)	–0.3004(2)	0.103(3)	0.107(3)	0.107(3)	0.009(2)	0.050(2)	–0.015(2)
C(18)	8*f*	0.1252(3)	–0.1534(4)	–0.3110(2)	0.089(3)	0.097(3)	0.084(3)	0.018(2)	0.044(2)	–0.007(2)
C(19)	8*f*	0.1777(2)	–0.1007(2)	–0.2398(2)	0.042(3)	0.079(4)	0.040(3)	0.022(3)	0.007(2)	–0.004(3)
C(20)	8*f*	0.5163(2)	0.4083(3)	0.3679(2)	0.024(2)	0.024(2)	0.020(2)	0.002(2)	0.006(2)	0.002(2)
C(21)	8*f*	0.5089(2)	0.4535(2)	0.4373(2)	0.021(2)	0.023(2)	0.020(2)	–0.000(2)	0.005(2)	–0.003(2)
C(22)	8*f*	0.4724(2)	0.4037(2)	0.4771(2)	0.023(2)	0.021(2)	0.023(2)	–0.001(2)	0.008(2)	–0.002(2)
C(23)	8*f*	0.4638(2)	0.4504(2)	0.5383(2)	0.027(2)	0.024(2)	0.025(2)	–0.007(2)	0.012(2)	–0.001(2)
C(24)	8*f*	0.4530(3)	0.2946(3)	0.4642(2)	0.032(2)	0.026(2)	0.023(2)	–0.005(2)	0.011(2)	–0.005(2)
O(1)	8*f*	0.4655(2)	0.3433(2)	0.3274(2)	0.032(2)	0.028(1)	0.026(1)	–0.008(1)	0.011(1)	–0.006(1)
O(2)	8*f*	0.5719(2)	0.4349(2)	0.3539(2)	0.027(2)	0.053(2)	0.034(2)	–0.011(1)	0.015(1)	–0.012(1)
O(3)	8*f*	0.5052(2)	0.2335(2)	0.4833(2)	0.045(2)	0.026(2)	0.048(2)	–0.002(1)	0.021(2)	0.002(1)
O(4)	8*f*	0.3776(2)	0.2757(2)	0.4381(2)	0.036(2)	0.027(2)	0.069(2)	–0.012(1)	0.021(2)	–0.005(1)
Mn(1)	4*e*	½	0.26099(6)	¼	0.0250(4)	0.0229(4)	0.0193(4)	0	0.0083(3)	0
N(1)	8*f*	0.3732(2)	0.2194(2)	0.1620(2)	0.029(2)	0.023(2)	0.024(2)	0.001(1)	0.010(1)	–0.004(1)
N(2)	8*f*	0.5035(2)	0.1246(2)	0.1730(2)	0.026(2)	0.028(2)	0.024(2)	0.003(1)	0.007(1)	–0.001(1)
N(3)	8*f*	0.3245(2)	–0.0891(2)	–0.0503(2)	0.025(2)	0.028(2)	0.028(2)	0.004(1)	0.006(1)	–0.006(1)
N(4)	8*f*	0.2171(2)	–0.0057(2)	–0.0629(2)	0.022(2)	0.029(2)	0.030(2)	0.001(1)	0.004(1)	–0.006(1)
Cl(1)	8*f*	0.2160(1)	–0.0021(1)	–0.2524(1)	0.097(1)	0.086(1)	0.102(2)	0.007(1)	0.046(1)	0.018(1)
F(1)	8*f*	0.1672(2)	–0.2635(2)	–0.0862(2)	0.089(2)	0.050(2)	0.036(2)	–0.025(2)	0.028(2)	0.008(1)

Acknowledgment. The authors thank the Key Laboratory of Preparation and Applications of Environmental Friendly Materials and Institute Foundation of Siping City (no. 2009011) for supporting this work.

References

1. Wang, X.-L.; Bi, Y.-F.; Lin, H.-Y.; Liu, G.-C.: Three Novel Cd(II) Metal-Organic Frameworks Constructed from Mixed Ligands of Dipyrido[3,2-*d*:2',3'-*f*]quinoxaline and Benzene-dicarboxylate: From a 1-D Ribbon, 2-D Layered Network, to a 3-D Architecture. Cryst. Growth Des. **7** (2007) 1086-1091.
2. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. **A64** (2008) 112-122.

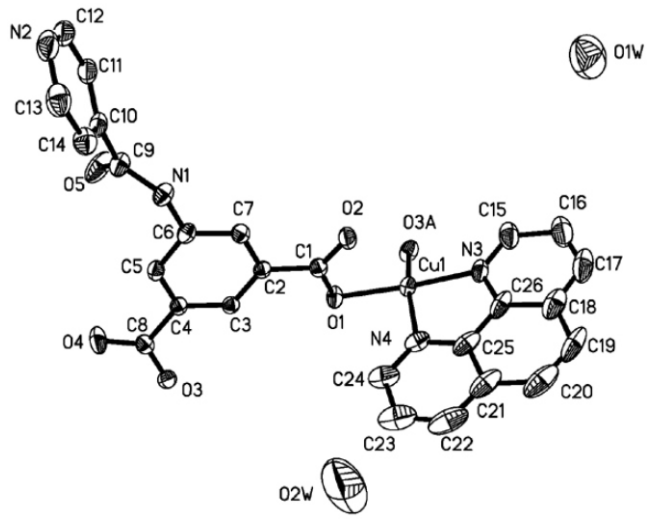
Z. Kristallogr. NCS **226** (2011) 341-342 / **DOI** 10.1524/ncrs.2011.0153 **341**

Crystal structure of (1,10-phenanthroline-κ^2N:N')-(μ_2-5-isonicotinamidoisophthalato-κ^2O^1,O^3)copper(II) monohydrate, $Cu(C_{12}H_8N_2)(C_{14}H_8N_2O_5) \cdot H_2O$

Yi-Fang Deng, Man-Sheng Chen*, Dai-Zhi Kuang and Zhi-Min Chen

Hengyang Normal University, Key Laboratory of Functional Organometallic Materials, Department of Chemistry and Materials Science, Hengyang 421008, Hunan, P. R. China

Received November 19, 2010, in revised form April 30, 2011, accepted and available on-line June 17, 2011; CCDC no. 1267/3298



Abstract

$C_{26}H_{18}CuN_4O_6$, monoclinic, $C12/c1$ (no. 15), a = 27.347(5) Å, b = 13.317(3) Å, c = 13.523(3) Å, β = 110.869(2)°, V = 4601.8 Å^3, Z = 8, $R_{gt}(F)$ = 0.065, $wR_{ref}(F^2)$ = 0.159, T = 293 K.

Source of material

A mixture of $Cu(CH_3CO_2)_2 \cdot 2H_2O$ (0.040 g, 0.1 mmol), 5-isonicotinamidoisophthalic acid (iaip, 0.028 g, 0.1 mmol), NaOH (0.081 g, 0.2 mmol), phen (0.020 g, 0.1 mmol), CH_3CH_2OH (2 mL) and H_2O (8 mL) was sealed in a 15 ml Teflon-lined stainless steel reactor, which was heated at 413 K for 72 h and then cooled to room temperature. Blue needle-like crystals of the title compound were collected.

Experimental details

H atoms bonded to C atoms were placed geometrically and treated as riding. The water H atoms found from Fourier difference maps were refined with restraints for d(O—H) = 0.8499 - 0.8501 Å and U_{iso}(H) = 1.2 U_{eq}(O). The number of disordered water molecules was established by the thermogravimetric analysis.

Discussion

The rapid expanding field of crystal engineering of one-, two- and three-dimensional coordination architectures is of great current interests for their structural as well as for their potential applications as functional materials [1]. Among them, metal-organic frameworks (MOFs) with carboxylate-containing ligands have been extensively studied because the carboxylate groups can vary coordination modes resulting in formation of different structures. Particularly, copper complexes with the heterocycle have been investigated extensively to date [3,4]. It is well known that multicarboxylate with pyridine functional group have good coordination capacity as well as the amide group, a fascinating functional group with two different types of hydrogen bonding sites [5,6].

In the title complex, the central Cu(II) ion is four-coordinated by two N atoms from phen ligands, two carboxylate O atoms from two iaip ligands in a square planar coordination. Furthermore, carboxylate groups of the iaip ligand adopt the mono-dentate coordination mode to connect two Cu(II) atoms into an infinite chain, whereas the pyridyl group is not participating in coordination. There are weak π-π interactions between the aromatic groups within the chains between the central benzene rings and benzene and pyridyl rings of iaip with a centroid-centroid distances of 3.6315(6) Å, 3.7245(7) Å, respectively. Then the π-π interactions interlink the chains into layer, which are connected together through the N–H···O and O–H···O hydrogen bonding interactions to give the 3D supramolecular architecture.

Table 1. Data collection and handling.

Crystal:	blue needle, size 0.10 × 0.15 × 0.20 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	10.02 cm^{-1}
Diffractometer, scan mode:	Bruker SMART APEX CCD, φ/ω
$2\theta_{max}$:	50.0°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	11196, 4042
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 3105
$N(param)_{refined}$:	341
Program:	SHELXTL [7]

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

Atom	Site	Occ.	x	y	z	U_{iso}
H(3)	8f		0.7625	0.6260	0.3179	0.041
H(5)	8f		0.8349	0.7331	0.6116	0.045
H(7)	8f		0.7318	0.5056	0.5635	0.045
H(11)	8f		0.8901	0.4977	0.9570	0.067
H(12)	8f		0.8907	0.5024	1.1266	0.078
H(13)	8f		0.7987	0.7346	1.0661	0.088
H(14)	8f		0.7892	0.7302	0.8866	0.074
H(15)	8f		0.6039	0.1643	0.1874	0.085

* Correspondence author (e-mail: cmsniu@163.com)

Table 2. Continued.

Atom	Site	Occ.	x	y	z	U_{iso}
H(16)	8*f*		0.5208	0.0860	0.1321	0.111
H(17)	8*f*		0.4476	0.1813	0.0832	0.114
H(19)	8*f*		0.4032	0.3609	0.0640	0.099
H(20)	8*f*		0.4145	0.5235	0.0700	0.109
H(22)	8*f*		0.4764	0.6772	0.1092	0.110
H(23)	8*f*		0.5588	0.7354	0.1671	0.112
H(24)	8*f*		0.6295	0.6229	0.2103	0.085
H(1)	8*f*		0.7653	0.6110	0.7332	0.053
H(1WA)	8*f*	0.575	0.4196	0.2079	0.5929	0.154
H(1WB)	8*f*	0.575	0.4235	0.1479	0.6785	0.154
H(2WA)	8*f*	0.425	0.5120	0.9016	0.1744	0.120
H(2WB)	8*f*	0.425	0.5421	0.9241	0.1152	0.120

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)	8*f*		0.64040(2)	0.38788(4)	0.20276(4)	0.0293(3)	0.0424(4)	0.0378(3)	–0.0023(3)	0.0090(2)	–0.0053(3)
C(1)	8*f*		0.7042(2)	0.4817(3)	0.3584(4)	0.028(2)	0.036(3)	0.047(3)	0.006(2)	0.012(2)	–0.001(2)
C(2)	8*f*		0.7417(2)	0.5550(3)	0.4299(3)	0.025(2)	0.032(2)	0.041(2)	0.006(2)	0.009(2)	0.001(2)
C(3)	8*f*		0.7681(2)	0.6244(3)	0.3914(3)	0.031(2)	0.034(2)	0.036(2)	0.004(2)	0.010(2)	–0.002(2)
C(4)	8*f*		0.8027(2)	0.6913(3)	0.4592(4)	0.026(2)	0.035(2)	0.045(3)	0.003(2)	0.009(2)	–0.001(2)
C(5)	8*f*		0.8109(2)	0.6874(3)	0.5649(4)	0.030(2)	0.036(2)	0.043(3)	–0.000(2)	0.008(2)	–0.007(2)
C(6)	8*f*		0.7853(2)	0.6184(3)	0.6052(3)	0.028(2)	0.046(3)	0.038(2)	0.004(2)	0.011(2)	–0.003(2)
C(7)	8*f*		0.7501(2)	0.5526(3)	0.5369(3)	0.026(2)	0.041(3)	0.043(3)	0.001(2)	0.010(2)	0.002(2)
C(8)	8*f*		0.8307(2)	0.7705(3)	0.4198(4)	0.034(3)	0.037(3)	0.049(3)	0.001(2)	0.016(2)	–0.001(2)
C(9)	8*f*		0.8401(2)	0.6142(4)	0.7930(4)	0.043(3)	0.066(3)	0.041(3)	–0.006(3)	0.014(2)	–0.003(2)
C(10)	8*f*		0.8395(2)	0.6148(4)	0.9024(4)	0.041(3)	0.059(3)	0.042(3)	–0.015(2)	0.012(2)	–0.011(3)
C(11)	8*f*		0.8700(2)	0.5469(4)	0.9766(4)	0.050(3)	0.057(3)	0.054(3)	–0.017(3)	0.011(3)	–0.010(3)
C(12)	8*f*		0.8710(2)	0.5516(5)	1.0778(4)	0.066(4)	0.073(4)	0.048(3)	–0.027(3)	0.011(3)	0.000(3)
C(13)	8*f*		0.8170(3)	0.6849(5)	1.0426(5)	0.077(4)	0.082(4)	0.070(4)	–0.020(3)	0.036(3)	–0.028(3)
C(14)	8*f*		0.8117(2)	0.6838(4)	0.9352(4)	0.064(4)	0.063(4)	0.058(3)	–0.012(3)	0.022(3)	–0.007(3)
C(15)	8*f*		0.5730(3)	0.2040(5)	0.1675(4)	0.075(4)	0.091(4)	0.044(3)	–0.036(3)	0.017(3)	–0.009(3)
C(16)	8*f*		0.5235(3)	0.1571(6)	0.1346(5)	0.096(5)	0.117(5)	0.060(4)	–0.052(4)	0.021(4)	–0.007(4)
C(17)	8*f*		0.4807(3)	0.2138(7)	0.1072(5)	0.061(4)	0.161(6)	0.058(4)	–0.046(4)	0.016(3)	–0.002(4)
C(18)	8*f*		0.4818(2)	0.3181(7)	0.1118(4)	0.052(3)	0.153(5)	0.032(3)	–0.017(4)	0.014(3)	–0.001(3)
C(19)	8*f*		0.4377(2)	0.3869(7)	0.0852(5)	0.035(3)	0.174(6)	0.039(3)	–0.004(4)	0.013(2)	–0.005(4)
C(20)	8*f*		0.4448(3)	0.4822(7)	0.0898(5)	0.064(4)	0.170(6)	0.041(3)	0.026(4)	0.020(3)	0.007(4)
C(21)	8*f*		0.4935(3)	0.5304(7)	0.1216(4)	0.059(4)	0.148(5)	0.029(3)	0.026(4)	0.019(3)	0.009(3)
C(22)	8*f*		0.5046(3)	0.6307(7)	0.1286(5)	0.098(5)	0.132(5)	0.045(3)	0.053(4)	0.028(3)	0.009(4)
C(23)	8*f*		0.5525(3)	0.6651(6)	0.1609(5)	0.121(6)	0.098(5)	0.060(4)	0.049(5)	0.033(4)	–0.001(4)
C(24)	8*f*		0.5948(3)	0.5972(5)	0.1866(4)	0.087(4)	0.075(4)	0.053(3)	0.029(3)	0.027(3)	0.004(3)
C(25)	8*f*		0.5383(2)	0.4646(5)	0.1482(4)	0.049(3)	0.112(4)	0.028(2)	0.022(3)	0.015(2)	0.009(3)
C(26)	8*f*		0.5317(2)	0.3575(6)	0.1431(4)	0.036(3)	0.132(4)	0.025(2)	–0.008(3)	0.014(2)	0.000(3)
N(1)	8*f*		0.7932(2)	0.6140(3)	0.7152(3)	0.031(2)	0.064(3)	0.038(2)	–0.002(2)	0.013(2)	–0.001(2)
N(2)	8*f*		0.8464(2)	0.6194(5)	1.1121(4)	0.088(4)	0.094(4)	0.045(3)	–0.042(3)	0.024(3)	–0.016(3)
N(3)	8*f*		0.5766(2)	0.3030(3)	0.1705(3)	0.041(3)	0.066(3)	0.036(2)	–0.016(2)	0.009(2)	–0.007(2)
N(4)	8*f*		0.5878(2)	0.4993(3)	0.1788(3)	0.052(3)	0.061(3)	0.041(2)	0.019(2)	0.017(2)	0.004(2)
O(1)	8*f*		0.7000(1)	0.4806(2)	0.2615(2)	0.041(2)	0.054(2)	0.042(2)	–0.015(2)	0.012(2)	–0.011(2)
O(2)	8*f*		0.6776(1)	0.4260(3)	0.3934(3)	0.045(2)	0.051(2)	0.050(2)	–0.016(2)	0.014(2)	–0.001(2)
O(3)	8*f*		0.8159(1)	0.7825(2)	0.3200(3)	0.037(2)	0.051(2)	0.047(2)	–0.007(2)	0.009(2)	0.012(2)
O(4)	8*f*		0.8657(1)	0.8198(3)	0.4825(3)	0.063(3)	0.068(3)	0.056(2)	–0.035(2)	0.026(2)	–0.017(2)
O(5)	8*f*		0.8818(2)	0.6124(4)	0.7786(3)	0.036(2)	0.161(5)	0.051(2)	–0.004(3)	0.014(2)	0.004(3)
O(1W)	8*f*	0.575(8)	0.4387(3)	0.1650(5)	0.6361(6)	0.097(8)	0.109(7)	0.21(1)	–0.038(6)	0.092(8)	–0.044(7)
O(2W)	8*f*	0.425(8)	0.5111(3)	0.9252(5)	0.1154(6)	0.11(1)	0.099(9)	0.120(9)	0.030(7)	0.075(8)	–0.019(7)

Acknowledgments. This work was supported by the Construct Program of the Key Discipline in Hunan Province, the Foundation of Educational Department of Hunan Province (grant no. 10C0473) and the Science Foundation of Hengyang Normal University (10B67).

References

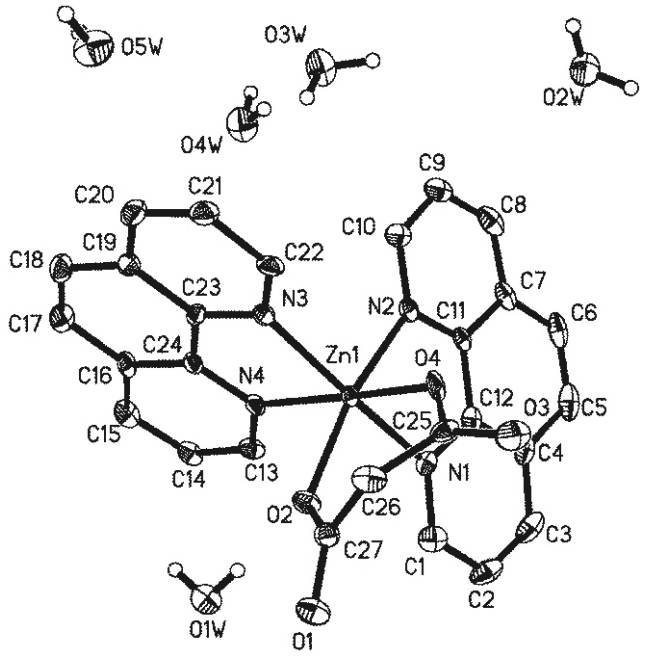
1. Kitagawa, S.; Kondo, M.: Functional Micropore Chemistry of Crystalline Metal Complex-Assembled Compounds . Bull. Chem. Soc. Jpn. **71** (1998) 1739-1753.
2. Blake, A. J.; Champness, N. R.; Hubberstey, P.; Li, W. S.; Withersby, M. A.; Schröder, M.: Inorganic crystal engineering using self-assembly of tailored building-blocks. Coord. Chem. Rev. **183** (1999) 117-138.
3. Huang, X. C.; Zhang, J. P.; Lin, Y. Y.; Yu, X. L.; Chen, X. M.: Two mixed valence copper(I,II) imidazolate coordination polymers: metal-valence tuning approach for new topological structures. Chem. Commum. (2004) 1100-1101.
4. Masciocchi, N.; Bruni, S.; Cariati, E.; Cariati, F.; Galli, S.; Sironi. A.: Extended polymorphism in copper(II) imidazolate polymers: A spectroscopic and XRPD structural study. Inorg. Chem. **40** (2001) 5897-5905.
5. Huyskens, P. L.: Factors governing the influence of a first hydrogen on the formation of a second one by the same molecule or ion. J. Am. Chem. Soc. **99** (1977) 2578-2582.
6. Lee, C. M.; Kumler, W. D.: The dipole moment and structure of the imide Group. III. straight chain imides >N–H···O=C< Hydrogen Bonding and a Case of O=C–H···O=C< Hydrogen Bonding. J. Am. Chem. Soc. **84** (1962) 571-578.
7. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. **A64** (2008) 112-122.

Crystal structure of bis(1,10-phenanthroline-κ^2N,N')-(malonato-κ^2O^1,O^3)zinc(II) pentahydrate, $Zn(C_{12}H_8N_2)_2(C_3H_2O_4) \cdot 5H_2O$

Xue Nie* and Jing-Nian Qu

Hengyang Normal University, Department of Chemistry and Materials Science, Hengyang 421008, Hunan, P. R. China

Received January 4, 2011, accepted and available on-line June 17, 2011; CCDC no. 1267/3354



Abstract

$C_{27}H_{28}N_4O_9Zn$, triclinic, $P\bar{1}$ (no. 2), a = 10.380(2) Å, b = 10.580(3) Å, c = 13.059(2) Å, α = 84.682(2)°, β = 76.965(3)°, γ = 72.834(2)°, V = 1334.4 Å^3, Z = 2, $R_{gt}(F)$ = 0.040, $wR_{ref}(F^2)$ = 0.097, T = 291 K.

Source of material

A mixture of $ZnSO_4 \cdot 7H_2O$ (0.029 g, 0.1 mmol), malonic acid (H_2L, 0.011 g, 0.1 mmol), NaOH (0.041 g, 0.1 mmol), 1,10-phenanthroline (0.019 g, 0.1 mmol), CH_3CH_2OH (4 mL) and H_2O (6 mL) was sealed in a 15 ml Teflon-lined stainless steel reactor, which was heated at 393 K for 72 h and then it was cooled to room temperature. Colorless block-shaped crystals of the title compound were collected.

Experimental details

Hydrogen atoms were placed geometrically and treated as riding with d(C—H) = 0.93 Å (aromatic) or 0.97 Å (acyclic), d(O—H) = 0.85 Å and U_{iso}(H) = 1.2 U_{eq}(C,O).

Discussion

There is considerable interest in the study of transition complexes containing carboxylate ligands due to their novel topology and excellent properties [1-6]. Furthermore, zinc, as one of the most important trace elements, plays a versatile role in biological systems caused by its structural and catalytic role in enzymes [7,8]. Therefore, many efforts have been made on the study of synthetic analogues of zinc enzymes in the hope of clarifying the mechanism of their action.

In the title crystal structure, the Zn(II) ion is six-coordinated by four N atoms from two phen molecules and two carboxylate O atoms from one L^{2-} ligands in a slightly distorted octahedral coordination with O4 and N4 at the apical positions. Other two carboxylate O atoms are not coordinating. The bond lengths d(Zn—N) and d(Zn—O) are in the normal ranges.

In the crystal structure, there are abundant strong O–H···O hydrogen bonds between the uncoordinated O atoms of carboxyl groups and water molecules, which link single complex into a three-dimensional framwork.

Table 1. Data collection and handling.

Crystal:	colorless bolck, size 0.14 × 0.20 × 0.24 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	9.83 cm^{-1}
Diffractometer, scan mode:	Bruker Smart APEX CCD, φ/ω
$2\theta_{max}$:	52°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	13993, 5236
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 4851
$N(param)_{refined}$:	370
Program:	SHELXTL [9]

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

Atom	Site	x	y	z	U_{iso}
H(1A)	2*i*	0.9374	0.0280	0.6714	0.045
H(2A)	2*i*	1.0580	–0.1720	0.5906	0.053
H(3A)	2*i*	0.9417	–0.2926	0.5343	0.054
H(5A)	2*i*	0.7120	–0.3134	0.5062	0.051
H(6A)	2*i*	0.4798	–0.2431	0.5461	0.046
H(8A)	2*i*	0.2604	–0.0678	0.6259	0.048
H(9A)	2*i*	0.1622	0.1309	0.7064	0.045
H(10A)	2*i*	0.3002	0.2489	0.7422	0.038
H(13A)	2*i*	0.7381	–0.0279	0.8743	0.035
H(14A)	2*i*	0.7184	–0.0742	1.0514	0.036
H(15A)	2*i*	0.5760	0.0869	1.1695	0.042
H(17A)	2*i*	0.3955	0.3090	1.1974	0.044
H(18A)	2*i*	0.2722	0.5014	1.1299	0.045
H(20A)	2*i*	0.2241	0.6489	0.9678	0.042
H(21A)	2*i*	0.2692	0.6745	0.7893	0.042
H(22A)	2*i*	0.4223	0.5052	0.6864	0.035
H(26A)	2*i*	0.7076	0.4980	0.6369	0.041
H(26B)	2*i*	0.8433	0.4731	0.5507	0.041
H(1X)	2*i*	0.8963	0.2004	0.8401	0.048
H(1Y)	2*i*	0.8802	0.1636	0.9460	0.048

* Correspondence author (e-mail: xuehuanie@126.com)

Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
H(2X)	2*i*	0.0151	0.3453	0.1366	0.065
H(2Y)	2*i*	0.1286	0.2722	0.0667	0.065
H(3X)	2*i*	0.0796	0.4957	0.6727	0.056
H(3Y)	2*i*	0.1389	0.5629	0.7266	0.056

Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
H(4X)	2*i*	0.1009	0.3840	0.8602	0.063
H(4Y)	2*i*	0.0423	0.2945	0.9240	0.063
H(5X)	2*i*	1.0299	–0.0188	0.8783	0.061
H(5Y)	2*i*	1.0258	–0.1433	0.9203	0.061

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)	2*i*	0.8893(3)	–0.0210(3)	0.6477(2)	0.035(2)	0.036(2)	0.039(2)	–0.012(1)	–0.007(1)	0.007(1)
C(2)	2*i*	0.9626(3)	–0.1418(3)	0.5995(3)	0.030(2)	0.036(2)	0.051(2)	0.006(1)	0.003(1)	0.004(1)
C(3)	2*i*	0.8934(3)	–0.2128(3)	0.5667(3)	0.047(2)	0.031(2)	0.041(2)	–0.001(1)	0.010(1)	–0.005(1)
C(4)	2*i*	0.7496(3)	–0.1694(2)	0.5801(2)	0.050(2)	0.019(1)	0.019(1)	–0.003(1)	–0.004(1)	0.0031(9)
C(5)	2*i*	0.6684(4)	–0.2373(3)	0.5447(2)	0.083(2)	0.023(1)	0.022(1)	–0.016(2)	–0.013(1)	0.006(1)
C(6)	2*i*	0.5299(4)	–0.1932(3)	0.5660(2)	0.077(2)	0.031(1)	0.019(1)	–0.030(2)	–0.017(1)	0.010(1)
C(7)	2*i*	0.4589(3)	–0.0738(3)	0.6176(2)	0.049(2)	0.027(1)	0.021(1)	–0.020(1)	–0.018(1)	0.014(1)
C(8)	2*i*	0.3162(3)	–0.0214(3)	0.6421(2)	0.050(2)	0.053(2)	0.030(1)	–0.034(2)	–0.019(1)	0.020(1)
C(9)	2*i*	0.2576(3)	0.0969(3)	0.6895(2)	0.029(1)	0.056(2)	0.028(1)	–0.016(1)	–0.009(1)	0.017(1)
C(10)	2*i*	0.3413(3)	0.1664(3)	0.7123(2)	0.028(1)	0.044(2)	0.021(1)	–0.011(1)	–0.005(1)	0.015(1)
C(11)	2*i*	0.5355(3)	0.0041(2)	0.6465(2)	0.032(1)	0.027(1)	0.014(1)	–0.013(1)	–0.0097(9)	0.0068(9)
C(12)	2*i*	0.6836(3)	–0.0471(2)	0.6290(2)	0.038(1)	0.024(1)	0.017(1)	–0.009(1)	–0.007(1)	0.0071(9)
C(13)	2*i*	0.6790(3)	0.0354(3)	0.9213(2)	0.026(1)	0.034(1)	0.027(1)	–0.008(1)	–0.011(1)	0.012(1)
C(14)	2*i*	0.6684(3)	0.0069(3)	1.0273(2)	0.035(1)	0.036(1)	0.025(1)	–0.017(1)	–0.013(1)	0.014(1)
C(15)	2*i*	0.5817(3)	0.1018(3)	1.0975(2)	0.045(2)	0.045(2)	0.022(1)	–0.023(1)	–0.011(1)	0.014(1)
C(16)	2*i*	0.5016(3)	0.2219(3)	1.0581(2)	0.036(1)	0.037(1)	0.013(1)	–0.019(1)	–0.005(1)	0.0024(9)
C(17)	2*i*	0.4076(3)	0.3224(3)	1.1248(2)	0.039(2)	0.052(2)	0.021(1)	–0.023(1)	0.003(1)	0.001(1)
C(18)	2*i*	0.3351(3)	0.4380(3)	1.0847(2)	0.036(2)	0.051(2)	0.026(1)	–0.019(1)	0.003(1)	–0.010(1)
C(19)	2*i*	0.3548(3)	0.4622(3)	0.9741(2)	0.023(1)	0.032(1)	0.032(1)	–0.010(1)	–0.004(1)	–0.009(1)
C(20)	2*i*	0.2867(3)	0.5812(3)	0.9265(2)	0.030(1)	0.033(1)	0.041(2)	–0.006(1)	–0.002(1)	–0.014(1)
C(21)	2*i*	0.3131(3)	0.5961(3)	0.8210(2)	0.027(1)	0.030(1)	0.046(2)	0.000(1)	–0.013(1)	–0.006(1)
C(22)	2*i*	0.4062(3)	0.4940(3)	0.7592(2)	0.022(1)	0.027(1)	0.036(1)	0.001(1)	–0.015(1)	0.002(1)
C(23)	2*i*	0.4500(2)	0.3641(2)	0.9057(2)	0.020(1)	0.021(1)	0.020(1)	–0.0065(9)	–0.0009(9)	–0.0048(9)
C(24)	2*i*	0.5217(2)	0.2419(2)	0.9492(2)	0.024(1)	0.029(1)	0.017(1)	–0.009(1)	–0.0076(9)	0.0005(9)
C(25)	2*i*	0.7182(2)	0.3692(3)	0.5295(2)	0.020(1)	0.029(1)	0.025(1)	0.001(1)	–0.0003(9)	0.008(1)
C(26)	2*i*	0.7806(3)	0.4298(3)	0.5965(2)	0.031(1)	0.024(1)	0.047(2)	–0.007(1)	–0.011(1)	0.010(1)
C(27)	2*i*	0.8586(3)	0.3378(2)	0.6726(2)	0.026(1)	0.025(1)	0.032(1)	–0.008(1)	–0.007(1)	–0.004(1)
N(1)	2*i*	0.7535(2)	0.0252(2)	0.6604(2)	0.029(1)	0.026(1)	0.021(1)	–0.0063(9)	–0.0011(8)	–0.0016(8)
N(2)	2*i*	0.4776(2)	0.1201(2)	0.6932(2)	0.029(1)	0.027(1)	0.019(1)	–0.0094(9)	–0.0083(8)	0.0022(8)
N(3)	2*i*	0.4729(2)	0.3804(2)	0.8016(2)	0.024(1)	0.024(1)	0.019(1)	–0.0035(8)	–0.0090(8)	0.0031(8)
N(4)	2*i*	0.6074(2)	0.1510(2)	0.8820(2)	0.024(1)	0.028(1)	0.018(1)	–0.0070(8)	–0.0096(8)	0.0022(8)
O(1)	2*i*	0.9787(2)	0.3391(2)	0.6713(2)	0.035(1)	0.044(1)	0.050(1)	–0.0188(9)	–0.0134(9)	0.003(1)
O(2)	2*i*	0.7984(2)	0.2653(2)	0.7356(2)	0.0279(9)	0.032(1)	0.033(1)	–0.0140(8)	–0.0112(8)	0.0077(8)
O(3)	2*i*	0.7436(2)	0.3892(2)	0.4339(2)	0.036(1)	0.071(2)	0.029(1)	–0.009(1)	–0.0051(9)	0.024(1)
O(4)	2*i*	0.6369(2)	0.3009(2)	0.5741(1)	0.044(1)	0.046(1)	0.0104(8)	–0.0196(9)	–0.0109(7)	0.0050(7)
O(1W)	2*i*	0.9384(2)	0.1693(2)	0.8897(2)	0.044(1)	0.034(1)	0.043(1)	–0.0116(9)	–0.0145(9)	0.0064(9)
O(2W)	2*i*	0.0797(3)	0.2733(3)	0.1285(2)	0.049(1)	0.071(2)	0.043(1)	–0.017(1)	–0.007(1)	–0.009(1)
O(3W)	2*i*	0.0798(2)	0.5202(2)	0.7328(2)	0.057(1)	0.060(1)	0.035(1)	–0.036(1)	–0.005(1)	0.004(1)
O(4W)	2*i*	0.1087(3)	0.3290(2)	0.9118(2)	0.057(1)	0.059(2)	0.049(1)	–0.032(1)	–0.007(1)	–0.000(1)
O(5W)	2*i*	1.0707(2)	–0.1012(2)	0.8743(2)	0.050(1)	0.034(1)	0.067(2)	–0.012(1)	–0.008(1)	–0.001(1)
Zn(1)	2*i*	0.62469(3)	0.21697(3)	0.72004(2)	0.0219(2)	0.0209(2)	0.0128(1)	–0.0068(1)	–0.0044(1)	

Acknowledgment. This work was supported by Hengyang Bureau of Science & Technology (grant no. 2009KJ28).

References

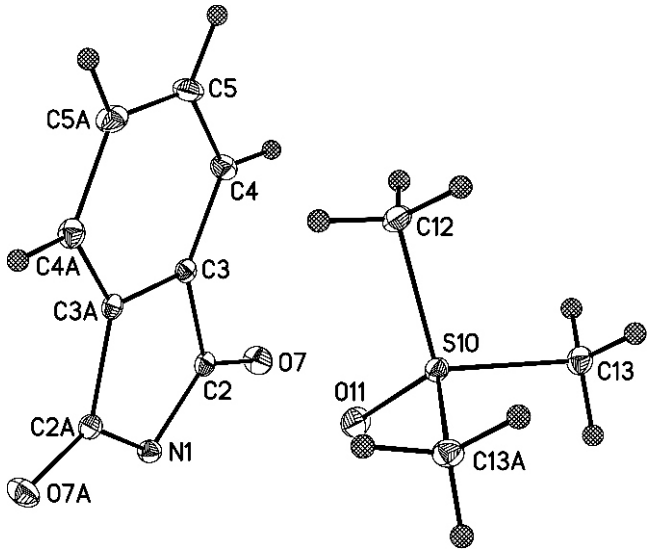
1. Batten, S. R.; Robson, R.: Interpenetrating Nets: Ordered, Periodic Entanglement. Angew. Chem., Int., Ed. **37** (1998) 1460-1494.
2. Kitagawa, S.; Kondo, M.: Functional Micropore Chemistry of Crystalline Metal Complex-Assembled Compounds. Bull. Chem. Soc. Jpn. **71** (1998) 1739-1753.
3. Kong, X. J.; Ren, Y. P.; Long, L. S.; Zheng, Z. P.; Huang, R. B.; Zheng, L. S.: A Keplerate Magnetic Cluster Featuring an Icosidodecahedron of Ni(II) Ions Encapsulating a Dodecahedron of La(III) Ions. J. Am. Chem. Soc. **129** (2007) 7016-7017.
4. Mrozinski, J.: New trends of molecular magnetism. Coord. Chem. Rev. **249** (2005) 2534-2548.
5. Wang, Y.; Huang, Y. Q.; Liu, G. X.; Okamuraz, T.-A.; Doi, M.; Sheng, Y. W.; Sun, W. Y.; Ueyama, N.: New Metal-Organic Frameworks with Large Cavities: Selective Sorption and Desorption of Solvent Molecules. Chem. Eur. J. **13** (2007) 7523-7531.
6. Zou, R. Q.; Sakurai, H.; Han, S.; Zhong, R. Q.; Xu, Q.: Probing the Lewis Acid Sites and CO Catalytic Oxidation Activity of the Porous Metal-Organic Polymer [Cu(5-methylisophthalate)]. J. Am. Chem. Soc. **129** (2007) 8402-8403.
7. Parkin, G.: Synthetic Analogues Relevant to the Structure and Function of Zinc Enzymes. Chem. Rev. **104** (2004) 699-768.
8. Vallee, B. L.; Auld, D. S.: Zinc coordination, function, and structure of zinc enzymes and other proteins. Biochemistry **29** (1990) 5647-5659.
9. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. **A64** (2008) 112-122.

Crystal structure of trimethylsulfoxonium phthalimide, $[C_3H_9SO][C_8H_4NO_2]$

Eyad Mallah[*,I], Qutaiba Abu-Salem[II], Wael Abu Dayyih[I], Mohammed Hamad[I], Manfred Steimann[III] and Caecilia Maichle-Mössmer[III]

[I] Petra University, Faculty of Pharmacy and Medical Sciences, P. O. Box 961343, Amman 11196, Jordan
[II] University of Al al-Bayt, Faculty of Science, Department of Chemistry, Al-Mafraq, Jordan
[III] Institut für Anorganische Chemie der Universität Tübingen, Auf der Morgenstelle 18, 72076 Tübingen, Germany

Received February 21, 2011, accepted and available on-line June 17, 2011; CCDC no. 1267/3411



Abstract

$C_{11}H_{13}NO_3S$, orthorhombic, *Pnma* (no. 62), $a = 8.445(1)$ Å, $b = 10.958(1)$ Å, $c = 12.084(2)$ Å, $V = 1118.2$ Å^3, $Z = 4$, $R_{gt}(F) = 0.054$, $wR_{ref}(F^2) = 0.108$, $T = 173$ K.

Source of material

Trimethylsulfoxonium iodide (0.250 g, 1.14 mmol) was added at room temperature. To a solution containing thallium phthalimide (0.397 g, 1.13 mmol) in methanol (30 ml). After stirring overnight, the filtered solution was evaporated to dryness, and the resulting solid was washed with Et_2O (yield 0.220 g, 35 %). The title compound was recrystallized from methanol/Et_2O as colorless crystals.

Discussion

Phthalimide [1(*H*)-isoindoline-1,3(2*H*)-dione] and its derivatives are very important compounds. They are used in the synthesis of antimicrobal activity, as anti drogens and agents for treating tumour necrosis factor. Certain phthalimide derivatives are used as herbicides and for reducing bacterial contamination. Phthalimide forms salts with potassium and thallium due to its high acidity caused by electrophilic carbonyl groups attached to the nitrogen atom. Potassium phthalimide is used in the Gabriel synthesis of primary amines and by reacting with thallium nitrate in aqueous solution produces thallium phthalimide which can give many phthalimide derivatives by reacting with salts containing iodide.

* Correspondence author (e-mail: eyad782002@yahoo.com)

The resulted salt crystallizes with one molecular anion and one cation in the symmetric unit. In the crystal structure, the bond lengths and angles of the anion are quite similar to those reported for potassium phthalimide structure [1].

The bonds are most significantly different in the region near N atom which is the deprotonation site. As a result of deprotonation the internal ring angle at the nitrogen atom in the protonated neutral molecule closes from 112.8(2)° [2] to 107.9(3)° (N1) in its anion. The opening of each of the internal ring angles at the adjacent carbon atoms C2 and C2A by 4 - 5° over-compensates for the closing of the angle at N1 by 4.9°. This suggests that all three angular changes are a consequence of the deprotonation. In addition the C—O bond length [1.231(3) Å] is slightly increased by about 0.03 Å and C—N bond length [1.369(3) Å] is slightly decreased by 0.01 Å. These results and the symmetry about N1 indicate also a symmetric p-electron distribution in the sense of an effective delocalization within the ring. There are no hydrogen interactions in the structure and it is interesting to note that the three S—C bond lengths in the cation are similar (2× 1.750(3) Å and 1× 1.753(4) Å), and the three O–S–C bond angles are slightly similar (2× 112.85(11)° and 113.06(18)°). The molecular anion is planar; the two carbonyl groups are not displaced from the mean plane of their attached molecular anion ring.

Table 1. Data collection and handling.

Crystal:	colorless needle, size 0.05 × 0.05 × 0.30 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	2.80 cm^{-1}
Diffractometer, scan mode:	STOE IPDS 2, φ
$2\theta_{max}$:	52.74°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	15073, 1201
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 1048
$N(param)_{refined}$:	107
Programs:	SHELXS-97, SHELXL-97 [3]

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

Atom	Site	*x*	*y*	*z*	U_{iso}
H(4)	8*d*	0.545(4)	0.536(3)	0.645(3)	0.040(9)
H(5)	8*d*	0.401(4)	0.644(3)	0.781(3)	0.05(1)
H(12A)	8*d*	0.210(4)	0.678(3)	0.552(3)	0.037(9)
H(12B)	4*c*	0.055(6)	¾	0.522(4)	0.04(1)
H(13A)	8*d*	0.022(4)	0.634(3)	0.330(2)	0.024(7)
H(13B)	8*d*	0.170(4)	0.620(3)	0.253(3)	0.044(9)
H(13C)	8*d*	0.169(4)	0.552(3)	0.366(3)	0.044(9)

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*c*	0.7896(4)	¾	0.4195(2)	0.022(2)	0.023(2)	0.020(1)	0	0.002(1)	0
C(2)	8*d*	0.7336(3)	0.6490(2)	0.4734(2)	0.018(1)	0.024(1)	0.021(1)	–0.001(1)	–0.004(1)	–0.002(1)
C(3)	8*d*	0.6320(3)	0.6865(2)	0.5700(2)	0.016(1)	0.022(1)	0.019(1)	–0.000(1)	–0.0047(9)	0.002(1)
C(4)	8*d*	0.5486(3)	0.6211(3)	0.6477(2)	0.025(1)	0.025(1)	0.028(1)	–0.001(1)	0.000(1)	0.004(1)
C(5)	8*d*	0.4656(3)	0.6867(3)	0.7276(2)	0.025(1)	0.039(2)	0.024(1)	–0.004(1)	0.006(1)	0.006(1)
O(7)	8*d*	0.7625(2)	0.5425(2)	0.4478(2)	0.040(1)	0.022(1)	0.038(1)	0.0030(9)	0.0078(9)	–0.0047(8)
S(10)	4*c*	0.2239(1)	¾	0.38169(7)	0.0171(4)	0.0212(4)	0.0164(4)	0	–0.0016(3)	0
O(11)	4*c*	0.3936(3)	¾	0.3654(2)	0.018(1)	0.048(2)	0.027(2)	0	–0.001(1)	0
C(12)	4*c*	0.1693(5)	¾	0.5217(3)	0.029(2)	0.026(2)	0.017(2)	0	–0.002(2)	0
C(13)	8*d*	0.1314(3)	0.6217(3)	0.3246(2)	0.028(2)	0.020(1)	0.023(1)	–0.001(1)	–0.001(1)	–0.004(1)

Acknowledgment. X-ray data were collected at the University of Tübingen using a Stoe IPDS 2 diffractometer, we would like to acknowledge the Deanship of Scientific Research at Petra University for their support and kind cooperation.

References

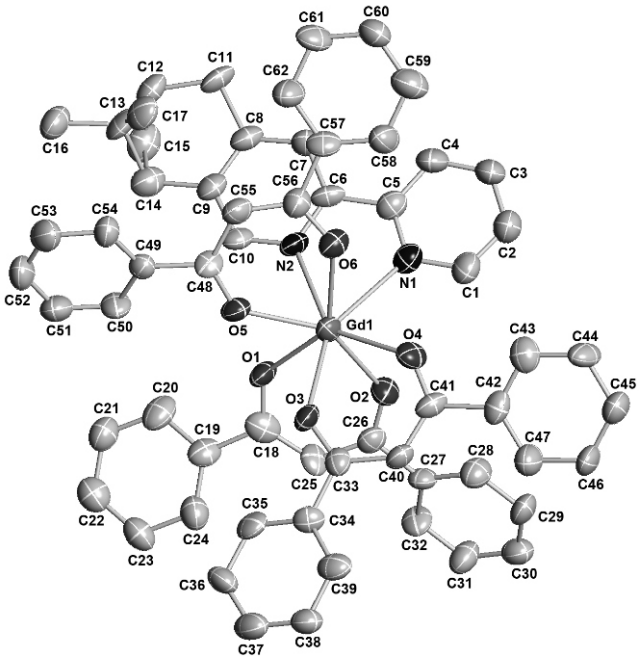
1. Nagel, N.; Bock, H.; Bats, J. W.: Potassium Phthalimide. Acta Crystallogr. **C52** (1996) 1344.
2. Ng, S. W.: Structure of 1*H*-isoindole-1,3(2*H*)-dione (Phthalimide). Acta Crystallogr. **C48** (1992) 1694-1695.
3. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. **A64** (2008) 112-122.

Crystal structure of tris(dibenzoylmethanato)-[(*R*,*R*)-6,6-dimethyl-3-pyridin-2-yl-5,6,7,8-tetrahydro-5,7-methanoisoquinoline)]-gadolinium(III), $Gd(C_{15}H_{11}O_2)_3(C_{17}H_{18}N_2)$

Xi-Li Li* and Xiaoxia Niu

Zhengzhou University of Light Industry, Henan Provincial Key Laboratory of Surface & Interface Science, Zhengzhou 450002, P. R. China

Received December 10, 2010, accepted and available on-line June 17, 2011; CCDC no. 1267/3328



Abstract

$C_{62}H_{51}GdN_2O_6$, monoclinic, $P2_1$ (no. 4), a = 9.504(2) Å, b = 20.748(5) Å, c = 12.704(3) Å, β = 92.432(4)°, V = 2502.8 Å^3, Z = 2, $R_{gt}(F)$ = 0.052, $wR_{ref}(F^2)$ = 0.118, T = 298 K.

Source of material

The chiral ligand (*R*,*R*)-6,6-dimethyl-3-pyridin-2-yl-5,6,7,8-tetrahydro-5,7-methanoiso- quinoline was prepared by the procedures [1] and $Gd(dbm)_3 \cdot 2H_2O$ was synthesized according to [2]. A solution of $Gd(dbm)_3 \cdot 2H_2O$ (86 mg, 0.1 mmol) in ethanol (10 mL) was added to a solution of chiral ligand (25 mg, 0.1 mmol) in acetone (10 mL). The mixture was stirred 10 minutes and kept at RT. Yellow single crystals of title complex suitable for X-ray analysis were obtained in 73 % yield by slow evaporation of the solvent over two weeks.

Experimental details

H atoms were included in calculated positions and treated as riding atoms with d(C—H) = 0.93 (aromatic), 0.97 (methylene) or 0.96 (methyl) Å and U_{iso}(H) = 1.2 or 1.5 U_{eq}(C). The Flack parameter is 0.02(1).

* Correspondence author (e-mail: lixl@zzuli.edu.cn)

Discussion

Chiral lanthanide complexes have attracted considerable attention of research in the field of coordination chemistry, material science and life science due to their diverse applications in asymmetric catalysis, enantioselective synthesis, medical diagnotic and therapy [3-7]. Among them, the Gd-based complexes are commonly used as chiral shift reagents for resolving NMR spectra [8].

The introduction of the chiral bipyridine derivative ligand results in the chirality of the title compound, which crystallizes with space group $P2_1$. The chirality is dominated by the two centers C12 and C14 of the bipyridine derivative. the Gd(III) ion is coordinated by six oxygen atoms from three β-diketonate ligands and two nitrogen atoms of chiral pinene bipyridine. The arrangement of O_6N_2 donors can be best approximated as a distorted square antiprism. The bond lengths d(Gd—O) are in the range of 2.328(5) - 2.386(7) Å and d(Gd—N) are 2.574(5) and 2.599(5) Å, respectively. The O3, O4, O5, O6 (bottom plane) and O1, O2, N1, N2 atoms (top plane) comprise the two square-basic planes of the antiprism with mean deviations of 0.072(3) and 0.113(3) Å from each plane, their dihedral angle is 1.7(2)°.

The present compound was synthesized from the starting materials (*R*,*R*)-(–)-6,6-dimethyl-3-pyridin-2-yl-5,6,7,8-tetrahydro-5,7- methanoisoquinoline, while the reported compound was obtained from (*S*,*S*)-(–)-6,6-dimethyl-3-pyridin-2-yl-5,6,7,8-tetrahydro-5,7- methanoisoquinoline. They are a pair of enantiomers, but the synthetic pathways are different [9,10].

Table 1. Data collection and handling.

Crystal:	yellow block, size 0.22 × 0.24 × 0.30 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	13.81 cm^{-1}
Diffractometer, scan mode:	Bruker SMART APEX CCD, φ/ω
$2\theta_{max}$:	52°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	13499, 8459
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 7308
$N(param)_{refined}$:	642
Programs:	SHELXS-97, SHELXL-97 [11]

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

Atom	Site	x	y	z	U_{iso}
H(1)	2*a*	0.7362	0.6454	–0.0679	0.066
H(2)	2*a*	0.5965	0.6692	–0.2112	0.076
H(3)	2*a*	0.3914	0.7256	–0.1893	0.072
H(4)	2*a*	0.3287	0.7545	–0.0245	0.075
H(7)	2*a*	0.2849	0.7803	0.1272	0.058

Table 2. Continued.

Atom	Site	*x*	*y*	*z*	U_{iso}
H(10)	2*a*	0.5710	0.6980	0.3886	0.048
H(11A)	2*a*	0.1908	0.8570	0.2885	0.062
H(11B)	2*a*	0.0958	0.7949	0.2890	0.062
H(12)	2*a*	0.1010	0.8407	0.4640	0.061
H(14)	2*a*	0.4213	0.7396	0.5297	0.072
H(15A)	2*a*	0.1600	0.7158	0.4330	0.079
H(15B)	2*a*	0.1646	0.7436	0.5508	0.079
H(16A)	2*a*	0.2626	0.8910	0.6129	0.094
H(16B)	2*a*	0.4055	0.8552	0.6375	0.094
H(16C)	2*a*	0.2628	0.8175	0.6418	0.094
H(17A)	2*a*	0.5060	0.8838	0.4721	0.090
H(17B)	2*a*	0.3727	0.9252	0.4406	0.090
H(17C)	2*a*	0.4237	0.8713	0.3645	0.090
H(20)	2*a*	0.6767	0.6086	0.5168	0.074
H(21)	2*a*	0.6794	0.5857	0.6957	0.072
H(22)	2*a*	0.8407	0.5154	0.7655	0.072
H(23)	2*a*	0.9800	0.4531	0.6560	0.066
H(24)	2*a*	0.9753	0.4767	0.4753	0.069
H(25)	2*a*	0.8889	0.4766	0.3163	0.056
H(28)	2*a*	0.9207	0.5209	–0.0120	0.066
H(29)	2*a*	0.9852	0.4354	–0.1205	0.066
H(30)	2*a*	0.9722	0.3320	–0.0585	0.067
H(31)	2*a*	0.8940	0.3102	0.1075	0.073

Table 2. Continued.

Atom	Site	*x*	*y*	*z*	U_{iso}
H(32)	2*a*	0.8333	0.3956	0.2160	0.058
H(35)	2*a*	1.1168	0.5995	0.4161	0.060
H(36)	2*a*	1.2827	0.5509	0.5335	0.067
H(37)	2*a*	1.4865	0.5095	0.4718	0.072
H(38)	2*a*	1.5415	0.5206	0.2987	0.060
H(39)	2*a*	1.3777	0.5706	0.1840	0.065
H(40)	2*a*	1.2151	0.5915	0.0812	0.053
H(43)	2*a*	0.9712	0.7172	–0.1340	0.067
H(44)	2*a*	1.0197	0.7071	–0.3116	0.068
H(45)	2*a*	1.1670	0.6274	–0.3691	0.072
H(46)	2*a*	1.2629	0.5534	–0.2486	0.070
H(47)	2*a*	1.2111	0.5589	–0.0711	0.074
H(50)	2*a*	0.7932	0.7276	0.5227	0.063
H(51)	2*a*	0.7805	0.7455	0.6993	0.073
H(52)	2*a*	0.7843	0.8514	0.7638	0.073
H(53)	2*a*	0.8028	0.9355	0.6535	0.075
H(54)	2*a*	0.8059	0.9181	0.4733	0.059
H(55)	2*a*	0.7187	0.8930	0.3146	0.068
H(58)	2*a*	0.7270	0.8526	–0.0225	0.074
H(59)	2*a*	0.5994	0.9220	–0.1354	0.084
H(60)	2*a*	0.4485	0.9981	–0.0673	0.069
H(61)	2*a*	0.4377	1.0083	0.1142	0.070
H(62)	2*a*	0.5598	0.9380	0.2264	0.073

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)	2*a*	0.6522(9)	0.6673(4)	–0.0586(6)	0.068(4)	0.045(6)	0.052(4)	0.006(3)	0.004(3)	–0.008(3)
C(2)	2*a*	0.5706(7)	0.6816(7)	–0.1444(5)	0.068(4)	0.071(5)	0.051(3)	0.008(7)	0.002(3)	–0.008(7)
C(3)	2*a*	0.4491(9)	0.7148(4)	–0.1310(6)	0.069(5)	0.059(5)	0.051(4)	0.028(4)	–0.009(4)	0.001(4)
C(4)	2*a*	0.412(1)	0.7320(4)	–0.0340(7)	0.070(5)	0.058(5)	0.058(5)	0.031(4)	0.001(4)	0.006(4)
C(5)	2*a*	0.4998(7)	0.7156(4)	0.0512(6)	0.042(3)	0.044(4)	0.056(4)	–0.003(3)	0.008(3)	–0.001(3)
C(6)	2*a*	0.4608(6)	0.7304(3)	0.1608(6)	0.026(3)	0.032(4)	0.070(4)	0.005(2)	0.004(3)	0.004(3)
C(7)	2*a*	0.3424(7)	0.7638(4)	0.1818(6)	0.041(3)	0.055(5)	0.049(4)	0.008(3)	–0.002(3)	–0.001(3)
C(8)	2*a*	0.3086(9)	0.7729(4)	0.2860(7)	0.045(4)	0.038(5)	0.063(5)	0.014(3)	0.019(4)	0.002(3)
C(9)	2*a*	0.3964(7)	0.7493(3)	0.3639(6)	0.049(4)	0.033(4)	0.054(4)	0.005(3)	0.010(3)	–0.004(3)
C(10)	2*a*	0.5137(7)	0.7160(3)	0.3351(5)	0.039(3)	0.028(3)	0.052(4)	0.008(3)	0.009(3)	0.005(3)
C(11)	2*a*	0.1828(7)	0.8139(4)	0.3171(6)	0.044(4)	0.043(5)	0.069(5)	0.016(3)	0.024(3)	–0.005(4)
C(12)	2*a*	0.1811(8)	0.8170(4)	0.4372(6)	0.054(4)	0.042(5)	0.057(4)	0.002(3)	0.016(3)	–0.017(4)
C(13)	2*a*	0.3209(9)	0.8339(4)	0.4906(8)	0.059(5)	0.043(5)	0.070(6)	0.008(4)	0.017(4)	–0.026(4)
C(14)	2*a*	0.3607(9)	0.7599(4)	0.4749(7)	0.056(4)	0.056(5)	0.069(5)	0.010(4)	0.012(4)	0.006(4)
C(15)	2*a*	0.197(1)	0.7491(5)	0.4801(7)	0.070(5)	0.062(6)	0.069(5)	–0.013(4)	0.021(4)	–0.007(4)
C(16)	2*a*	0.312(1)	0.8510(5)	0.6063(6)	0.077(5)	0.057(5)	0.055(4)	0.008(4)	0.017(4)	–0.008(4)
C(17)	2*a*	0.4146(8)	0.8832(5)	0.4369(6)	0.058(4)	0.058(6)	0.064(5)	–0.002(4)	–0.006(4)	–0.030(4)
C(18)	2*a*	0.815(1)	0.5608(5)	0.3649(8)	0.038(4)	0.051(6)	0.053(6)	–0.008(4)	0.008(4)	–0.002(5)
C(19)	2*a*	0.8280(9)	0.5465(4)	0.4793(8)	0.048(5)	0.036(5)	0.060(5)	–0.006(3)	0.010(4)	0.004(4)
C(20)	2*a*	0.739(1)	0.5780(4)	0.5448(8)	0.081(6)	0.035(5)	0.071(6)	0.001(4)	0.026(5)	–0.006(4)
C(21)	2*a*	0.741(1)	0.5648(5)	0.6524(7)	0.068(6)	0.060(6)	0.054(5)	0.004(5)	0.014(4)	–0.004(4)
C(22)	2*a*	0.834(1)	0.5216(7)	0.6930(8)	0.062(5)	0.064(7)	0.052(6)	–0.019(5)	0.002(4)	0.004(4)
C(23)	2*a*	0.9216(9)	0.4853(4)	0.6279(6)	0.059(4)	0.057(5)	0.048(4)	–0.006(4)	–0.011(3)	0.011(4)
C(24)	2*a*	0.9176(9)	0.4992(4)	0.5198(6)	0.074(5)	0.055(5)	0.045(4)	–0.001(4)	0.000(4)	–0.002(4)
C(25)	2*a*	0.8528(8)	0.5156(4)	0.2910(5)	0.063(5)	0.042(4)	0.036(3)	–0.002(3)	0.010(3)	0.012(3)
C(26)	2*a*	0.8416(7)	0.5234(4)	0.1817(5)	0.032(3)	0.046(4)	0.049(4)	0.005(3)	0.007(3)	–0.004(3)
C(27)	2*a*	0.8745(7)	0.4658(3)	0.1126(5)	0.043(3)	0.033(4)	0.044(3)	0.013(3)	0.001(3)	0.005(3)
C(28)	2*a*	0.9171(8)	0.4787(4)	0.0122(6)	0.063(5)	0.045(5)	0.056(4)	0.001(4)	0.010(3)	0.004(4)
C(29)	2*a*	0.9549(8)	0.4275(4)	–0.0530(6)	0.059(4)	0.061(5)	0.046(4)	0.016(4)	0.011(3)	–0.016(4)
C(30)	2*a*	0.9464(8)	0.3660(4)	–0.0157(6)	0.057(4)	0.047(5)	0.062(5)	0.013(3)	–0.005(4)	–0.006(4)
C(31)	2*a*	0.9004(9)	0.3526(4)	0.0842(6)	0.079(5)	0.047(5)	0.058(4)	0.008(4)	0.019(4)	–0.006(4)
C(32)	2*a*	0.8642(9)	0.4035(3)	0.1488(6)	0.071(5)	0.021(3)	0.053(4)	–0.004(3)	–0.001(3)	–0.004(3)
C(33)	2*a*	1.1297(7)	0.6234(3)	0.2145(5)	0.051(4)	0.028(4)	0.039(3)	–0.003(3)	0.002(3)	–0.001(3)
C(34)	2*a*	1.2356(8)	0.5889(3)	0.2889(6)	0.033(3)	0.034(4)	0.053(4)	–0.007(3)	0.004(3)	0.003(3)
C(35)	2*a*	1.2018(9)	0.5839(4)	0.3928(6)	0.061(4)	0.028(4)	0.060(4)	0.006(3)	0.004(4)	–0.010(3)
C(36)	2*a*	1.301(1)	0.5543(5)	0.4623(7)	0.064(5)	0.053(6)	0.049(5)	0.008(4)	–0.018(4)	0.001(4)
C(37)	2*a*	1.4236(9)	0.5304(4)	0.4252(7)	0.058(5)	0.049(5)	0.072(5)	0.013(4)	–0.018(4)	–0.015(4)
C(38)	2*a*	1.4567(8)	0.5361(4)	0.3226(6)	0.050(4)	0.042(4)	0.058(4)	0.013(3)	–0.005(3)	–0.002(3)
C(39)	2*a*	1.3583(9)	0.5662(4)	0.2548(7)	0.056(4)	0.038(4)	0.068(5)	0.004(3)	–0.010(4)	–0.009(4)
C(40)	2*a*	1.1428(7)	0.6173(4)	0.1048(5)	0.039(3)	0.047(4)	0.048(4)	0.014(3)	0.008(3)	–0.008(3)

Table 3. Continued.

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(41)	2*a*	1.0563(7)	0.6468(3)	0.0312(6)	0.041(3)	0.032(4)	0.058(4)	0.008(3)	0.016(3)	0.004(3)
C(42)	2*a*	1.0884(8)	0.6382(4)	–0.0841(6)	0.052(4)	0.048(4)	0.047(4)	–0.008(3)	0.008(3)	–0.014(3)
C(43)	2*a*	1.0288(7)	0.6841(7)	–0.1567(5)	0.060(3)	0.056(4)	0.052(3)	–0.006(6)	0.000(3)	–0.010(7)
C(44)	2*a*	1.0594(7)	0.6780(6)	–0.2631(5)	0.066(4)	0.050(5)	0.055(3)	0.022(5)	0.014(3)	0.020(5)
C(45)	2*a*	1.1467(9)	0.6301(5)	–0.2983(6)	0.064(5)	0.068(6)	0.048(4)	0.012(4)	0.013(4)	–0.013(4)
C(46)	2*a*	1.2039(9)	0.5858(4)	–0.2256(6)	0.072(5)	0.065(6)	0.038(3)	0.022(4)	0.015(3)	–0.008(3)
C(47)	2*a*	1.174(1)	0.5893(4)	–0.1185(6)	0.073(5)	0.067(6)	0.045(4)	0.015(4)	0.010(4)	0.004(4)
C(48)	2*a*	0.7997(8)	0.8068(4)	0.3627(7)	0.040(4)	0.025(4)	0.051(5)	–0.009(3)	0.009(3)	–0.002(4)
C(49)	2*a*	0.7961(8)	0.8212(4)	0.4791(7)	0.031(3)	0.041(5)	0.039(4)	0.005(3)	–0.005(3)	–0.006(3)
C(50)	2*a*	0.792(1)	0.7695(4)	0.5484(7)	0.085(6)	0.020(4)	0.053(4)	0.011(3)	0.000(4)	0.002(3)
C(51)	2*a*	0.786(1)	0.7800(5)	0.6531(8)	0.065(5)	0.056(6)	0.062(5)	0.022(4)	0.004(4)	0.004(4)
C(52)	2*a*	0.789(1)	0.8441(7)	0.6918(7)	0.065(6)	0.075(8)	0.042(5)	0.016(5)	0.008(4)	–0.001(4)
C(53)	2*a*	0.7982(9)	0.8938(5)	0.6269(7)	0.062(5)	0.066(6)	0.058(5)	0.011(4)	–0.011(4)	–0.014(4)
C(54)	2*a*	0.8009(8)	0.8832(4)	0.5190(5)	0.053(4)	0.058(5)	0.037(3)	0.004(3)	0.004(3)	–0.008(3)
C(55)	2*a*	0.7453(8)	0.8530(5)	0.2893(6)	0.051(4)	0.068(6)	0.051(4)	0.013(4)	0.009(3)	0.004(4)
C(56)	2*a*	0.7300(8)	0.8417(4)	0.1844(6)	0.048(4)	0.049(5)	0.047(4)	0.001(3)	0.003(3)	–0.004(3)
C(57)	2*a*	0.6534(7)	0.8884(3)	0.1128(6)	0.047(3)	0.029(4)	0.065(4)	0.000(3)	0.002(3)	0.009(3)
C(58)	2*a*	0.6674(9)	0.8834(5)	0.0048(6)	0.060(5)	0.077(6)	0.049(4)	0.025(4)	0.010(3)	0.009(4)
C(59)	2*a*	0.591(1)	0.9252(5)	–0.0630(8)	0.067(5)	0.072(7)	0.070(6)	0.012(5)	–0.009(4)	0.014(5)
C(60)	2*a*	0.5017(8)	0.9712(4)	–0.0226(6)	0.056(4)	0.059(5)	0.055(4)	0.012(4)	–0.012(3)	0.001(4)
C(61)	2*a*	0.4937(9)	0.9764(4)	0.0862(7)	0.058(4)	0.051(5)	0.065(5)	0.014(4)	0.009(4)	0.027(4)
C(62)	2*a*	0.5679(9)	0.9347(4)	0.1539(7)	0.070(5)	0.056(5)	0.057(4)	0.018(4)	0.009(4)	0.008(4)
Gd(1)	2*a*	0.80811(3)	0.68252(2)	0.19401(2)	0.0407(2)	0.0530(2)	0.0384(1)	0.0115(2)	0.00700(9)	–0.0005(2)
N(1)	2*a*	0.6189(5)	0.6829(5)	0.0401(4)	0.049(2)	0.043(3)	0.054(3)	0.003(4)	0.005(2)	–0.010(5)
N(2)	2*a*	0.5514(6)	0.7077(3)	0.2362(4)	0.045(3)	0.036(3)	0.049(3)	0.011(2)	0.014(2)	0.002(2)
O(1)	2*a*	0.7656(6)	0.6178(2)	0.3393(4)	0.060(3)	0.035(3)	0.044(3)	0.015(2)	0.017(2)	–0.001(2)
O(2)	2*a*	0.8044(7)	0.5747(3)	0.1347(5)	0.054(3)	0.042(3)	0.041(3)	0.000(2)	0.004(2)	0.011(3)
O(3)	2*a*	1.0343(5)	0.6546(2)	0.2558(3)	0.051(3)	0.040(3)	0.038(2)	0.010(2)	0.011(2)	–0.006(2)
O(4)	2*a*	0.9537(4)	0.6819(4)	0.0490(3)	0.056(2)	0.045(2)	0.044(2)	0.007(4)	0.007(2)	0.018(4)
O(5)	2*a*	0.8418(6)	0.7508(2)	0.3383(4)	0.048(3)	0.034(3)	0.052(3)	0.011(2)	0.000(2)	–0.006(2)
O(6)	2*a*	0.7761(6)	0.7916(3)	0.1387(5)	0.050(3)	0.047(4)	0.050(4)	0.001(3)	0.012(2)	0.001(3)

Acknowledgment. This work was financially supported by the Doctorial Foundation (grant no. 000491) of Zhengzhou University of Light Industry.

References

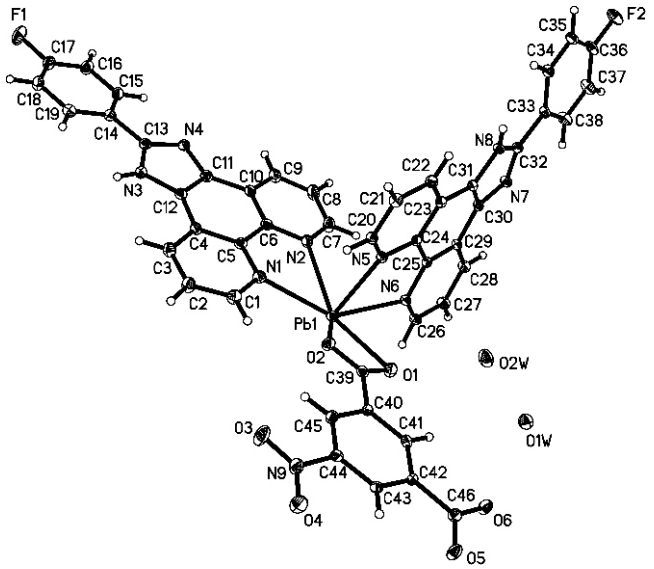
1. Hayoz, P.; Zelewsky, A. V.: New versatile optically active bipyridines as building blocks for helicating and caging ligands. Tetrahedron Lett. **33** (1992) 5165-5170.
2. Carles, R. G.; Ohlmann, R. C.: Europium thenoyltrifluoroacetonate, preparation and fluorescence properties. J. Inorg. Nucl. Chem. **27** (1965) 255-257.
3. Helen, C. A.: Chiral Lanthanide Complexes: Coordination Chemistry and Applications. Chem. Rev. **102** (2002) 1807-1850.
4. Crassous, J.: Chiral transfer in coordination complexes: towards molecular materials. Chem. Soc. Rev. **38** (2009) 830-845.
5. Fu, G. C.: Applications of planar-chiral heterocycles as ligands in asymmetric catalysis. Acc. Chem. Res. **39** (2006) 853-860.
6. Inanaga, J.; Furuno, H.; Hayano, T.: Asymmetric Catalysis and Amplification with Chiral Lanthanide Complexes. Chem. Rev. **102** (2002) 2211-2225.
7. Muller, G.; Maupin, C. L.; Riehl, J. P.; Birkedal, H.; Piguet, C.; Bunzli, G. J.: Structural, Photophysical and Chiro-Optical Properties of Lanthanide Complexes with a Bis(benzimidazole)pyridine-Based Chiral Ligand. Eur. J. Inorg. Chem. (2003) 4065-4072.
8. Aime, S.; Crich, S. G.; Gianolio, E.; Giovenzana, G. B.; Terreno, L. T.: High sensitivity lanthanide(III) based probes for MR-medical imaging Coord. Chem. Rev. **250** (2006) 1562-1579.
9. Li, X.-L.; Zheng, Y.; Zuo, J.-L.; Song, Y.; You, X.-Z.: Synthesis, crystal structure and triboluminescence of a pair of Eu(III)-based enantiomers. Polyhedron **26** (2007) 5257.
10. Li, X.-L.; He, L.-F.: Tris(dibenzoylmethanido-κ^2O,O')-[(6*S*,8*S*)-(+)-7,7-dimethyl-3-(2-pyridyl)-5,6,7,8-tetrahydro-6,8-methanoisoquinoline--κ^2N,N']gadolinium(III). Acta Crystallogr. **E65** (2009) m1050.
11. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. **A64** (2008) 112-122.

Crystal structure of (2-(4-fluorophenyl)-1*H*-imidazo[4,5-*f*][1,10]-phenanthroline)-(5-nitro-1,3-benzenedicarboxylato)lead(II) sesquihydrate, $Pb(C_{19}H_{11}N_4F)_2(C_8H_3NO_6) \cdot 1.5H_2O$

Xiu-Yan Wang*[,I,II], Shuai Ma[I,II] and Yu He[I,II]

[I] Jilin Normal University, College of Chemistry, Siping 136000, P. R. China
[II] Key Laboratory of Preparation and Applications of Environment-Friendly Materials, Jilin Normal University, Ministry of Education, Siping 136000, P. R. China

Received February 6, 2011, accepted and available on-line June 23, 2011; CCDC no. 1267/3390



Abstract

$C_{92}H_{56}F_4N_{18}O_{15}Pb_2$, monoclinic, *P*12/*c*1 (no. 13), $a = 18.290(1)$ Å, $b = 10.6611(6)$ Å, $c = 20.872(1)$ Å, $\beta = 100.122(1)°$, $V = 4006.6$ Å^3, $Z = 2$, $R_{gt(F)} = 0.039$, $wR_{ref(F^2)} = 0.096$, $T = 293$ K.

Source of material

The pH value of a mixture of $Pb(NO_3)_2$ (0.5 mmol), 5-nitro-1,3-benzenedicarboxylic acid (1,3-H_2bdc, 0.5 mmol) and 2-(4-fluorophenyl)-1*H*-imidazo[4,5-*f*][1,10]phenanthroline (L, 1 mmol) in 13 mL distilled water was adjusted between 5 and 6 by addition of triethylamine. The resultant solution was heated at 462 K in a Teflon-lined stainless steel autoclave for five days. The reaction system was then slowly cooled to room temperature. Pale yellow crystals of the title compound suitable for single crystal X-ray diffraction analysis were collected by filtration, washed several times with distilled water and dried in air at ambient temperature (28 % yield based on Pb).

Experimental details

All H atoms were positioned geometrically with d(N—H) = 0.86 Å, d(C—H) = 0.93 Å and treated as riding with U_{iso}(H) = 1.2 U_{eq}(C,N). The hydrogen atoms of O1W and O2W were not located from the difference Fourier maps.

* Correspondence author (e-mail: wangxiuyan2001@yahoo.com.cn)

Discussion

1,10-Phenanthroline (phen) is a common ligand in the field of coordination complex due to its strong ability to coordinate the metal atoms. There are many reports on the coordination compounds constructed from phen or its derivatives [1].

In the title crystal structure, the central Pb(II) atom is six-coordinated by four nitrogen atoms from two different ligands, and two carboxylate oxygen atoms from one 1,3-bdc anion in a distorted octahedral manner. The Pb—O and Pb—N bond lengths are in the normal ranges. In addition, the hydrogen bonds N3–H3A···O2W (d(N3–H3A···O2W) = 2.864(7) Å, ∠N3–H3A···O2W = 172.0°) and N8–H8A···O5 (d(N8–H8A···O5) = 2.727(6) Å, ∠N8–H8A···O5 = 161.9°) stabilize the molecular packing.

Table 1. Data collection and handling.

Crystal:	pale yellow block, size 0.18 × 0.23 × 0.31 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	42.90 cm^{-1}
Diffractometer, scan mode:	Bruker APEX CCD, φ/ω
$2\theta_{max}$:	50.12°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	20302, 7070
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 5631
$N(param)_{refined}$:	591
Programs:	SHELXS-97, SHELXL-97 [2]

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

Atom	Site	x	y	z	U_{iso}
H(1)	4*g*	0.5585	0.4277	–0.0707	0.064
H(2)	4*g*	0.5313	0.5474	–0.1636	0.065
H(3)	4*g*	0.6104	0.7074	–0.1810	0.059
H(7)	4*g*	0.8533	0.4791	0.1312	0.070
H(8)	4*g*	0.9432	0.6289	0.1223	0.075
H(9)	4*g*	0.9218	0.7719	0.0391	0.065
H(15)	4*g*	0.9349	1.0367	–0.1130	0.060
H(16)	4*g*	0.9781	1.2036	–0.1681	0.071
H(18)	4*g*	0.7864	1.2147	–0.2926	0.073
H(19)	4*g*	0.7421	1.0475	–0.2388	0.067
H(20)	4*g*	0.5738	0.5349	0.0911	0.047
H(21)	4*g*	0.5485	0.6751	0.1671	0.051
H(22)	4*g*	0.6264	0.6889	0.2674	0.048
H(26)	4*g*	0.8244	0.1345	0.1479	0.054
H(27)	4*g*	0.9183	0.1391	0.2368	0.056
H(28)	4*g*	0.9172	0.2937	0.3148	0.053
H(34)	4*g*	0.7986	0.8243	0.4452	0.049

Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
H(35)	4*g*	0.8616	0.9312	0.5344	0.057
H(37)	4*g*	1.0063	0.6483	0.5721	0.071
H(38)	4*g*	0.9451	0.5422	0.4816	0.067
H(41)	4*g*	0.5040	0.0075	0.1185	0.043
H(43)	4*g*	0.3023	–0.0450	0.0114	0.042
H(45)	4*g*	0.4297	0.2397	–0.0303	0.047
H(3A)	4*g*	0.7107	0.8734	–0.1846	0.051
H(8A)	4*g*	0.7341	0.6915	0.3666	0.039

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*g*	0.5917(3)	0.4903(6)	–0.0777(3)	0.039(4)	0.062(4)	0.058(4)	–0.018(3)	0.003(3)	0.004(3)
C(2)	4*g*	0.5744(4)	0.5628(6)	–0.1337(3)	0.042(4)	0.067(4)	0.050(4)	–0.010(3)	–0.004(3)	0.011(3)
C(3)	4*g*	0.6214(4)	0.6568(6)	–0.1442(3)	0.042(4)	0.058(4)	0.046(4)	–0.001(3)	0.004(3)	0.002(3)
C(4)	4*g*	0.6865(3)	0.6761(5)	–0.0990(3)	0.041(3)	0.046(3)	0.032(3)	–0.006(3)	0.007(3)	–0.003(3)
C(5)	4*g*	0.7013(3)	0.5956(5)	–0.0433(3)	0.035(3)	0.038(3)	0.043(3)	–0.007(3)	0.008(3)	–0.003(3)
C(6)	4*g*	0.7703(3)	0.6080(5)	0.0036(3)	0.046(4)	0.043(3)	0.038(3)	–0.011(3)	0.008(3)	–0.006(3)
C(7)	4*g*	0.8448(4)	0.5351(7)	0.0965(3)	0.053(4)	0.078(5)	0.040(3)	–0.025(4)	–0.003(3)	0.012(3)
C(8)	4*g*	0.8995(4)	0.6263(7)	0.0919(3)	0.054(4)	0.086(5)	0.043(4)	–0.033(4)	–0.003(3)	0.003(4)
C(9)	4*g*	0.8870(4)	0.7097(6)	0.0425(3)	0.051(4)	0.067(4)	0.043(4)	–0.028(3)	0.006(3)	–0.002(3)
C(10)	4*g*	0.8218(4)	0.7023(5)	–0.0033(3)	0.050(4)	0.047(3)	0.035(3)	–0.016(3)	0.006(3)	–0.004(3)
C(11)	4*g*	0.8047(3)	0.7840(6)	–0.0592(3)	0.044(4)	0.045(3)	0.044(3)	–0.011(3)	0.010(3)	–0.005(3)
C(12)	4*g*	0.7405(3)	0.7698(5)	–0.1041(3)	0.040(3)	0.038(3)	0.040(3)	–0.002(3)	0.011(3)	–0.005(3)
C(13)	4*g*	0.8082(4)	0.9230(5)	–0.1317(3)	0.050(4)	0.038(3)	0.042(3)	–0.009(3)	0.017(3)	–0.003(3)
C(14)	4*g*	0.8323(4)	1.0285(5)	–0.1691(3)	0.056(4)	0.040(3)	0.041(3)	0.000(3)	0.013(3)	–0.003(3)
C(15)	4*g*	0.9045(4)	1.0730(6)	–0.1486(3)	0.055(4)	0.050(3)	0.043(3)	–0.014(3)	0.001(3)	0.005(3)
C(16)	4*g*	0.9306(4)	1.1716(6)	–0.1816(3)	0.063(5)	0.057(4)	0.059(4)	–0.013(4)	0.013(4)	0.010(3)
C(17)	4*g*	0.8856(5)	1.2199(6)	–0.2337(3)	0.084(6)	0.050(4)	0.050(4)	0.000(4)	0.031(4)	0.009(3)
C(18)	4*g*	0.8156(5)	1.1783(6)	–0.2564(3)	0.082(6)	0.056(4)	0.043(4)	0.008(4)	0.010(4)	0.009(3)
C(19)	4*g*	0.7893(4)	1.0796(6)	–0.2238(3)	0.066(5)	0.052(4)	0.048(4)	–0.005(3)	0.006(4)	–0.005(3)
C(20)	4*g*	0.6052(3)	0.5379(5)	0.1313(3)	0.038(3)	0.046(3)	0.032(3)	–0.011(3)	–0.002(3)	0.002(3)
C(21)	4*g*	0.5899(3)	0.6233(6)	0.1767(3)	0.029(3)	0.048(3)	0.051(4)	0.002(3)	0.003(3)	0.003(3)
C(22)	4*g*	0.6361(3)	0.6319(5)	0.2362(3)	0.040(3)	0.039(3)	0.040(3)	0.003(3)	0.003(3)	0.002(3)
C(23)	4*g*	0.6983(3)	0.5521(5)	0.2487(2)	0.029(3)	0.035(3)	0.032(3)	–0.002(2)	0.005(2)	0.000(2)
C(24)	4*g*	0.7083(3)	0.4626(5)	0.2004(2)	0.028(3)	0.033(3)	0.029(3)	–0.006(2)	0.004(2)	0.001(2)
C(25)	4*g*	0.7686(3)	0.3732(5)	0.2126(2)	0.036(3)	0.033(3)	0.029(3)	–0.003(2)	0.006(2)	0.003(2)
C(26)	4*g*	0.8244(4)	0.1985(5)	0.1782(3)	0.057(4)	0.039(3)	0.042(3)	0.004(3)	0.016(3)	–0.013(3)
C(27)	4*g*	0.8809(4)	0.1991(5)	0.2320(3)	0.046(4)	0.044(3)	0.050(4)	0.010(3)	0.010(3)	–0.006(3)
C(28)	4*g*	0.8802(3)	0.2907(5)	0.2780(3)	0.042(4)	0.047(3)	0.043(3)	0.007(3)	0.004(3)	–0.004(3)
C(29)	4*g*	0.8226(3)	0.3800(5)	0.2689(2)	0.034(3)	0.035(3)	0.029(3)	0.001(2)	0.005(2)	–0.003(2)
C(30)	4*g*	0.8146(3)	0.4770(5)	0.3149(2)	0.034(3)	0.041(3)	0.025(3)	0.005(3)	–0.002(2)	0.001(2)
C(31)	4*g*	0.7538(3)	0.5549(5)	0.3060(2)	0.042(3)	0.033(3)	0.027(3)	0.001(2)	0.006(3)	0.000(2)
C(32)	4*g*	0.8304(3)	0.6027(5)	0.3957(2)	0.039(3)	0.033(3)	0.032(3)	0.004(3)	0.003(3)	–0.001(2)
C(33)	4*g*	0.8646(3)	0.6715(5)	0.4544(2)	0.036(3)	0.044(3)	0.029(3)	0.003(3)	0.002(2)	–0.002(2)
C(34)	4*g*	0.8403(3)	0.7885(5)	0.4706(3)	0.039(3)	0.047(3)	0.036(3)	0.008(3)	0.002(3)	0.000(3)
C(35)	4*g*	0.8774(4)	0.8521(6)	0.5239(3)	0.053(4)	0.047(3)	0.043(3)	–0.003(3)	0.012(3)	–0.013(3)
C(36)	4*g*	0.9380(4)	0.7972(6)	0.5613(3)	0.046(4)	0.071(4)	0.032(3)	–0.010(3)	0.000(3)	–0.020(3)
C(37)	4*g*	0.9644(4)	0.6829(6)	0.5465(3)	0.046(4)	0.080(5)	0.045(4)	0.021(4)	–0.009(3)	–0.015(3)
C(38)	4*g*	0.9276(4)	0.6199(6)	0.4926(3)	0.055(4)	0.060(4)	0.046(4)	0.023(3)	–0.007(3)	–0.013(3)
C(39)	4*g*	0.5503(3)	0.2096(5)	0.0605(3)	0.045(4)	0.047(3)	0.034(3)	–0.015(3)	0.016(3)	–0.009(3)
C(40)	4*g*	0.4785(3)	0.1368(5)	0.0471(2)	0.041(3)	0.033(3)	0.028(3)	–0.008(2)	0.012(3)	–0.001(2)
C(41)	4*g*	0.4668(3)	0.0317(5)	0.0844(2)	0.035(3)	0.043(3)	0.027(3)	0.001(3)	0.002(2)	0.000(2)
C(42)	4*g*	0.4018(3)	–0.0368(5)	0.0722(2)	0.038(3)	0.032(3)	0.031(3)	–0.006(2)	0.006(3)	0.003(2)
C(43)	4*g*	0.3468(3)	–0.0009(5)	0.0206(2)	0.032(3)	0.036(3)	0.037(3)	–0.008(2)	0.003(3)	–0.003(2)
C(44)	4*g*	0.3593(3)	0.1003(5)	–0.0163(3)	0.040(3)	0.035(3)	0.035(3)	–0.005(3)	–0.002(3)	–0.002(2)
C(45)	4*g*	0.4235(3)	0.1709(5)	–0.0044(3)	0.043(3)	0.038(3)	0.038(3)	–0.001(3)	0.011(3)	0.003(3)
C(46)	4*g*	0.3901(3)	–0.1533(5)	0.1113(3)	0.036(3)	0.043(3)	0.043(3)	–0.004(3)	–0.002(3)	0.002(3)
N(1)	4*g*	0.6525(3)	0.5052(4)	–0.0339(2)	0.036(3)	0.047(3)	0.047(3)	–0.011(2)	0.006(2)	–0.002(2)
N(2)	4*g*	0.7818(3)	0.5249(5)	0.0539(2)	0.045(3)	0.057(3)	0.034(3)	–0.018(3)	0.005(2)	0.000(2)
N(3)	4*g*	0.7435(3)	0.8596(4)	–0.1504(2)	0.047(3)	0.040(3)	0.040(3)	–0.004(2)	0.007(2)	0.002(2)
N(4)	4*g*	0.8468(3)	0.8810(4)	–0.0767(2)	0.050(3)	0.040(2)	0.040(3)	–0.016(2)	0.010(3)	–0.002(2)
N(5)	4*g*	0.6623(2)	0.4600(4)	0.1420(2)	0.029(2)	0.036(2)	0.032(2)	–0.004(2)	0.002(2)	–0.001(2)
N(6)	4*g*	0.7708(3)	0.2818(4)	0.1671(2)	0.045(3)	0.036(2)	0.032(2)	–0.005(2)	0.010(2)	–0.005(2)
N(7)	4*g*	0.8634(3)	0.5067(4)	0.3713(2)	0.040(3)	0.041(3)	0.034(2)	0.008(2)	–0.001(2)	–0.005(2)
N(8)	4*g*	0.7639(2)	0.6336(4)	0.3586(2)	0.033(3)	0.031(2)	0.033(2)	0.006(2)	0.003(2)	–0.004(2)
N(9)	4*g*	0.3005(3)	0.1321(5)	–0.0719(3)	0.052(4)	0.058(3)	0.047(3)	–0.008(3)	–0.007(3)	0.012(3)
O(1)	4*g*	0.6020(2)	0.1700(4)	0.1023(2)	0.040(3)	0.063(3)	0.047(2)	–0.018(2)	–0.002(2)	0.008(2)
O(2)	4*g*	0.5552(2)	0.3066(3)	0.0270(2)	0.042(2)	0.045(2)	0.051(2)	–0.015(2)	0.007(2)	0.004(2)
O(1W)	2*f*	½	–0.0202(6)	¼	0.068(4)	0.060(4)	0.049(3)	0	0.002(3)	0

Table 3. Continued.

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(3)	4*g*	0.3076(3)	0.2289(5)	–0.1021(3)	0.078(4)	0.087(4)	0.078(4)	–0.030(3)	–0.027(3)	0.046(3)
O(2W)	4*g*	0.6278(3)	0.1173(5)	0.2384(2)	0.069(4)	0.107(4)	0.048(3)	–0.019(3)	–0.003(3)	–0.004(3)
O(4)	4*g*	0.2467(3)	0.0657(5)	–0.0844(2)	0.056(3)	0.079(3)	0.072(3)	–0.027(3)	–0.025(3)	0.020(3)
O(5)	4*g*	0.3308(2)	–0.2117(4)	0.0916(2)	0.045(3)	0.061(3)	0.062(3)	–0.022(2)	–0.007(2)	0.021(2)
O(6)	4*g*	0.4389(3)	–0.1832(4)	0.1577(2)	0.054(3)	0.056(3)	0.054(3)	–0.017(2)	–0.015(2)	0.019(2)
F(1)	4*g*	0.9106(3)	1.3208(4)	–0.2650(2)	0.107(4)	0.084(3)	0.087(3)	–0.007(3)	0.040(3)	0.040(2)
F(2)	4*g*	0.9733(2)	0.8590(4)	0.6147(2)	0.054(2)	0.094(3)	0.049(2)	–0.009(2)	–0.006(2)	–0.032(2)
Pb(1)	4*g*	0.69111(1)	0.32580(2)	0.05121(1)	0.0374(1)	0.0411(1)	0.0367(1)	–0.0080(1)	0.0049(1)	–0.0036(1)

Acknowledgments. The authors thank the Key Laboratory of Preparation and Applications of Environment-Friendly Materials and Institute Foundation of Siping City (grant no. 2009011) for supporting this work.

References

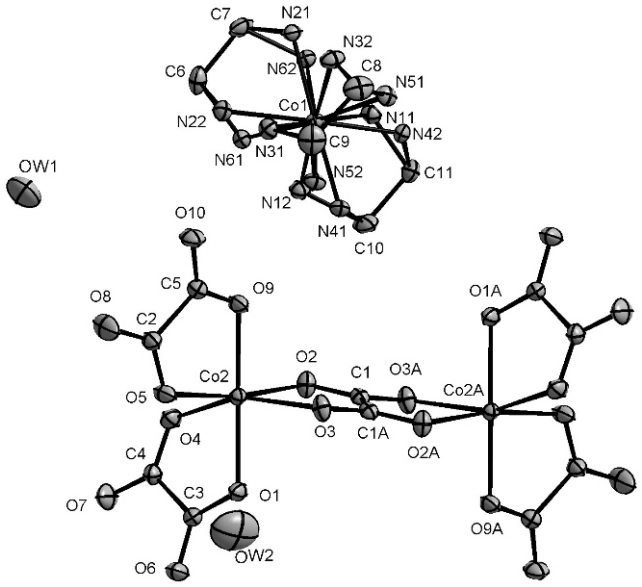
1. Kong, Z.-G.; Wang, M.; Ma, X.-Y.; Wang, Q.-W.: *catena*-Poly[[aqua(11-chloropyrido[2′,3′:2,3]pyrimidino[5,6-*f*][1,10]phenanthroline-κ^2N^4,N^5)cadmium(II)]-benzene-1,4-dicarboxylato-$\kappa^3O^1,O^{1'}:O^4$]: an inclined interpenetrating (6,3) network. Acta Crystallogr. **C65** (2009) m472-m474.
2. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. **A64** (2008) 112-122.

Crystal structure of bis[tris(ethylenediamine)cobalt(III)] pentaoxalatocobaltate(II) tetrahydrate, $[Co(C_2H_8N_2)_3]_2[Co_2(C_2O_4)_5] \cdot 4H_2O$

Jaeun Kang[I], Seungmoon Pyo[I], Hoseop Yun[II] and Junghwan Do[*,I]

[I] Konkuk University, Department of Chemistry, Seoul 147-701, Republic of Korea
[II] Ajou University, Division of Energy Systems Reseach and Department of Chemistry, Suwon 441-749, Republic of Korea

Received November 30, 2010, accepted and available on-line June 17, 2011; CCDC no. 1267/3315



Abstract

$C_{22}H_{56}Co_4N_{12}O_{24}$, triclinic, $P\bar{1}$ (no. 2), a = 7.988(2) Å, b = 10.218(2) Å, c = 12.873(3) Å, α = 100.85(3)°, β = 92.14(3)°, γ = 93.57(3)°, V = 1028.6 Å^3, Z = 1, $R_{gt}(F)$ = 0.037, $wR_{ref}(F^2)$ = 0.119, T = 293 K.

Source of material

A mixture of CoO · $6H_2O$ (0.0582 g, 0.2 mmol), oxalic acid (0.018 g, 0.2 mmol), ethylenediamine (0.013 ml, 0.2 mmol), and water (0.6 ml) was sealed under vacuum in a Pyrex tube and heated to 150 °C for 2 days under autogenous pressure, followed by cooling to 30 °C with 10 °C/h. The solid products were recovered by vacuum filtration and washed with water. Red polyhedral crystals suitable for analysis with unidentified white powder were obtained.

Experimental details

The hydrogen atoms of lattice water molecules were not located (large thermal parameters of oxygen atoms). Also, all hydrogen atoms on ethylenediamine cannot be found due to the disorder of all nitrogen atoms.

Discussion

The crystal structure of the title compound comprises discrete centrosymmetric dinuclear $[Co_2(C_2O_4)_5]^{6-}$ anions, mononuclear $[Co(C_2H_8N_2)_3]^{3+}$ cations, and water molecules. The anionic dimer contains four terminal chelating and one bridging bis-bidentate oxalate ligands. Each Co2 atom is coordinated in a slightly distorted octahedral manner by six oxygen atoms of three oxalate ligands in the range of 77.83(9)° - 114.98(10)° and 156.40(9)° - 170.74(9)°. The cobalt-to-bridging oxalate bond lengths are slightly longer than those involving the terminal oxalate ligands. A similar trend can be observed in several other $[M_2(C_2O_4)_5]^{n-}$ anionic complexes (M = Fe, Cr, Ni, Zn; n = 4 or 6) [1-7]. The BVS calculation for Co in $[Co_2(C_2O_4)_5]^{6-}$ anions gives a value of 2.02, indicating an oxidation state of +2 [8]. Co1 in $[Co(en)_3]^{3+}$ is coordinated to three ethylenediamine molecules in a slightly distorted octahedral manner. Two nitrogen atoms in each ethylenediamine molecule are disordered almost equally over two positions, giving two possible conformations, *gauche*- and and *syn*- conformation. The *gauche*-conformation is considered more likely since it minimizes nitrogen-nitrogen repulsions and is usually observed for $M(en)_3$ cations [9-12]. Therefore, two sets of *gauche*-conformational $[Co(en)_3]^{3+}$ cations are almost equally distributed in the structure, i.e., one set of N1–C6–C7–N4, N5–C8–C9–N8, N9–C10–C11–N12, and the other set of N2–C6–C7–N3, N6–C8–C9–N7, N10–C10–C11–N11, with torsional angles in the range of 56.51(3)° - 61.76(3)°. The other possible arrangement is *synperiplanar*. However, the *syn*-conformation of ethylenediamine in octahedral $M(en)_3$ geometry is energetically unfavorable and is not reported yet. The crystal packing of the title complex is stabilized by hydrogen bonds between the $[Co(C_2H_8N_2)_3]^{3+}$ cations and $[Co_2(C_2O_4)_5]^{6-}$ anions. Besides, two inequivalent lattice water molecules are further hydrogen bonded among to the monomeric cations, dimeric anions, or to each other in a complex arrangement.

Table 1. Data collection and handling.

Crystal:	red polyhedral, size 0.16 × 0.23 × 0.26 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	16.86 cm^{-1}
Diffractometer, scan mode:	Regaku R-AXIS RAPID, ω
$2\theta_{max}$:	54.96°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	10220, 4659
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 4070
$N(param)_{refined}$:	340
Programs:	SHELXS-97, SHELXL-97 [13], DIAMOND [14]

* Correspondence author (e-mail: junghwan@konkuk.ac.kr)

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}
Co(1)	2*i*		0.07526(4)	0.27340(3)	0.25000(3)	0.0186(2)	0.0232(2)	0.0223(2)	0.0020(1)	0.0006(1)	0.0052(1)
Co(2)	2*i*		–0.40012(5)	0.70669(4)	0.16424(3)	0.0313(2)	0.0232(2)	0.0213(2)	0.0060(2)	–0.0025(2)	0.0012(1)
O(1)	2*i*		–0.6136(3)	0.7944(2)	0.1282(2)	0.028(1)	0.026(1)	0.049(1)	–0.0011(8)	–0.0102(9)	0.0076(9)
O(2)	2*i*		–0.3360(3)	0.6228(2)	0.0116(2)	0.039(1)	0.032(1)	0.027(1)	–0.0077(9)	0.0064(9)	0.0019(8)
O(3)	2*i*		–0.5692(3)	0.5295(2)	0.1280(2)	0.048(1)	0.029(1)	0.0215(9)	–0.0023(9)	0.0097(9)	0.0030(8)
O(4)	2*i*		–0.2985(3)	0.8965(2)	0.1490(2)	0.025(1)	0.035(1)	0.052(1)	0.0000(8)	–0.001(1)	0.007(1)
O(5)	2*i*		–0.4245(3)	0.7865(3)	0.3250(2)	0.057(2)	0.048(1)	0.025(1)	0.031(1)	–0.003(1)	0.0004(9)
O(6)	2*i*		–0.7081(3)	0.9945(2)	0.1360(2)	0.034(1)	0.035(1)	0.070(2)	0.012(1)	–0.006(1)	0.005(1)
O(7)	2*i*		–0.3846(3)	1.1015(3)	0.1618(3)	0.050(2)	0.027(1)	0.090(2)	–0.009(1)	–0.014(2)	0.008(1)
O(8)	2*i*		–0.3044(5)	0.7885(3)	0.4829(2)	0.114(3)	0.077(2)	0.024(1)	0.054(2)	–0.011(1)	–0.008(1)
O(9)	2*i*		–0.2392(3)	0.5958(2)	0.2383(2)	0.052(1)	0.038(1)	0.029(1)	0.024(1)	–0.004(1)	–0.0020(9)
O(10)	2*i*		–0.1476(3)	0.5670(3)	0.3967(2)	0.056(2)	0.044(1)	0.039(1)	0.022(1)	–0.008(1)	0.012(1)
OW(1)	2*i*		0.3275(6)	0.9464(5)	0.4064(4)	0.097(3)	0.096(3)	0.128(4)	0.043(3)	0.006(3)	–0.020(3)
OW(2)	2*i*		–0.8754(6)	0.7436(6)	0.2686(5)	0.078(3)	0.151(5)	0.196(6)	–0.012(3)	0.034(3)	0.064(5)
N(11)	2*i*	0.542(8)	0.1450(5)	0.2200(5)	0.1030(3)	0.026(2)	0.029(2)	0.024(2)	0.005(2)	0.006(2)	0.005(2)
N(12)	2*i*	0.458	0.0237(7)	0.4115(5)	0.1639(4)	0.035(3)	0.028(3)	0.026(3)	0.008(2)	0.000(2)	0.006(2)
N(21)	2*i*	0.544(8)	0.2994(5)	0.2357(5)	0.3035(4)	0.023(2)	0.029(2)	0.034(2)	0.004(2)	–0.004(2)	0.009(2)
N(22)	2*i*	0.456	0.1586(7)	0.4200(6)	0.3724(4)	0.031(3)	0.032(3)	0.028(3)	0.003(2)	–0.001(2)	0.002(2)
N(31)	2*i*	0.545(8)	–0.0114(6)	0.3067(5)	0.3916(3)	0.030(2)	0.033(3)	0.025(2)	0.003(2)	0.005(2)	0.005(2)
N(32)	2*i*	0.455	0.1079(7)	0.1371(6)	0.3323(5)	0.030(3)	0.036(3)	0.040(3)	0.002(2)	–0.002(2)	0.019(2)
N(41)	2*i*	0.571(7)	–0.1367(5)	0.3124(4)	0.1845(3)	0.023(2)	0.030(2)	0.033(2)	0.008(2)	–0.001(2)	0.002(2)
N(42)	2*i*	0.429	–0.0004(7)	0.1423(5)	0.1264(4)	0.025(3)	0.023(3)	0.028(3)	0.000(2)	–0.007(2)	0.001(2)
N(51)	2*i*	0.565(8)	–0.0061(5)	0.0819(4)	0.2463(4)	0.028(2)	0.025(2)	0.037(2)	–0.001(2)	0.004(2)	0.010(2)
N(52)	2*i*	0.435	–0.1527(7)	0.2824(6)	0.3058(5)	0.023(3)	0.032(3)	0.035(3)	0.006(2)	0.005(2)	0.009(2)
N(61)	2*i*	0.545(7)	0.1658(5)	0.4566(4)	0.2658(4)	0.027(2)	0.022(2)	0.031(2)	0.003(2)	–0.003(2)	0.002(2)
N(62)	2*i*	0.455	0.3089(6)	0.2766(5)	0.2096(4)	0.022(3)	0.027(3)	0.031(3)	0.002(2)	–0.001(2)	0.003(2)
C(1)	2*i*		–0.4322(3)	0.5268(3)	–0.0334(2)	0.032(1)	0.022(1)	0.020(1)	0.005(1)	0.003(1)	0.0065(9)
C(2)	2*i*		–0.3263(4)	0.7438(3)	0.3876(2)	0.042(2)	0.033(2)	0.027(1)	0.013(1)	–0.002(1)	0.003(1)
C(3)	2*i*		–0.5942(4)	0.9187(3)	0.1366(2)	0.028(1)	0.026(1)	0.031(1)	0.004(1)	–0.005(1)	0.003(1)
C(4)	2*i*		–0.4088(4)	0.9794(3)	0.1499(2)	0.032(1)	0.026(1)	0.036(2)	–0.002(1)	–0.004(1)	0.005(1)
C(5)	2*i*		–0.2270(4)	0.6264(3)	0.3374(2)	0.031(1)	0.027(1)	0.031(1)	0.004(1)	–0.001(1)	0.005(1)
C(6)	2*i*		0.3204(4)	0.4732(3)	0.3496(3)	0.040(2)	0.038(2)	0.037(2)	–0.013(1)	0.003(1)	–0.004(1)
C(7)	2*i*		0.4168(4)	0.3542(4)	0.3098(3)	0.023(1)	0.044(2)	0.056(2)	–0.004(1)	–0.011(1)	0.015(2)
C(8)	2*i*		–0.0587(5)	0.0761(4)	0.3594(3)	0.042(2)	0.052(2)	0.053(2)	–0.002(2)	0.006(2)	0.031(2)
C(9)	2*i*		–0.1444(5)	0.2010(4)	0.4003(3)	0.049(2)	0.058(2)	0.044(2)	–0.006(2)	0.021(2)	0.014(2)
C(10)	2*i*		–0.0978(5)	0.3296(4)	0.0695(3)	0.060(2)	0.058(2)	0.030(2)	0.027(2)	–0.014(2)	0.004(2)
C(11)	2*i*		–0.0079(4)	0.2066(3)	0.0300(2)	0.040(2)	0.039(2)	0.027(1)	0.003(1)	–0.005(1)	–0.001(1)

Acknowledgment. This work was supported by the National Research Foundation of Korea Grant funded by the Korean Govenment (grant no. KRF-2008-314-C00190).

References

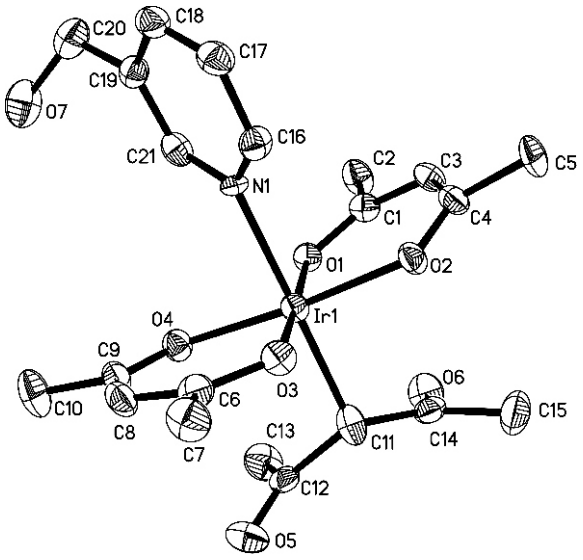
1. Vaidhyanathan, R.; Natarajan, S.; Rao, C. N. R.: Synthesis of a Hierarchy of Zinc Oxalate Sturctures from Amine Oxalates. J. Chem. Soc., Dalton Trans. (2001) 699-706.
2. Armentano, D.; De Munno, G.; Lloret, F.; Julve, M.: Bi and Tris(oxalato)-ferrate(III) Complexes as Precursors of Polynuclear Compounds. CrystEngComm **7** (2005) 57-66.
3. Armentano, D.; De Munno, G.; Faus, J.; Lloret, F.; Julve, M.: Syntheses, Crystal Structures, and Magnetic Properties of the Oxalato-Bridged Mixed-Valence Complexes $[Fe^{II}(bpm)_3]_2[Fe^{III}_2(ox)_5] \cdot 8H_2O$ and $Fe^{II}(bpm)_3Na(H_2O)_2Fe(ox)_3 \cdot 4H_2O$ (bpm = 2,2′-Bipyrimidine). Inorg. Chem. **40** (2001) 655-660.
4. Román, P.; Guzmán-Miralles, C.; Luque, A.; Beitia, J. I.; Cano, J.; Lloret, F.; Julve, M.; Alvarez, S.: Influenece of the Peripheral Ligand Atoms on the Exchange Interaction in Oxalato-Bridged Nickel(II) Complexes: An Orbital Model. Crystal Structures and Magnetic Properties of $(H_3dien)_2[Ni_2(ox)_5] \cdot 12H_2O$ and $[Ni_2(dien)_2(H_2O)_2(ox)]Cl_2$. Inorg. Chem. **35** (1996) 3741-3751.
5. Coronado, E.; Galán-Mascarós, J. R.; Gómez-Garcí, C. J.: Charge Transfer Salts of Tetrathiafulvalene Derivatives with Magnetic Iron(III) Oxalate Complexes: $[TTF]_7[Fe(ox)_3]_2 \cdot 4H_2O$, $[TTF]_5[Fe_2(ox)_5] \cdot 2PhMe \cdot 2H_2O$ and $[TMTTF]_4[Fe_2(ox)_5] \cdot PhCN \cdot 4H_2O$ (TMTTF = tetramethyltetrathiafulvalene). J. Chem. Soc., Dalton Trans. (2000) 205-210.
6. Rashid, S.; Turner, S. S.; Day, P.; Light, M. E.; Hursthouse, M. B.: Molecular Charge-Transfer Salt of BEDT-TTF [Bis(ethylenedithio)tetrathiafulvalene] with the Oxalate-Bridged Dimeric Anion $[Fe_2(C_2O_4)_5]^{4-}$. Inorg. Chem. **39** (2000) 2426-2428.
7. Masters, V. M.; Sharrad, C. A.; Bernhardt, P. V.; Gahan, L. R.; Moubaraki, B.; Murray, K. S.: Synthesis, Structure and Magnetism of the Oxalato-Bridged Chromium(III) Complex $[NBun_4]_4[Cr_2(ox)_5] \cdot 2CHCl_3$. J. Chem. Soc., Dalton Trans. (1998) 413-416.
8. Brese, N. E.; O'Keeffe, M.: Bond-Valence Parameters for Solids. Acta Crystallogr. **B47** (1991) 192-197.
9. Hea, X.; Zhang, P.; Song, T.-Y.; Mu, Z.-C.; Yu, J.-H.; Wang, Y.; Xu, J.-N.: Hydrothermal Synthesis and Structure of a Molybdenum(VI) Phosphate Cluster and a Three Dimensional Cobalt Molybdenum(V) Phosphate. Polyhedron **23** (2004) 2153-2159.
10. Bontchev, R. P.; Venturini, E. L.; Nyman, M.: Copper-Linked Hexaniobate Lindqvist Clusters-Variations on a Theme. Inorg. Chem. **46** (2007) 4483-4491.
11. Takamizawa, S.; Akatsuka, T.; Ueda, T.: Gas-Conforming Transformability of an Ionic Single-Crystal Host Consisting of Discrete Charged Components. Angew. Chem., Int. Ed. **47** (2008) 1689-1692.
12. Matiková-Mal'arová, M.; Cernák, J.; Massa, W.; Varret, F.: Three Co(III)-Fe(II) Complexes Based on Hexacyanoferrates: Syntheses, Spectroscopic and Structural Characterizations. Inorg. Chim. Acta **362** (2009) 443-448.
13. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. **A64** (2008) 112-122.
14. Brandenburg, K.: DIAMOND. Visual Crystal Structure Information System. Version 3.2f. Crystal Impact, Bonn, Germany 1998.

Crystal structure of bis(acetylacetonato-κ^2O,O')-(diacetylmethanido-κC)-(3-pyridylmethanol)iridium(III), $Ir(C_5H_7O_2)_3(C_6H_7NO)$

Qiao-Wen Chang, Chang-Yi Hu, Jia-Lin Chen, Qing-Song Ye, Xi-Zhu Chen, Li-Qiao Chen, Yao Yu and Wei-Ping Liu*

State Key Laboratory of Advanced Technologies for Platinum Metals, Kunming Institute of Precious Metal, Kunming 650106, P. R. China

Received December 24, 2010, accepted and available on-line June 17, 2011; CCDC no. 1267/3343



Abstract

$C_{21}H_{28}IrNO_7$, monoclinic, *C*1*c*1 (no. 9), a = 16.938(2) Å, b = 8.0768(8) Å, c = 16.265(2) Å, β = 95.124(1)°, V = 2216.3 Å^3, Z = 4, $R_{gt}(F)$ = 0.028, $wR_{ref}(F^2)$ = 0.053, T = 298 K.

Source of material

The titled complex was prepared by refluxing aquabis(acetylacetonato-κ^2O,O')(diacetylmethanido-κC)iridium(III) and a large excess of 3-pyridylmethanol, and then the insoluble residual was filtered off. The filtrate was slowly cooled to room temperature along with evaporation, a yellow crystalline product precipitated. Single crystals were selected from the product for the X-ray diffraction analysis.

Experimental details

All the hydrogen atoms were positioned geometrically with d(C—H) = 0.93 - 0.98 Å, d(O—H) = 0.82 Å and refined as riding with U_{iso}(H) = 1.2 or 1.5 U_{eq}(C) and U_{iso}(H) = 1.5 U_{eq}(O). The refined Flack parameter of 0.004(9) implies that the absolute structure is correct.

Discussion

In the title crystal structure, the Ir atom is six-coordinated and situated in a slightly distorted octahedral environment, formed by four oxygen atoms of two acetylacetone ligands, one carbon atom of one acetylacetone ligand and one N atom of 3-pyridylmethanol. The average O–Ir–O chelating angle is 95.135°. The average Ir—O bond length of two acetylacetone ligands is 2.025(4) Å, Ir—C bond length is found to be 2.09(2) Å, which agree with the literature data of $Ir(C_5H_7O_2)_3$, $Ir(C_5H_7O_2)_3(H_2O)$, $Ir(C_5H_7O_2)_3(C_2H_6SO)$ and $Ir(C_5H_7O_2)_3(CH_3CN) \cdot 1.5H_2O$ [1-5]. The Ir—N bond length is found to be 2.13(1) Å. Change in the coordination mode of one acetylacetonate ligand of tris(acetylacetonato-*O*,*O*)iridium(III) lead to the formation of the direct Ir-C bond . In this complex, the average Ir—O, Ir—C and Ir—N bond lengths are close to each other. The Ir—C bond length is found to be between a Ir—C σ-bond (2.00 - 2.02 Å) and a Ir—C π-bond (2.27 - 2.31 Å) [3]. The crystal structure also reveals that there are two different types of coordinated acac ligands: a conventional bidentate (O-bonded acac ligand) and a γ-C bonded acac ligand in the title complex, as Periana proposed [3].

The crystal packing is stablilized by extensive hydrogen bonds formed between 3-pyridinemethanol and carbonyl O atoms of the acetylacetone ligand with d(O7–H7···O6) of 2.864(8) Å and ∠O7–H7···O6 = 164.3°.

Table 1. Data collection and handling.

Crystal:	yellow block, size 0.12 × 0.14 × 0.26 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	60.65 cm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD, φ/ω
$2\theta_{max}$:	56.4°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	7210, 3791
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 3397
$N(param)_{refined}$:	278
Programs:	SHELXS-97, SHELXL-97 [6], DIAMOND [7]

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

Atom	Site	x	y	z	U_{iso}
H(7)	4*a*	0.6107	0.4127	0.2983	0.104
H(2A)	4*a*	0.2386	0.7592	0.4057	0.079
H(2B)	4*a*	0.3151	0.8082	0.4617	0.079
H(2C)	4*a*	0.3138	0.6455	0.4090	0.079
H(3)	4*a*	0.3283	1.0699	0.3974	0.048
H(5A)	4*a*	0.4258	1.3422	0.3174	0.078
H(5B)	4*a*	0.3462	1.3382	0.3596	0.078
H(5C)	4*a*	0.3455	1.3818	0.2656	0.078
H(7A)	4*a*	0.4850	1.0374	–0.0558	0.083
H(7B)	4*a*	0.5446	0.8904	–0.0622	0.083
H(7C)	4*a*	0.5622	1.0281	0.0048	0.083
H(8)	4*a*	0.5140	0.6500	0.0001	0.054

* Correspondence author (e-mail: liuweiping0917@126.com)

Table 2. Continued.

Atom	Site	*x*	*y*	*z*	U_{iso}
H(10A)	4*a*	0.5095	0.3714	0.1142	0.101
H(10B)	4*a*	0.4689	0.3777	0.0238	0.101
H(10C)	4*a*	0.4178	0.3436	0.0978	0.101
H(11)	4*a*	0.2857	0.9477	0.0612	0.055
H(13A)	4*a*	0.1710	0.5800	0.1095	0.095
H(13B)	4*a*	0.2489	0.5732	0.1692	0.095
H(13C)	4*a*	0.2408	0.4637	0.0893	0.095
H(15A)	4*a*	0.1623	1.1393	0.0947	0.102

Table 2. Continued.

Atom	Site	*x*	*y*	*z*	U_{iso}
H(15B)	4*a*	0.2467	1.1776	0.1381	0.102
H(15C)	4*a*	0.1740	1.1607	0.1908	0.102
H(16)	4*a*	0.5312	1.0789	0.2137	0.047
H(17)	4*a*	0.6525	1.0814	0.2877	0.055
H(18)	4*a*	0.6928	0.8524	0.3670	0.054
H(20A)	4*a*	0.6759	0.5627	0.3949	0.073
H(20B)	4*a*	0.5966	0.5692	0.4375	0.073
H(21)	4*a*	0.4891	0.6410	0.2923	0.048

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}
Ir(1)	4*a*	0.38668(3)	0.86191(2)	0.17848(3)	0.0385(1)	0.0298(1)	0.0291(1)	–0.0001(3)	0.00554(7)	0.0010(3)
N(1)	4*a*	0.4998(7)	0.859(1)	0.2476(6)	0.025(4)	0.038(5)	0.025(5)	0.004(3)	–0.009(3)	–0.004(3)
O(1)	4*a*	0.3397(3)	0.7651(5)	0.2778(3)	0.040(3)	0.036(3)	0.030(3)	0.002(2)	0.007(2)	0.004(2)
O(2)	4*a*	0.3767(3)	1.1003(5)	0.2149(3)	0.055(3)	0.025(2)	0.035(2)	0.001(2)	0.003(2)	–0.003(2)
O(3)	4*a*	0.4391(3)	0.9613(5)	0.0830(3)	0.046(3)	0.038(3)	0.037(3)	–0.004(2)	0.009(2)	0.006(2)
O(4)	4*a*	0.4061(3)	0.6230(5)	0.1473(3)	0.046(3)	0.033(3)	0.040(3)	0.001(2)	0.006(2)	0.001(2)
O(5)	4*a*	0.2791(3)	0.6804(7)	–0.0046(3)	0.079(4)	0.080(4)	0.036(3)	–0.002(3)	0.001(3)	–0.008(3)
O(6)	4*a*	0.1755(3)	0.8587(6)	0.1999(3)	0.053(3)	0.066(4)	0.063(4)	–0.002(3)	0.024(3)	0.000(3)
O(7)	4*a*	0.5934(3)	0.4161(7)	0.3437(4)	0.072(4)	0.043(3)	0.095(5)	0.003(3)	0.020(3)	0.017(3)
C(1)	4*a*	0.3258(5)	0.8551(9)	0.3383(5)	0.037(5)	0.042(4)	0.034(5)	–0.003(4)	0.006(4)	0.002(4)
C(2)	4*a*	0.2955(5)	0.7579(9)	0.4105(5)	0.076(6)	0.045(5)	0.041(4)	0.003(4)	0.022(4)	0.003(4)
C(3)	4*a*	0.3374(4)	1.0254(8)	0.3463(4)	0.048(4)	0.045(4)	0.028(4)	–0.002(3)	0.009(3)	–0.009(3)
C(4)	4*a*	0.3606(4)	1.1377(8)	0.2884(4)	0.040(4)	0.041(4)	0.034(4)	–0.002(3)	0.005(3)	–0.011(3)
C(5)	4*a*	0.3704(5)	1.3157(8)	0.3096(5)	0.072(6)	0.023(4)	0.062(5)	0.002(3)	0.013(4)	–0.008(3)
C(6)	4*a*	0.4772(5)	0.865(1)	0.0351(6)	0.035(5)	0.058(6)	0.037(5)	0.002(4)	0.008(4)	0.002(4)
C(7)	4*a*	0.5213(4)	0.964(1)	–0.0250(5)	0.053(5)	0.066(5)	0.050(5)	–0.007(4)	0.018(4)	0.001(4)
C(8)	4*a*	0.4828(4)	0.6970(9)	0.0382(4)	0.049(4)	0.050(5)	0.038(4)	0.003(3)	0.012(3)	–0.012(3)
C(9)	4*a*	0.4490(4)	0.5855(9)	0.0893(4)	0.044(4)	0.042(4)	0.043(4)	0.004(3)	0.008(3)	–0.012(3)
C(10)	4*a*	0.4625(6)	0.4031(9)	0.0805(6)	0.094(7)	0.038(5)	0.075(6)	0.006(4)	0.032(5)	–0.008(4)
C(11)	4*a*	0.279(1)	0.870(1)	0.106(1)	0.048(8)	0.035(7)	0.058(8)	–0.005(5)	0.025(6)	–0.005(5)
C(12)	4*a*	0.2611(6)	0.702(2)	0.0664(7)	0.027(4)	0.043(6)	0.040(5)	0.000(4)	–0.007(4)	0.000(4)
C(13)	4*a*	0.2276(5)	0.568(1)	0.1126(5)	0.073(6)	0.049(5)	0.068(6)	–0.014(4)	0.005(4)	–0.002(4)
C(14)	4*a*	0.2133(4)	0.941(1)	0.1526(5)	0.035(4)	0.054(5)	0.039(4)	0.004(3)	–0.007(3)	0.000(4)
C(15)	4*a*	0.1977(5)	1.1204(9)	0.1432(6)	0.070(6)	0.050(5)	0.085(7)	0.022(4)	0.004(5)	0.005(5)
C(16)	4*a*	0.5474(4)	0.9875(9)	0.2456(5)	0.044(4)	0.030(4)	0.043(5)	0.000(3)	0.001(4)	0.007(3)
C(17)	4*a*	0.6197(4)	0.9893(9)	0.2893(4)	0.045(4)	0.044(4)	0.048(4)	–0.009(3)	0.004(3)	–0.007(3)
C(18)	4*a*	0.6439(4)	0.8528(9)	0.3361(4)	0.038(4)	0.058(5)	0.040(4)	0.000(4)	0.005(3)	–0.011(4)
C(19)	4*a*	0.5946(4)	0.7174(8)	0.3363(4)	0.040(4)	0.041(4)	0.036(4)	0.006(3)	0.007(3)	0.004(3)
C(20)	4*a*	0.6186(5)	0.565(1)	0.3845(5)	0.055(5)	0.063(5)	0.064(6)	0.011(4)	0.006(4)	0.013(5)
C(21)	4*a*	0.5236(6)	0.731(2)	0.2916(7)	0.046(6)	0.032(5)	0.043(5)	–0.008(5)	0.012(5)	–0.004(4)

Acknowledgments. This work was financially supported by Science and Technology Development Program of Yunnan Province (grant nos. 2008IA008, 2008CF002, 2009CD133 and 2009CI019).

References

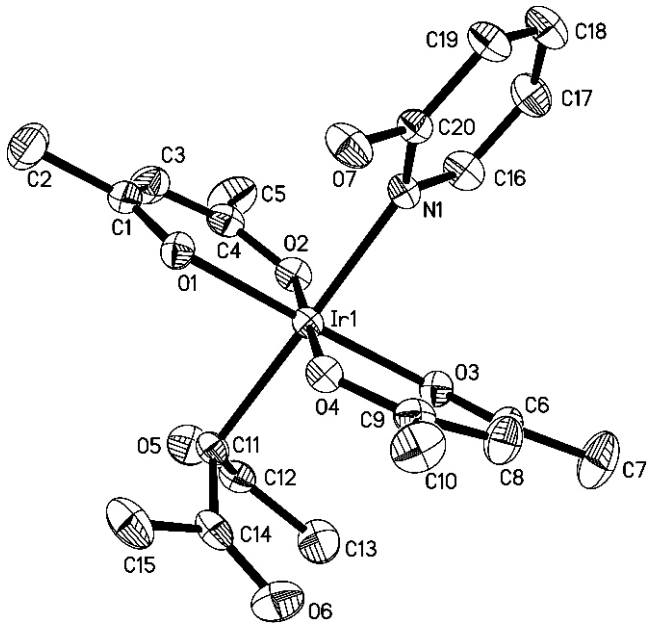
1. Isakova, V. G.; Baidina, I. A.; Morozova, N. B.; Igumenov, I. K.: γ-Halogenated iridium(III)acetylacetonates. Polyhedron **19** (2000) 1097-1103.
2. Chang, Q. W.; Xie, M. J.; Liu, W. P.; Chen, X. Z.; Ye, Q. S.: Bis-(acetylacetonato-2*O*,*O'*)aqua(diacetylmethanido-*C*)iridium(III). Acta Crystallogr. **E65** (2009) m1264.
3. Matsumoto, T.; Periana, R. A.; Taube, D. J.; Yoshida, H.: Regioselective hydrophenylation of olefins catalyzed by an Ir(III) complex. J. Mol. Catal. **A180** (2002) 1-18.
4. Jiang, J.; Xie, M. J.; Chang, Q. W.; Chen, J. L.; Xie, X. T.; Ye, Q. S.; Chen, X. Z.; Yu, Y.; Liu, W. P.: Crystal structure of bis(acetylacetonato-κ^2*O*,*O'*)-(diacetylmethanido-κ*C*)-(dimethylsulfoxide-*S*)iridium(III), $Ir(C_5H_7O_2)_3(C_2H_6SO)$. Z. Kristallogr. NCS **225** (2010) 575-576.
5. Chang, Q. W.; Hu, C, Y.; Pan, Z. F.; Chen, J. L.; Ye, Q. S.; Chen, X. Z.; Yu, Y.; Liu, W. P.: Crystal structure of bis(acetylacetonato-κ^2*O*,*O'*)-(diacetylmethanido-κ*C*)-(acetonitrile-*N*)iridium(III) sesquihydrate, $Ir(C_5H_7O_2)_3(CH_3CN) \cdot 1.5H_2O$. Z. Kristallogr. NCS **225** (2010) 667-668.
6. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. **A64** (2008) 112-122.
7. Brandenburg, K.: DIAMOND. Visual Crystal Structure Information System. Version 3.2c. Crystal Impact, Bonn, Germany 1998.

Crystal structure of bis(acetylacetonato-κ^2O,O')-(diacetylmethanido-κC)-(2-hydroxypyridine)iridium(III), $Ir(C_5H_7O_2)_3(C_5H_5NO)$

Qiao-Wen Chang, Chang-Yi Hu, Jia-Lin Chen, Qing-Song Ye, Xi-Zhu Chen, Yao Yu, Li-Qiao Chen and Wei-Ping Liu*

State Key Laboratory of Advanced Technologies for Platinum Metals, Kunming Institute of Precious Metal, Kunming 650106, P. R. China

Received December 24, 2010, accepted and available on-line June 17, 2011; CCDC no. 1267/3344



Abstract

$C_{20}H_{26}IrNO_7$, orthorhombic, *Pbca* (no. 61), a = 9.4798(8) Å, b = 14.646(1) Å, c = 31.842(3) Å, V = 4421.0 Å^3, Z = 8, $R_{gt}(F)$ = 0.036, $wR_{ref}(F^2)$ = 0.074, T = 293 K.

Source of material

The title complex was prepared by mixing the aqueous solution of aquabis(acetylacetonato-κ^2O,O')(diacetylmethanido-κC)-iridium(III) and equimolar amount of 2-hydroxypyridine. After one week, a yellow crystalline product precipitated. Single crystals were selected from the product for the X-ray diffraction analysis.

Experimental details

All the hydrogen atoms were positioned geometrically with d(C—H) = 0.93 - 0.98 Å, d(O—H) = 0.82 Å and refined as riding with U_{iso}(H) = 1.2 or 1.5 U_{eq}(C) and U_{iso}(H) = 1.5 U_{eq}(O).

Discussion

In the title complex, the Ir atom is six-coordinated and situated in a slightly distorted octahedral environment, formed by four oxygen atoms of two acetylacetone ligands, one carbon atom of one acetylacetone ligand and one N atom of 2-hydroxypyridine. The average O–Ir–O chelating angle is 94.1(1)°. The average Ir—O bond length of two acetylacetone ligands is 2.023(3) Å, Ir—C bond length is found to be 2.162(5) Å, which agree with the literature data of $Ir(C_5H_7O_2)_3$, $Ir(C_5H_7O_2)_3(H_2O)$, $Ir(C_5H_7O_2)_3(C_2H_6SO)$ and $Ir(C_5H_7O_2)_3(CH_3CN) \cdot 1.5H_2O$ [1-5]. Ir—N bond length is found to be 2.140(4) Å. Changes in the coordination mode of one acetylacetonate ligand of tris(acetyacetonato-O,O)iridium(III) lead to the formation of a direct Ir—C bond. The average Ir—O, Ir—C and Ir—N bond lengths are close to each other. Ir—C bond length is found to be between Ir—C σ-bond (2.00 - 2.02 Å) and Ir—C π-bond (2.27 - 2.31 Å). In the crystal structure of the title complex there are two different types of coordinating acac ligands: a conventional bidentate (O-bonded acac ligand) and a γ-C bonded acac ligand, as Periana proposed [3]. The crystal packing of the title complex is stablilized by extensive hydrogen bonds formed between 2-hydroxypyridine and carbonyl O atoms of the acetylacetone ligand with d(O7–H7···O5) = 2.618(5) Å and ∠O7–H7···O5 = 165.9°.

Table 1. Data collection and handling.

Crystal:	yellow block, size 0.12 × 0.15 × 0.19 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	60.79 cm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD, φ/ω
$2\theta_{max}$:	56.74°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	28671, 5364
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 3751
$N(param)_{refined}$:	269
Programs:	SHELXS-97, SHELXL-97 [6], DIAMOND [7]

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

Atom	Site	x	y	z	U_{iso}
H(7)	8*c*	0.1448	0.4073	0.6475	0.072
H(2A)	8*c*	0.5749	0.5605	0.7659	0.093
H(2B)	8*c*	0.4403	0.4994	0.7710	0.093
H(2C)	8*c*	0.4429	0.5772	0.7373	0.093
H(3)	8*c*	0.6736	0.3963	0.7603	0.061
H(5A)	8*c*	0.8133	0.2073	0.7118	0.099
H(5B)	8*c*	0.7781	0.2484	0.7560	0.099
H(5C)	8*c*	0.9040	0.2878	0.7298	0.099
H(7A)	8*c*	0.6912	0.2567	0.5108	0.107
H(7B)	8*c*	0.5368	0.2539	0.4932	0.107
H(7C)	8*c*	0.5805	0.1894	0.5302	0.107
H(8)	8*c*	0.4030	0.3751	0.5125	0.057
H(10A)	8*c*	0.2026	0.5107	0.5569	0.081
H(10B)	8*c*	0.2862	0.5127	0.5144	0.081
H(10C)	8*c*	0.3214	0.5836	0.5498	0.081

* Correspondence author (e-mail: liuweiping0917@126.com)

Table 2. Continued.

Atom	Site	*x*	*y*	*z*	U_{iso}
H(11)	8*c*	0.7555	0.5265	0.6508	0.039
H(13A)	8*c*	1.0150	0.3747	0.5808	0.089
H(13B)	8*c*	0.9263	0.4491	0.5572	0.089
H(13C)	8*c*	0.8568	0.3556	0.5694	0.089
H(15A)	8*c*	0.6990	0.6919	0.6098	0.089
H(15B)	8*c*	0.5860	0.6315	0.6326	0.089

Table 2. Continued.

Atom	Site	*x*	*y*	*z*	U_{iso}
H(15C)	8*c*	0.5621	0.6617	0.5860	0.089
H(16)	8*c*	0.5462	0.1989	0.6398	0.053
H(17)	8*c*	0.3963	0.0799	0.6474	0.061
H(18)	8*c*	0.1575	0.1079	0.6580	0.064
H(19)	8*c*	0.0788	0.2567	0.6581	0.055

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}
Ir(1)	8*c*	0.57132(2)	0.39919(1)	0.633268(6)	0.0231(1)	0.0273(1)	0.0325(1)	0.00097(9)	–0.00159(8)	0.00115(9)
N(1)	8*c*	0.4088(4)	0.3007(3)	0.6443(1)	0.029(2)	0.027(2)	0.037(2)	–0.000(2)	–0.004(2)	0.001(2)
O(1)	8*c*	0.5125(3)	0.4787(2)	0.6820(1)	0.029(2)	0.037(2)	0.036(2)	0.003(2)	–0.001(2)	–0.005(2)
O(2)	8*c*	0.6984(3)	0.3185(2)	0.6683(1)	0.029(2)	0.037(2)	0.043(2)	0.004(2)	–0.006(2)	0.007(2)
O(3)	8*c*	0.6220(3)	0.3180(2)	0.5838(1)	0.033(2)	0.035(2)	0.038(2)	0.005(2)	–0.000(2)	–0.003(2)
O(4)	8*c*	0.4408(3)	0.4786(2)	0.5991(1)	0.028(2)	0.031(2)	0.038(2)	0.003(2)	–0.003(2)	0.002(2)
O(5)	8*c*	0.9569(4)	0.4304(3)	0.6506(1)	0.032(2)	0.064(3)	0.066(3)	0.003(2)	–0.002(2)	0.003(2)
O(6)	8*c*	0.7298(5)	0.5475(3)	0.5541(1)	0.076(3)	0.072(3)	0.049(2)	0.004(3)	0.003(2)	0.016(2)
O(7)	8*c*	0.2300(4)	0.4036(3)	0.6515(1)	0.030(2)	0.034(2)	0.079(3)	0.002(2)	0.005(2)	0.001(2)
C(1)	8*c*	0.5563(5)	0.4655(4)	0.7195(2)	0.040(3)	0.043(3)	0.036(3)	–0.010(3)	0.006(3)	–0.004(2)
C(2)	8*c*	0.4984(7)	0.5316(5)	0.7513(2)	0.081(5)	0.062(5)	0.044(3)	0.006(4)	0.007(3)	–0.010(3)
C(3)	8*c*	0.6503(6)	0.3968(4)	0.7319(2)	0.057(4)	0.059(4)	0.036(3)	0.000(4)	–0.005(3)	0.007(3)
C(4)	8*c*	0.7125(5)	0.3302(4)	0.7079(2)	0.032(3)	0.043(4)	0.045(3)	–0.003(3)	–0.005(2)	0.010(3)
C(5)	8*c*	0.8109(7)	0.2623(5)	0.7282(2)	0.066(4)	0.084(5)	0.050(4)	0.029(4)	–0.006(3)	0.016(4)
C(6)	8*c*	0.5502(6)	0.3211(4)	0.5492(2)	0.050(4)	0.047(4)	0.033(3)	–0.006(3)	–0.002(3)	–0.006(3)
C(7)	8*c*	0.5936(7)	0.2487(5)	0.5180(2)	0.096(6)	0.064(5)	0.055(4)	0.027(4)	–0.011(4)	–0.022(4)
C(8)	8*c*	0.4462(6)	0.3836(4)	0.5385(2)	0.049(3)	0.051(4)	0.042(3)	0.009(3)	–0.012(3)	–0.006(3)
C(9)	8*c*	0.3996(5)	0.4572(4)	0.5622(2)	0.027(3)	0.044(3)	0.040(3)	0.000(2)	–0.002(2)	0.006(3)
C(10)	8*c*	0.2928(6)	0.5219(4)	0.5442(2)	0.050(4)	0.061(4)	0.052(3)	0.015(3)	–0.008(3)	0.011(3)
C(11)	8*c*	0.7463(5)	0.4920(4)	0.6246(1)	0.026(3)	0.032(3)	0.041(3)	–0.004(2)	–0.001(2)	0.000(2)
C(12)	8*c*	0.8779(6)	0.4412(4)	0.6194(2)	0.033(3)	0.037(3)	0.048(3)	–0.003(3)	0.003(3)	0.005(3)
C(13)	8*c*	0.9231(6)	0.4016(4)	0.5780(2)	0.041(3)	0.062(4)	0.075(4)	0.003(3)	0.015(3)	–0.013(4)
C(14)	8*c*	0.7052(6)	0.5595(4)	0.5914(2)	0.038(3)	0.035(3)	0.060(4)	–0.012(3)	–0.001(3)	0.000(3)
C(15)	8*c*	0.6315(6)	0.6437(4)	0.6063(2)	0.048(4)	0.034(4)	0.095(5)	–0.001(3)	0.001(4)	0.002(4)
C(16)	8*c*	0.4508(6)	0.2111(4)	0.6437(2)	0.034(3)	0.042(4)	0.056(4)	0.005(3)	–0.004(2)	0.006(3)
C(17)	8*c*	0.3621(7)	0.1394(4)	0.6483(2)	0.054(4)	0.029(3)	0.068(4)	0.000(3)	–0.004(3)	0.003(3)
C(18)	8*c*	0.2205(6)	0.1559(4)	0.6543(2)	0.051(4)	0.038(4)	0.070(4)	–0.013(3)	–0.004(3)	0.007(3)
C(19)	8*c*	0.1745(6)	0.2446(4)	0.6547(2)	0.034(3)	0.045(4)	0.060(4)	–0.008(3)	–0.001(3)	0.005(3)
C(20)	8*c*	0.2689(5)	0.3170(4)	0.6502(2)	0.031(3)	0.031(3)	0.034(3)	0.000(2)	–0.002(2)	0.004(2)

Acknowledgments. This work was financially supported by Science and Technology Development Program of Yunnan Province (grant nos. 2008IA008, 2008CF002, 2009CD133 and 2009CI019).

References

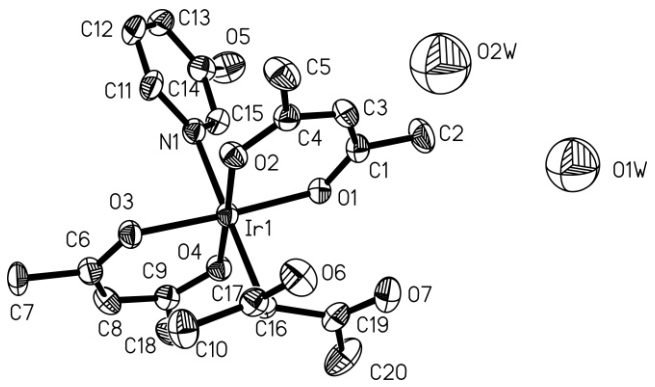
1. Isakova, V. G.; Baidina, I. A.; Morozova, N. B.; Igumenov, I. K.: γ-Halogenated iridium(III)acetylacetonates. Polyhedron **19** (2000) 1097-1103.
2. Chang, Q. W.; Xie, M. J.; Liu, W. P.; Chen, X. Z.; Ye, Q. S.: Bis-(acetylacetonato-2*O*,*O'*)aqua(diacetylmethanido-*C*)iridium(III). Acta Crystallogr. **E65** (2009) m1264.
3. Matsumoto, T.; Periana, R. A.; Taube, D. J.; Yoshida, H.: Regioselective hydrophenylation of olefins catalyzed by an Ir(III) complex. J. Mol. Catal. **A180** (2002) 1-18.
4. Jiang, J.; Xie, M. J.; Chang, Q. W.; Chen, J. L.; Xie, X. T.; Ye, Q. S.; Chen, X. Z.; Yu, Y.; Liu, W. P.: Crystal structure of bis(acetylacetonato-κ^2*O*,*O'*)-(diacetylmethanido-κ*C*)-(dimethylsulfoxide-*S*)iridium(III), $Ir(C_5H_7O_2)_3(C_2H_6SO)$. Z. Kristallogr. NCS **225** (2010) 575-576.
5. Chang, Q. W.; Hu, C, Y.; Pan, Z. F.; Chen, J. L.; Ye, Q. S.; Chen, X. Z.; Yu, Y.; Liu, W. P.: Crystal structure of bis(acetylacetonato-κ^2*O*,*O'*)-(diacetylmethanido-κ*C*)-(acetonitrile-*N*)iridium(III) sesquihydrate, $Ir(C_5H_7O_2)_3(CH_3CN)\cdot 1.5H_2O$. Z. Kristallogr. NCS **225** (2010) 667-668.
6. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. **A64** (2008) 112-122.
7. Brandenburg, K.: DIAMOND. Visual Crystal Structure Information System. Version 3.2c. Crystal Impact, Bonn, Germany 1998.

Crystal structure of bis(acetylacetonato-κ^2O,O')-(diacetylmethanido-κC)-(3-hydroxypyridine)iridium(III) dihydrate, $Ir(C_5H_7O_2)_3(C_5H_5NO) \cdot 2H_2O$

Qiao-Wen Chang, Chang-Yi Hu, Jia-Lin Chen, Qing-Song Ye, Xi-Zhu Chen, Yao Yu, Li-Qiao Chen and Wei-Ping Liu*

State Key Laboratory of Advanced Technologies for Platinum Metals, Kunming Institute of Precious Metal, Kunming 650106, P. R. China

Received January 4, 2011, accepted and available on-line June 17, 2011; CCDC no. 1267/3358



Abstract

$C_{20}H_{30}IrNO_9$, monoclinic, $P2_1/n$ (no. 14), a = 10.574(1) Å, b = 18.662(2) Å, c = 11.888(1) Å, β = 94.178(1)°, V = 2339.7 Å^3, Z = 4, $R_{gt}(F)$ = 0.038, $wR_{ref}(F^2)$ = 0.091, T = 298 K.

Source of material

The title complex was prepared by mixing the aqueous solution of aquabis(acetylacetonato-κ^2O,O')(diacetylmethanido-κC)-iridium(III) and equimolar amount of 3-hydroxypyridine. After two weeks, a yelleow crystalline product precipitated. Single crystals were selected from the product for the X-ray diffraction analysis.

Experimental details

The carbon-bound H atoms were positioned geometrically and refined as riding with d(C—H) = 0.93 - 0.98 Å and U_{iso}(H) = 1.2 U_{eq}(C). The oxygen atoms of water are refined isotropically.

Discussion

The asymmetric unit of the title crystal structure consists of a Ir(III) cation, three acetylacetonate anions, one 3-hydroypyridine molecule and two lattice water molecules. The Ir(III) cation is six-coordinated by four oxygen atoms of different acetyacetonate anions, one carbon atom of acetylacetonate anion and one N atom of 3-hydroxypyridine ligand in a slightly distorted octahedral environment. The average O–Ir–O chelating angle is 89.97°. The average Ir—O bond length is 2.016(4) Å, Ir—C bond length is 2.166(6) Å, which agree with the literature data for $Ir(C_5H_7O_2)_3$, $Ir(C_5H_7O_2)_3(H_2O)$ and $Ir(C_5H_7O_2)_3(C_2H_6SO)$ [1-5]. Ir—N bond length is found to be 2.088(5) Å.

In the crystal structure, there are intermolecular hydrogen bonds with d(O5–H5···O1W) = 2.593(8) Å, ∠O5–H5···O1W = 138.1°; d(O1W–H1W···O2W) = 3.101(9) Å, ∠O1W–H1W···O2W = 121.2°; d(O1W–H2W···O6) = 2.850(8) Å, ∠O1W–H2W···O6 = 130.5° and d(O1W–H2W···O7) = 3.019(9) Å, ∠O1W–H2W···O7 = 139.5°.

Table 1. Data collection and handling.

Crystal:	yellow prism, size 0.12 × 0.14 × 0.19 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	57.55 cm^{-1}
Diffractometer, scan mode:	Bruker SMART APEX II CCD, φ/ω
$2\theta_{max}$:	55°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	15209, 5290
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 3644
$N(param)_{refined}$:	277
Programs:	SHELXS-97, SHELXL-97 [6], DIAMOND [7]

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

Atom	Site	x	y	z	U_{iso}
H(5)	4*e*	–0.4142	0.0122	0.2191	0.100
H(2A)	4*e*	–0.3341	0.3666	0.0677	0.104
H(2B)	4*e*	–0.3472	0.3659	0.1982	0.104
H(2C)	4*e*	–0.3901	0.2992	0.1250	0.104
H(3)	4*e*	–0.1534	0.3611	0.2915	0.061
H(5A)	4*e*	0.1569	0.3129	0.3911	0.103
H(5B)	4*e*	0.0290	0.3310	0.4437	0.103
H(5C)	4*e*	0.0908	0.3870	0.3661	0.103
H(7A)	4*e*	0.3735	0.0981	0.0584	0.090
H(7B)	4*e*	0.3182	0.0269	0.0047	0.090
H(7C)	4*e*	0.3071	0.0423	0.1333	0.090
H(8)	4*e*	0.1305	0.0396	–0.1012	0.064
H(10A)	4*e*	–0.0720	0.0947	–0.2631	0.094
H(10B)	4*e*	–0.1811	0.0725	–0.1877	0.094
H(10C)	4*e*	–0.0673	0.0202	–0.2020	0.094
H(11)	4*e*	0.0493	0.1243	0.3053	0.064
H(12)	4*e*	–0.0508	0.0488	0.4215	0.073
H(13)	4*e*	–0.2578	0.0142	0.3739	0.074
H(15)	4*e*	–0.2493	0.1289	0.0924	0.057
H(16)	4*e*	0.1121	0.2568	–0.0862	0.047
H(18A)	4*e*	0.3793	0.3191	0.0606	0.099
H(18B)	4*e*	0.3282	0.2728	–0.0429	0.099
H(18C)	4*e*	0.3168	0.2443	0.0801	0.099
H(20A)	4*e*	–0.1517	0.3412	–0.2111	0.129
H(20B)	4*e*	–0.1417	0.2620	–0.1674	0.129
H(20C)	4*e*	–0.0344	0.2941	–0.2366	0.129
O(1W)	4*e*	0.4827(6)	0.9880(4)	0.3404(5)	0.110(2)
H(1W)	4*e*	0.4110	0.9978	0.3069	0.131
H(2W)	4*e*	0.4822	0.9462	0.3691	0.131
O(2W)	4*e*	0.7816(6)	0.9716(4)	0.5816(6)	0.129(3)
H(3W)	4*e*	0.8185	0.9595	0.6446	0.155
H(4W)	4*e*	0.8147	1.0035	0.5421	0.155

* Correspondence author (e-mail: liuweiping0917@126.com)

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}
Ir(1)	4*e*	–0.00518(2)	0.20807(1)	0.08562(2)	0.0360(1)	0.0362(2)	0.0368(2)	0.0049(1)	–0.00208(9)	–0.0027(1)
N(1)	4*e*	–0.0905(5)	0.1343(3)	0.1883(4)	0.042(3)	0.042(3)	0.040(3)	0.005(2)	–0.002(2)	–0.002(2)
O(1)	4*e*	–0.1715(4)	0.2609(2)	0.0774(3)	0.040(2)	0.037(3)	0.043(3)	0.003(2)	0.002(2)	0.000(2)
O(2)	4*e*	0.0667(4)	0.2588(3)	0.2257(3)	0.041(2)	0.053(3)	0.042(3)	0.002(2)	0.001(2)	–0.010(2)
O(3)	4*e*	0.1570(4)	0.1507(2)	0.0995(3)	0.044(2)	0.049(3)	0.043(3)	0.011(2)	–0.004(2)	–0.003(2)
O(4)	4*e*	–0.0778(4)	0.1538(2)	–0.0510(3)	0.046(3)	0.046(3)	0.043(3)	0.002(2)	0.001(2)	–0.005(2)
O(5)	4*e*	–0.3924(5)	0.0484(3)	0.1864(5)	0.082(4)	0.080(5)	0.089(4)	–0.030(3)	0.016(3)	0.014(3)
O(6)	4*e*	0.1788(5)	0.3773(3)	0.0878(4)	0.067(3)	0.059(4)	0.080(4)	–0.017(3)	0.005(3)	–0.023(3)
O(7)	4*e*	–0.0555(5)	0.3870(3)	–0.0329(4)	0.068(3)	0.056(4)	0.079(4)	0.015(3)	–0.001(3)	0.009(3)
C(1)	4*e*	–0.1975(6)	0.3060(3)	0.1526(6)	0.037(3)	0.036(4)	0.056(4)	0.001(3)	0.003(3)	0.001(3)
C(2)	4*e*	–0.3293(6)	0.3373(4)	0.1342(7)	0.048(4)	0.079(6)	0.082(6)	0.026(4)	0.004(4)	–0.008(5)
C(3)	4*e*	–0.1193(6)	0.3273(4)	0.2447(6)	0.058(4)	0.044(4)	0.052(4)	0.008(3)	0.011(3)	–0.011(3)
C(4)	4*e*	0.0039(6)	0.3051(3)	0.2769(5)	0.049(4)	0.042(4)	0.046(4)	0.000(3)	0.004(3)	0.001(3)
C(5)	4*e*	0.0768(7)	0.3369(5)	0.3787(6)	0.068(5)	0.081(6)	0.055(5)	0.003(4)	–0.001(4)	–0.029(4)
C(6)	4*e*	0.1811(6)	0.1001(4)	0.0323(6)	0.048(4)	0.045(4)	0.052(4)	0.004(3)	0.009(3)	0.001(3)
C(7)	4*e*	0.3063(6)	0.0636(4)	0.0596(6)	0.060(5)	0.052(5)	0.067(5)	0.029(4)	0.000(4)	0.001(4)
C(8)	4*e*	0.1001(6)	0.0771(4)	–0.0591(6)	0.052(4)	0.053(5)	0.056(5)	0.004(3)	0.013(3)	–0.016(3)
C(9)	4*e*	–0.0207(6)	0.1027(4)	–0.0958(5)	0.044(4)	0.038(4)	0.045(4)	–0.004(3)	0.004(3)	–0.002(3)
C(10)	4*e*	–0.0916(7)	0.0696(4)	–0.1962(6)	0.076(5)	0.062(5)	0.051(4)	–0.008(4)	0.004(4)	–0.021(4)
C(11)	4*e*	–0.0335(6)	0.1101(4)	0.2849(6)	0.054(4)	0.050(5)	0.055(4)	0.013(3)	–0.008(3)	0.010(3)
C(12)	4*e*	–0.0931(7)	0.0650(4)	0.3550(6)	0.069(5)	0.060(5)	0.052(5)	0.023(4)	–0.006(4)	0.013(4)
C(13)	4*e*	–0.2154(8)	0.0439(4)	0.3263(6)	0.083(6)	0.048(5)	0.055(5)	0.009(4)	0.015(4)	0.012(4)
C(14)	4*e*	–0.2742(7)	0.0673(4)	0.2263(6)	0.062(5)	0.041(4)	0.058(5)	–0.008(3)	0.013(4)	–0.004(3)
C(15)	4*e*	–0.2091(6)	0.1126(4)	0.1599(5)	0.049(4)	0.046(4)	0.047(4)	0.004(3)	0.001(3)	0.004(3)
C(16)	4*e*	0.0789(6)	0.2842(3)	–0.0244(5)	0.040(3)	0.041(4)	0.036(3)	0.002(3)	0.001(3)	–0.001(3)
C(17)	4*e*	0.1881(6)	0.3214(4)	0.0358(6)	0.045(4)	0.043(4)	0.051(4)	–0.007(3)	0.004(3)	0.003(3)
C(18)	4*e*	0.3143(6)	0.2863(4)	0.0332(7)	0.041(4)	0.060(5)	0.098(6)	–0.003(4)	0.001(4)	–0.005(4)
C(19)	4*e*	–0.0256(7)	0.3301(4)	–0.0746(6)	0.054(4)	0.047(5)	0.054(5)	–0.005(4)	–0.002(3)	0.013(4)
C(20)	4*e*	–0.0945(9)	0.3046(5)	–0.1821(7)	0.106(7)	0.079(7)	0.066(6)	–0.016(5)	–0.035(5)	0.019(5)

Acknowledgment. This work was financially supported by Science and Technology Development Program of Yunnan Province (grant nos. 2008IA008, 2008CF002, 2009CD133, 2009CI019).

References

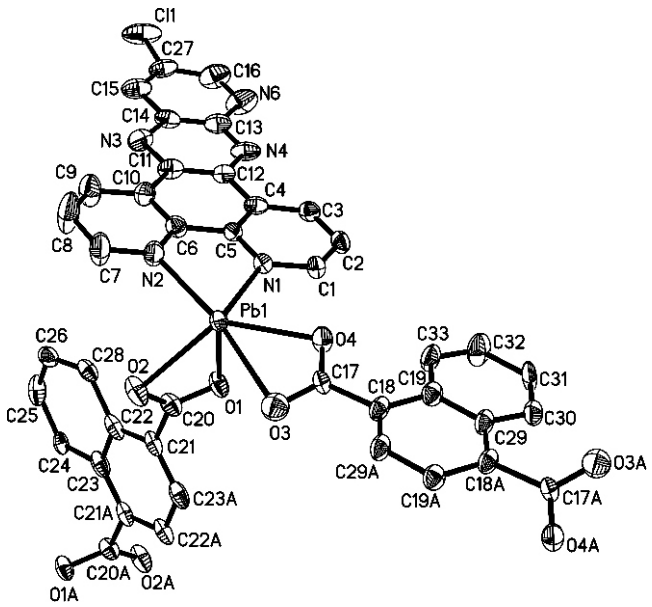
1. Isakova, V. G.; Baidina, I. A.; Morozova, N. B.; Igumenov, I. K.: γ-Halogenated iridium(III)acetylacetonates. Polyhedron **19** (2000) 1097-1103.
2. Chang, Q. W.; Xie, M. J.; Liu, W. P.; Chen, X. Z.; Ye, Q. S.: Bis(acetylacetonato-κ^2O,O')aqua(diacetylmethanido-κC)iridium(III). Acta Crystallogr. **E65** (2009) m1264.
3. Matsumoto, T.; Periana, R. A.; Taube, D. J.; Yoshida, H.: Regioselective hydrophenylation of olefins catalyzed by an Ir(III) complex. J. Mol. Catal. **A180** (2002) 1-18 .
4. Jiang, J.; Xie, M. J.; Chang, Q. W.; Chen, J. L.; Xie, X. T.; Ye, Q. S.; Chen, X. Z.; Yu, Y.; Liu, W. P.: Crystal structure of bis(acetylacetonato-κ^2O,O')-(diacetylmethanido-κC)-(dimethylsulfoxide-*S*)iridium(III), $Ir(C_5H_7O_2)_3(C_2H_6SO)$. Z. Kristallogr. NCS **225** (2010) 575-576.
5. Chang, Q. W.; Hu, C, Y.; Pan, Z. F.; Chen, J. L.; Ye, Q. S.; Chen, X. Z.; Yu, Y.; Liu, W. P.: Crystal structure of bis(acetylacetonato-κ^2O,O')-(diacetylmethanido-κC)-(acetonitrile-*N*)iridium(III) sesquihydrate, $Ir(C_5H_7O_2)_3(CH_3CN) \cdot 1.5H_2O$. Z. Kristallogr. NCS **225** (2010) 667-668.
6. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. **A64** (2008) 112-122.
7. Brandenburg, K.: DIAMOND. Visual Crystal Structure Information System. Version 3.2c. Crystal Impact, Bonn, Germany 1998.

Crystal structure of dipyrido[7,6-*a*:6′,7′-*c*]-3-chloropyrido[2,3-*b*]-quinoxaline)-(naphthalene-1,4-dicarboxylato)lead(II), $Pb(C_{17}H_8N_4Cl)(C_{12}H_6O_4)$

Ji-Ku Wang[*,I,II], Hao Chen[I,II] and Hong-Bin Xu[III]

[I] Jilin Normal University, College of Chemistry, Siping 136000, P. R. China
[II] Key Laboratory of Preparation and Applications of Environment-Friendly Materials, Jilin Normal University, Ministry of Education, P. R. China
[III] China Science and Technology Exchange Center, Ministry of Science and Technology, Beijing 100045, P. R. China

Received February 2, 2011, accepted and available on-line June 17, 2011; CCDC no. 1267/3386



Abstract

$C_{29}H_{14}ClN_4O_4Pb$, triclinic, $P\bar{1}$ (no. 2), a = 10.310(5) Å, b = 10.521(5) Å, c = 12.168(5) Å, α = 80.808(5)°, β = 81.973(5)°, γ = 79.638(5)°, V = 1273.3 Å^3, Z = 2, $R_{gt}(F)$ = 0.051, $wR_{ref}(F^2)$ = 0.138, T = 293 K.

Source of material

The pH value of a mixture of $Pb(NO_3)_2$ (0.5 mmol), naphthalene-1,4-dicarboxylatic acid (1,4-H_2ndc, 0.5 mmol) and dipyrido[7,6-*a*:6′,7′-*c*]-3-chloropyrido[2,3-*b*]quinoxaline (L, 0.5 mmol) in 10 mL distilled water was adjusted to between 5 and 6 by addition of triethylamine. The resultant solution was heated at 458 K in a Teflon-lined stainless steel autoclave for seven days. The reaction system was then slowly cooled to room temperature. Pale yellow crystals of the title compound suitable for single crystal X-ray diffraction analysis were collected from the final reaction system by filtration, washed several times with distilled water and dried in air at ambient temperature (yield 27 % based on Pb).

Experimental details

All H atoms were positioned geometrically d(C—H) = 0.93 Å and refined as riding with U_{iso}(H) = 1.2 U_{eq}(C). The naphthalene-1,4-dicarboxylate ligand is disordered over two positions in the fused-ring portion. The hydrogen atoms attached to C29' and C19' were not generated geometrically because of the disordered fused-ring portion.

Discussion

The current interest in coordination polymer frameworks not only stems from their potential applictions in microelectronics, nonlinear optics, porous materials, and catalysis, but also from their intriguing variety of topologies and entanglement motifs [1]. Recently, 1,10-phenanthroline (phen) derivatives have received intense interests in their coordination chemistry [2].

In the title complex, each Pb(II) atom is six-coordinated by two nitrogen atoms from one L ligand, and four carboxylate oxygen atoms from two different 1,4-ndc^{-2} ligands. The 1,4-ndc^{-2} ligands bridge neighboring Pb(II) atoms to form one-dimensional chains. The Pb···Pb distance bridged by 1,4-ndc^{-2} is about 11.72 Å. The L ligands are located on both sides of the one-dimensional chains. Further, the strong π-π interactions between the L ligands and the 1,4-ndc ligands of neighboring chains result in a 2D supramolecular structure [2].

Table 1. Data collection and handling.

Crystal:	pale yellow block, size 0.16 × 0.18 × 0.21 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	67.77 cm^{-1}
Diffractometer, scan mode:	Bruker APEX CCD, φ/ω
$2\theta_{max}$:	50.16°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	6666, 4456
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 3850
$N(param)_{refined}$:	385
Programs:	SHELXS-97, SHELXL-97 [3]

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

Atom	Site	Occ.	x	y	z	U_{iso}
H(1)	2*i*		0.4369	0.1788	0.0667	0.076
H(2)	2*i*		0.2571	0.2967	–0.0148	0.084
H(3)	2*i*		0.2754	0.3507	–0.2082	0.081
H(7)	2*i*		0.9847	0.0053	–0.2029	0.148
H(8)	2*i*		1.0046	0.0208	–0.3967	0.199
H(9)	2*i*		0.8537	0.1665	–0.4937	0.141
H(15)	2*i*		0.6070	0.3570	–0.7457	0.125
H(16)	2*i*		0.2259	0.5258	–0.7085	0.156
H(24)	2*i*	0.50	1.1326	0.6950	–0.2363	0.064
H(25)	2*i*	0.50	1.1339	0.5951	–0.3994	0.105

* Correspondence author (e-mail: wangjikujlnu@yahoo.com.cn)

Table 2. Continued.

Atom	Site	Occ.	x	y	z	U_{iso}
H(26)	2*i*	0.50	1.0581	0.4092	–0.3882	0.095
H(28)	2*i*	0.50	0.9689	0.3052	–0.2077	0.081
H(30)	2*i*	0.50	0.1927	0.1185	0.6115	0.096

Table 2. Continued.

Atom	Site	Occ.	x	y	z	U_{iso}
H(31)	2*i*	0.50	0.0792	0.2302	0.4642	0.106
H(32)	2*i*	0.50	0.1833	0.2397	0.2819	0.139
H(33)	2*i*	0.50	0.4009	0.1376	0.2470	0.099

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)	2*i*		0.446(1)	0.201(1)	–0.0108(9)	0.051(6)	0.070(7)	0.065(6)	–0.007(5)	–0.001(5)	–0.005(5)
C(2)	2*i*		0.336(1)	0.272(1)	–0.059(1)	0.044(6)	0.078(7)	0.087(8)	–0.004(5)	–0.004(5)	–0.014(6)
C(3)	2*i*		0.347(1)	0.303(1)	–0.1731(9)	0.060(6)	0.067(7)	0.076(7)	–0.001(5)	–0.020(5)	–0.013(5)
C(4)	2*i*		0.467(1)	0.264(1)	–0.2362(9)	0.082(7)	0.048(5)	0.068(6)	–0.014(5)	–0.025(5)	–0.006(4)
C(5)	2*i*		0.5742(9)	0.1939(9)	–0.1805(8)	0.051(5)	0.056(5)	0.058(5)	–0.012(4)	–0.006(4)	–0.009(4)
C(6)	2*i*		0.697(1)	0.154(1)	–0.2434(9)	0.063(7)	0.090(8)	0.061(6)	–0.016(6)	–0.015(5)	–0.002(5)
C(7)	2*i*		0.913(2)	0.045(2)	–0.241(1)	0.068(9)	0.19(2)	0.09(1)	0.01(1)	0.008(7)	–0.01(1)
C(8)	2*i*		0.929(2)	0.063(3)	–0.359(1)	0.10(1)	0.27(3)	0.08(1)	0.04(2)	0.017(9)	0.00(1)
C(9)	2*i*		0.836(2)	0.140(2)	–0.417(1)	0.076(9)	0.18(2)	0.079(9)	0.01(1)	–0.009(7)	0.01(1)
C(10)	2*i*		0.714(1)	0.180(1)	–0.361(1)	0.082(8)	0.094(9)	0.067(7)	–0.024(7)	0.005(6)	–0.008(6)
C(11)	2*i*		0.603(1)	0.255(1)	–0.4170(9)	0.11(1)	0.062(6)	0.056(6)	–0.023(6)	–0.028(6)	0.010(5)
C(12)	2*i*		0.482(1)	0.296(1)	–0.3573(9)	0.076(7)	0.058(6)	0.068(6)	–0.008(5)	–0.021(6)	–0.011(5)
C(13)	2*i*		0.393(2)	0.387(1)	–0.517(1)	0.11(1)	0.075(8)	0.083(9)	–0.012(8)	–0.042(8)	–0.009(6)
C(14)	2*i*		0.510(1)	0.353(1)	–0.578(1)	0.098(9)	0.063(7)	0.070(7)	–0.024(6)	–0.042(7)	0.008(5)
C(15)	2*i*		0.527(2)	0.381(1)	–0.702(1)	0.16(2)	0.063(8)	0.10(1)	–0.042(9)	–0.04(1)	–0.004(7)
C(16)	2*i*		0.299(2)	0.480(2)	–0.674(2)	0.16(2)	0.12(1)	0.11(1)	0.01(1)	–0.07(1)	–0.02(1)
C(17)	2*i*		0.6393(9)	0.027(1)	0.2729(8)	0.038(5)	0.061(6)	0.062(6)	–0.013(4)	0.001(4)	0.003(4)
C(18)	2*i*		0.566(1)	0.012(1)	0.3909(8)	0.083(7)	0.055(6)	0.051(5)	–0.022(5)	0.017(5)	–0.006(4)
C(20)	2*i*		0.900(1)	0.2545(9)	0.022(1)	0.055(6)	0.043(5)	0.091(8)	–0.011(5)	–0.010(5)	0.000(5)
C(21)	2*i*		0.9527(9)	0.382(1)	0.008(1)	0.033(5)	0.049(5)	0.108(9)	–0.008(4)	0.001(5)	–0.002(5)
C(22)	2*i*		1.003(1)	0.439(1)	–0.100(1)	0.036(5)	0.051(6)	0.13(1)	–0.008(4)	–0.005(6)	–0.007(6)
C(23)	2*i*		1.052(1)	0.559(1)	–0.106(1)	0.039(5)	0.047(6)	0.13(1)	0.002(4)	–0.005(6)	0.000(6)
C(24)	2*i*	0.50	1.101(2)	0.616(2)	–0.227(2)	0.039(9)	0.040(9)	0.07(1)	–0.002(7)	0.000(8)	0.010(8)
C(25)	2*i*	0.50	1.101(2)	0.555(2)	–0.330(2)	0.07(2)	0.06(1)	0.11(2)	0.01(1)	0.02(1)	0.02(1)
C(26)	2*i*	0.50	1.057(2)	0.447(3)	–0.324(2)	0.05(1)	0.08(2)	0.11(2)	0.00(1)	–0.02(1)	–0.04(2)
C(27)	2*i*		0.417(2)	0.443(1)	–0.744(1)	0.15(1)	0.073(8)	0.063(7)	–0.014(9)	–0.047(8)	–0.008(6)
C(28)	2*i*	0.50	1.003(2)	0.382(2)	–0.211(2)	0.04(1)	0.06(1)	0.10(2)	–0.004(9)	–0.02(1)	–0.00(1)
C(19)	2*i*		0.4272(8)	0.0668(8)	0.4083(6)	0.073(7)	0.064(6)	0.062(6)	–0.019(5)	0.005(5)	–0.003(5)
C(29)	2*i*		0.3649(9)	0.0611(9)	0.5175(6)	0.076(7)	0.067(7)	0.057(6)	–0.025(6)	0.019(5)	–0.006(5)
C(30)	2*i*	0.50	0.2345(9)	0.122(1)	0.5384(8)	0.07(2)	0.12(2)	0.05(1)	–0.03(1)	0.01(1)	–0.00(1)
C(31)	2*i*	0.50	0.1664(9)	0.189(2)	0.450(1)	0.04(1)	0.13(2)	0.08(2)	–0.02(1)	0.03(1)	0.01(1)
C(32)	2*i*	0.50	0.229(1)	0.195(2)	0.341(1)	0.11(2)	0.15(3)	0.06(2)	–0.02(2)	0.00(2)	0.03(2)
C(33)	2*i*	0.50	0.359(1)	0.134(1)	0.3200(6)	0.08(2)	0.11(2)	0.05(1)	–0.02(1)	0.01(1)	–0.00(1)
N(1)	2*i*		0.5634(7)	0.1630(7)	–0.0676(6)	0.051(4)	0.052(4)	0.057(5)	–0.009(4)	–0.008(3)	–0.002(3)
N(2)	2*i*		0.798(1)	0.082(1)	–0.1843(8)	0.062(6)	0.127(9)	0.064(6)	–0.003(6)	–0.003(5)	–0.016(6)
N(3)	2*i*		0.620(1)	0.284(1)	–0.5325(9)	0.120(9)	0.083(7)	0.077(7)	–0.033(7)	–0.005(6)	–0.011(5)
N(4)	2*i*		0.380(1)	0.361(1)	–0.4073(9)	0.124(9)	0.069(6)	0.091(7)	–0.007(6)	–0.060(7)	–0.010(5)
N(6)	2*i*		0.284(2)	0.454(1)	–0.566(1)	0.15(1)	0.14(1)	0.097(9)	0.03(1)	–0.071(9)	–0.021(8)
O(1)	2*i*		0.7784(7)	0.2542(7)	0.0471(7)	0.049(4)	0.058(4)	0.109(6)	–0.018(3)	0.007(4)	–0.005(4)
O(2)	2*i*		0.9787(8)	0.1549(7)	0.0017(9)	0.054(4)	0.052(4)	0.171(9)	–0.008(4)	–0.002(5)	–0.015(5)
O(3)	2*i*		0.761(1)	0.020(1)	0.2604(9)	0.099(3)	0.101(3)	0.099(3)	–0.016(1)	–0.011(1)	–0.014(1)
O(4)	2*i*		0.5772(7)	0.0533(8)	0.1913(6)	0.056(4)	0.096(6)	0.061(4)	–0.004(4)	–0.005(3)	0.006(4)
Cl(1)	2*i*		0.3995(7)	0.4896(4)	–0.8800(4)	0.271(7)	0.107(3)	0.110(3)	–0.055(4)	–0.113(4)	0.017(2)
Pb(1)	2*i*		0.76337(3)	0.03798(3)	0.03963(3)	0.0457(2)	0.0493(2)	0.0546(2)	–0.0115(2)	–0.0002(2)	–0.0011(1)

Acknowledgment. The authors thank the Key Laboratory of Preparation and Applications of Environment-Friendly Materials for supporting this work.

References

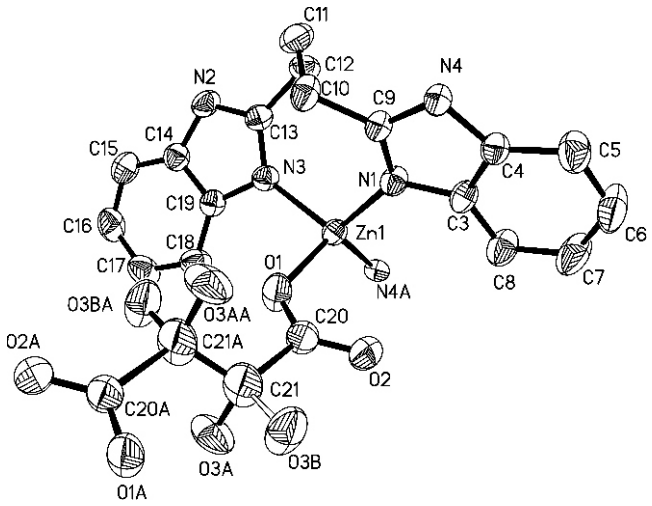
1. Wang, X.-L.; Bi, Y.-F.; Lin, H.-Y.; Liu, G.-C.: Three Novel Cd(II) Metal-Organic Frameworks Constructed from Mixed Ligands of Dipyrido[3,2-*d*:2′,3′-*f*]quinoxaline and Benzene-dicarboxylate: From a 1-D Ribbon, 2-D Layered Network, to a 3-D Architecture. Cryst. Growth Des. **7** (2007) 1086-1091.
2. Kong, Z.-G.; Wang, M.; Ma, X.-Y.; Wang, Q.-W.: *catena*-Poly[[aqua(11-chloropyrido[2′,3′:2,3]pyrimidino[5,6-*f*][1,10]phenanthroline)cadmium(II)]-benzene-1,4-dicarboxylato]: an inclined interpenetrating (6,3) network. Acta Crystallogr. **C65** (2009) m472-m474.
3. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. **A64** (2008) 112-122.

Crystal structure of bis{2,2′-(1,3-propanediyl)bis(1*H*-benzimidazole)}-(2,3-dihydroxybutanedioato)dizinc(II), $Zn_2(C_{17}H_{15}N_4)_2(C_4H_2O_6)$

Luan Jiang*

Baoji University of Arts and Sciences, Department of Chemistry and Chemical Engineering, Baoji 721013, Shaanxi, P. R. China

Received October 31, 2010, in revised form April 25, 2011, accepted and available on-line June 22, 2011; CCDC no. 1267/3268



Abstract

$C_{38}H_{32}N_8O_6Zn_2$, monoclinic, $P12_1/c1$ (no. 14), a = 9.501(5) Å, b = 18.589(5) Å, c = 10.296(5) Å, β = 96.572(5)°, V = 1806.5 Å^3, Z = 2, $R_{gt}(F)$ = 0.047, $wR_{ref}(F^2)$ = 0.128, T = 293 K.

Source of material

The compound was prepared by a hydrothermal method. A mixture of 2,2′-(1,2-ethanediyl)bis(1*H*-benzimidazole) (0.5 mmol), 2,3-dihydroxybutanedioic acid (0.5 mmol), $Zn(CH_3COO)_2$ (1 mmol) and water (10 ml) was stirred for 20 min and then transferred to a 23 ml Teflon-lined reactor. The reactor was kept at 433 K for 72 h under autogenous pressure. Single crystals were obtained after cooling to room temperature.

Experimental details

H111 atom bound to N2 and H3B atom were found in difference Fourier map and refined freely. The other H atoms were placed in calculated positions and refined in a riding-model approximation with d(C—H) = 0.95 - 0.99 Å, d(O—H) = 0.83 - 0.85 Å and U_{iso}(H) = 1.2 U_{eq}(C) or U_{iso}(H) = 1.5 U_{eq}(O). The hydroxy group of 2,3-dihydroxybutanedioate is disordered (O3A, O3B) with occupation of 0.482(7): 0.518(7).

Discussion

Bis-benzimidazoles are known to be strong chelating agents coordinating through both nitrogen atoms of the C=N group [1]. The benzimidazole ring system is interesting being present in clinically approved anthelmintics, antiulcers, antivirals, and antihistamines [2].

The molecule of the title complex has a crystallographic center of symmetry. The asymmetric unit contains one of the zinc complex and the Zn(II) has a distorted tetrahedral coordination formed by one O atoms from 2,3-dihydroxybutanedioate dianion and three N atoms (N1, N3, N4) from two 2,2′-(1,2-ethanediyl)bis(1*H*-benzimidazole) molecules. The bridging 2,3-dihydroxybutanedioate dianion and the intermolecular hydrogen bonds N–H···O^i (symmetry code i: x–1,y,z) play very important role in the formation, stability and crystallization of the title complex, assembling the molecules into a two-dimensional network.

Table 1. Data collection and handling.

Crystal:	colorless block, size 0.21 × 0.31 × 0.4 mm
Wavelength:	Mo K_α radiation (0.71069 Å)
μ:	13.87 cm^{-1}
Diffractometer, scan mode:	Bruker APEX CCD, φ/ω
$2\theta_{max}$:	50.14°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	9016, 3192
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 2369
$N(param)_{refined}$:	259
Programs:	SHELXS-97, SHELXL-97 [3]

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

Atom	Site	Occ.	x	y	z	U_{iso}
H(16)	4*e*		–0.1380	–0.1153	0.6260	0.062
H(10A)	4*e*		0.1499	0.1999	1.1571	0.047
H(10B)	4*e*		0.1500	0.1549	1.0286	0.047
H(15)	4*e*		–0.2716	–0.0302	0.7208	0.062
H(18)	4*e*		0.2018	0.0132	0.6583	0.054
H(12A)	4*e*		–0.1606	0.2419	0.8552	0.048
H(12B)	4*e*		–0.0042	0.2591	0.8312	0.048
H(8)	4*e*		0.4885	0.2884	0.7341	0.058
H(7)	4*e*		0.6476	0.3817	0.7813	0.073
H(11A)	4*e*		–0.0813	0.1930	1.0607	0.060
H(11B)	4*e*		–0.0332	0.2733	1.0534	0.060
H(6)	4*e*		0.6477	0.4476	0.9697	0.073
H(17)	4*e*		0.0941	–0.0958	0.6006	0.062
H(5)	4*e*		0.4953	0.4206	1.1225	0.057
H(3A)	4*e*	0.482	0.5202	–0.0748	0.8833	0.103
H(3B)	4*e*	0.518	0.690(1)	0.031(2)	1.09(1)	0.108
H(111)	4*e*		–0.242(6)	0.116(3)	0.827(5)	0.08(2)

* e-mail: fengguodong00805@163.com

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}
Zn(1)	4*e*		0.26153(5)	0.16711(2)	0.77071(4)	0.0287(3)	0.0321(3)	0.0271(3)	–0.0016(2)	0.0035(2)	0.0020(2)
N(1)	4*e*		0.2959(3)	0.2450(2)	0.9030(3)	0.035(2)	0.037(2)	0.024(2)	–0.007(2)	0.006(2)	–0.002(2)
C(3)	4*e*		0.3971(4)	0.2986(2)	0.9025(4)	0.032(2)	0.038(3)	0.029(2)	–0.006(2)	0.002(2)	0.006(2)
N(2)	4*e*		–0.1594(4)	0.1059(2)	0.7987(4)	0.027(2)	0.048(3)	0.048(2)	–0.007(2)	0.008(2)	–0.006(2)
C(16)	4*e*		–0.0969(5)	–0.0716(3)	0.6528(5)	0.051(3)	0.037(3)	0.063(3)	–0.013(2)	–0.006(3)	–0.006(2)
O(2)	4*e*		0.5701(3)	0.1338(2)	0.8668(3)	0.034(2)	0.047(2)	0.073(3)	–0.001(2)	0.009(2)	0.009(2)
C(20)	4*e*		0.4897(5)	0.0851(3)	0.8880(5)	0.036(3)	0.041(3)	0.049(3)	0.002(2)	0.002(2)	0.008(2)
N(3)	4*e*		0.0631(3)	0.1271(2)	0.7674(3)	0.028(2)	0.036(2)	0.034(2)	–0.000(2)	0.002(2)	–0.003(2)
C(10)	4*e*		0.1354(5)	0.2027(2)	1.0624(4)	0.046(3)	0.043(3)	0.028(2)	–0.017(2)	0.006(2)	–0.004(2)
C(13)	4*e*		–0.0519(4)	0.1534(2)	0.8110(4)	0.027(2)	0.040(3)	0.033(2)	0.000(2)	–0.000(2)	–0.001(2)
O(1)	4*e*		0.3593(3)	0.0813(2)	0.8449(3)	0.033(2)	0.046(2)	0.070(2)	–0.003(2)	–0.010(2)	0.023(2)
C(15)	4*e*		–0.1779(5)	–0.0213(3)	0.7078(5)	0.040(3)	0.054(3)	0.060(3)	–0.014(2)	0.006(2)	0.000(3)
C(18)	4*e*		0.1077(5)	0.0050(3)	0.6706(5)	0.031(2)	0.048(3)	0.055(3)	0.000(2)	0.004(2)	–0.013(2)
C(12)	4*e*		–0.0634(4)	0.2254(2)	0.8720(4)	0.029(2)	0.042(3)	0.048(3)	0.003(2)	0.005(2)	–0.009(2)
C(4)	4*e*		0.4000(4)	0.3369(2)	1.0181(4)	0.035(2)	0.031(2)	0.034(2)	–0.003(2)	0.007(2)	0.004(2)
C(19)	4*e*		0.0278(4)	0.0572(2)	0.7244(4)	0.029(2)	0.036(3)	0.032(2)	–0.002(2)	–0.002(2)	–0.000(2)
C(8)	4*e*		0.4898(5)	0.3145(3)	0.8113(5)	0.050(3)	0.060(3)	0.036(3)	–0.018(2)	0.013(2)	–0.010(2)
C(7)	4*e*		0.5835(5)	0.3702(3)	0.8399(5)	0.056(3)	0.082(4)	0.049(3)	–0.030(3)	0.024(3)	–0.011(3)
C(14)	4*e*		–0.1118(5)	0.0437(2)	0.7428(4)	0.038(2)	0.037(3)	0.039(3)	–0.004(2)	0.003(2)	–0.002(2)
C(11)	4*e*		–0.0191(5)	0.2253(3)	1.0201(5)	0.045(3)	0.055(3)	0.054(3)	–0.014(2)	0.023(2)	–0.017(2)
C(6)	4*e*		0.5842(6)	0.4096(3)	0.9543(5)	0.066(4)	0.064(4)	0.054(3)	–0.037(3)	0.015(3)	–0.007(3)
C(9)	4*e*		0.2436(4)	0.2516(2)	1.0181(4)	0.029(2)	0.031(2)	0.027(2)	–0.005(2)	0.003(2)	0.002(2)
C(17)	4*e*		0.0426(5)	–0.0596(3)	0.6360(5)	0.050(3)	0.041(3)	0.063(3)	0.002(2)	–0.003(3)	–0.015(2)
C(5)	4*e*		0.4939(5)	0.3941(3)	1.0457(5)	0.057(3)	0.047(3)	0.040(3)	–0.017(2)	0.008(2)	–0.008(2)
C(21)	4*e*		0.5481(5)	0.0161(3)	0.9607(7)	0.042(3)	0.063(4)	0.096(5)	0.007(3)	–0.014(3)	0.040(3)
O(3A)	4*e*	0.482(7)	0.5677(9)	–0.0396(4)	0.8681(7)	0.105(7)	0.053(5)	0.053(5)	0.027(4)	0.036(4)	0.000(4)
O(3B)	4*e*	0.518	0.6841(6)	0.0383(4)	1.0213(8)	0.035(4)	0.083(6)	0.094(6)	–0.006(4)	–0.009(4)	0.051(5)
N(4)	4*e*		0.3008(3)	0.3066(2)	1.0913(3)	0.030(2)	0.030(2)	0.028(2)	–0.005(2)	0.004(2)	0.001(2)

Acknowledgment. This work was financially supported by the Foundation for Young Teachers of Baoji University of Arts and Science (grant no. ZK09135).

References

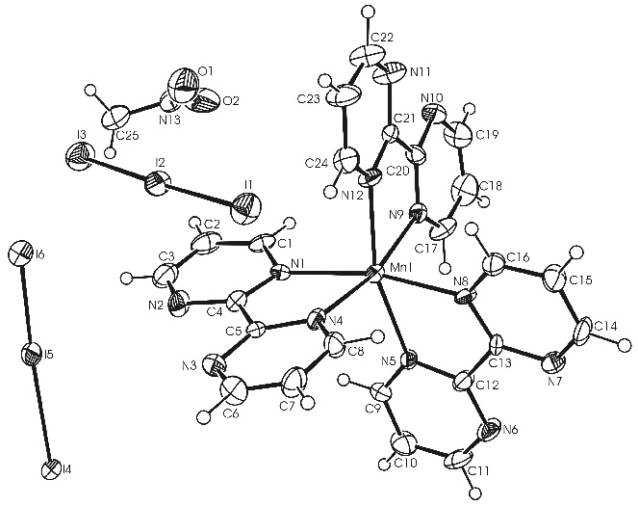
1. Sun, T.; Ke, L.; Yulin, L.: Aqua[1,3-bis(benzimidazol-2-yl)-2-oxapropane]diethanolmanganese(II) dipicrate ethanol disolvate. Acta Crystallogr. **E66** (2010) m1058-1059.
2. Harrell, C. C.; Kohli, P.; Siwy, Z.; Martin, C. R.: DNA-Nanotube Artificial Ion Channels. J. Am. Chem. Soc. **126** (2004) 15646-15647.
3. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. **A64** (2008) 112-122.

Crystal structure of tris(2,2′-bipyrimidine-κ^2N,N')manganese(II) bis(triiodide) — nitromethane (1:1), $[Mn(C_8H_6N_4)_3][I_3]_2 \cdot CH_3NO_2$

Kwang Ha*

Chonnam National University, School of Applied Chemical Engineering, Research Institute of Catalysis, Gwangju 500-757, Republic of Korea

Received March 19, 2011, accepted and available on-line June 23, 2011; CCDC no. 1267/3458



Abstract

$C_{25}H_{21}I_6MnN_{13}O_2$, triclinic, $P\bar{1}$ (no. 2), a = 11.246(1) Å, b = 14.016(1) Å, c = 14.042(1) Å, α = 60.163(2)°, β = 84.072(2)°, γ = 85.667(2)°, V = 1908.9 Å^3, Z = 2, $R_{gt}(F)$ = 0.067, $wR_{ref}(F^2)$ = 0.168, T = 200 K.

Source of material

To a solution of MnI_2 (0.3086 g, 1.000 mmol) in acetone (30 ml) was added 2,2′-bipyrimidine (bpym; 0.1588 g, 1.004 mmol) and stirred for 3 h at room temperature. After addition of pentane (30 ml) to the reaction mixture, the formed precipitate was then separated by filtration, washed with EtOH and ether and dried at 50 °C to give brown powder (0.3621 g). Crystals suitable for X-ray diffraction analysis were obtained by slow evaporation from a mixture of CH_3NO_2 and CH_3CN.

Experimental details

Hydrogen atoms were positioned geometrically and allowed to ride on their parent atoms with d(C—H) = 0.95 Å (CH) or 0.98 Å (CH_3) and U_{iso}(H) = 1.2 U_{eq}(C) or 1.5 $U_{eq}(C_{methyl})$. The highest peak (1.40 e Å^{-3}) and the deepest hole (–1.14 e Å^{-3}) in the difference Fourier map are located 1.12 Å and 1.09 Å from the atoms I1 and I5, respectively.

Discussion

The structure of the title compound consists of a mononuclear cationic complex $[Mn(bpym)_3]^{2+}$, two discrete I_3^- anions and a nitromethane solvent molecule. The structure is close to that of the Mn(II) complex $[Mn(phen)_3](I_3)_2$ (phen = 1,10-phenanthroline), which crystallizes in the hexagonal space group $R\bar{3}$ [1]. In the title complex, the Mn(II) ion is six-coordinated in a considerably distorted octahedral manner by six N atoms of the three bidentate 2,2′-bipyrimidine ligands. The complex approximates C_3 symmetry. The tight N–Mn–N chelating angles (∠N1–Mn1–N4 = 72.9(3)°, ∠N5–Mn1–N8 = 72.9(3)° and ∠N9–Mn1–N12 = 73.4(4)°) contribute to the distortion of the ocataheron. The apical angles ∠N1–Mn1–N8, ∠N4–Mn1–N9 and ∠N5–Mn1–N12 are 164.6(4)°, 167.4(4)° and 162.9(4)°, respectively. The distances d(Mn—N) are roughly equal (2.23(1) - 2.28(1) Å). The dihedral angles between the least-squares planes of the bpym ligands are 89.5(2)°, 87.0(3)° and 87.9(2)°. There are two types of triiodide anions, which differ in d(I—I) and their structures. One of them, I1–I2–I3, is approximately linear with d(I1—I2) = 2.941(1) Å, d(I2—I3) = 2.912(1) Å and ∠I1–I2–I3 = 178.04(5)°, whereas the other, I4–I5–I6, is slightly bent with ∠I4–I5–I6 = 171.40(5)° and reveals considerably different d(I4—I5) = 3.174(1) Å and d(I5—I6) = 2.796(2) Å. Numerous inter- and intramolecular π–π interactions between adjacent pyrimidine rings are present. The shortest distance between Cg1 (the centroid of ring N1–C4) and Cg2^i (ring N3–C6, symmetry code i: 1–x,1–y,1–z) is 3.790(9) Å, and the dihedral angle between the ring planes is 9.5(7)°. Moreover, the constituent ions and solvent molecules are linked by intermolecular C–H···N, C–H···O and C–H···I hydrogen bonds with d(C···N) = 3.35(2) Å, d(C···O) = 3.17(2) Å and 3.25(2) Å, and d(C···I) = 3.65(1) - 3.92(1) Å.

Table 1. Data collection and handling.

Crystal:	red-brown block, size 0.11 × 0.12 × 0.22 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	52.41 cm^{-1}
Diffractometer, scan mode:	Bruker SMART 1000 CCD, φ/ω
$2\theta_{max}$:	52.02°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	11742, 7374
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 4644
$N(param)_{refined}$:	425
Programs:	SHELXS-97, SHELXL-97 [2], ORTEP-3 [3], PLATON [4]

* e-mail: hakwang@chonnam.ac.kr

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

Atom	Site	x	y	z	U_{iso}
H(1)	2*i*	0.3768	0.2039	0.4949	0.039
H(2)	2*i*	0.3046	0.3406	0.3339	0.058
H(3)	2*i*	0.3765	0.5187	0.2569	0.057
H(6)	2*i*	0.8197	0.5952	0.4555	0.049
H(7)	2*i*	0.9152	0.4517	0.5927	0.053
H(8)	2*i*	0.8402	0.2784	0.6666	0.045
H(9)	2*i*	0.3704	0.2998	0.7083	0.043
H(10)	2*i*	0.2823	0.3216	0.8567	0.054
H(11)	2*i*	0.3776	0.2282	1.0199	0.063
H(14)	2*i*	0.8528	–0.0559	1.0588	0.054
H(15)	2*i*	0.9413	–0.0635	0.9031	0.050
H(16)	2*i*	0.8470	0.0352	0.7412	0.041
H(17)	2*i*	0.3698	0.0106	0.8037	0.049
H(18)	2*i*	0.2890	–0.1523	0.8366	0.067
H(19)	2*i*	0.3572	–0.2257	0.7281	0.057
H(22)	2*i*	0.8510	–0.0502	0.4288	0.060
H(23)	2*i*	0.9312	0.1043	0.4030	0.064
H(24)	2*i*	0.8342	0.1927	0.4961	0.045
H(25A)	2*i*	0.1369	0.3724	0.1299	0.109
H(25B)	2*i*	0.0335	0.3209	0.1007	0.109
H(25C)	2*i*	0.1651	0.3322	0.0412	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}
Mn(1)	2*i*	0.5927(2)	0.1696(2)	0.6538(1)	0.037(1)	0.025(1)	0.0191(9)	–0.0013(9)	–0.0018(8)	–0.0116(8)
N(1)	2*i*	0.5007(9)	0.2943(8)	0.5050(8)	0.036(6)	0.021(6)	0.026(5)	0.000(5)	–0.003(5)	–0.015(5)
N(2)	2*i*	0.502(1)	0.4806(9)	0.3589(8)	0.037(6)	0.039(7)	0.031(6)	0.002(5)	–0.017(5)	–0.013(5)
N(3)	2*i*	0.690(1)	0.5151(9)	0.4473(9)	0.051(7)	0.027(6)	0.035(6)	–0.005(5)	–0.006(5)	–0.016(5)
N(4)	2*i*	0.6970(9)	0.3230(8)	0.5770(7)	0.032(6)	0.028(6)	0.018(5)	–0.001(5)	–0.004(4)	–0.010(4)
N(5)	2*i*	0.4988(8)	0.1977(8)	0.7866(7)	0.026(5)	0.024(6)	0.018(5)	0.006(4)	–0.003(4)	–0.009(4)
N(6)	2*i*	0.504(1)	0.157(1)	0.9721(9)	0.049(7)	0.058(8)	0.028(6)	0.021(6)	–0.007(5)	–0.027(6)
N(7)	2*i*	0.706(1)	0.029(1)	0.9898(8)	0.054(8)	0.040(7)	0.025(6)	0.007(6)	0.005(5)	–0.018(5)
N(8)	2*i*	0.7055(9)	0.0844(8)	0.8013(8)	0.036(6)	0.030(6)	0.021(5)	–0.002(5)	0.000(4)	–0.018(5)
N(9)	2*i*	0.4985(9)	0.0162(8)	0.6958(8)	0.040(6)	0.024(6)	0.020(5)	–0.004(5)	–0.001(5)	–0.009(5)
N(10)	2*i*	0.496(1)	–0.1259(9)	0.6501(9)	0.061(8)	0.031(7)	0.043(7)	–0.003(6)	–0.005(6)	–0.023(6)
N(11)	2*i*	0.704(1)	–0.051(1)	0.521(1)	0.051(8)	0.064(9)	0.051(8)	–0.011(7)	0.009(6)	–0.044(7)
N(12)	2*i*	0.6992(9)	0.0928(9)	0.5641(8)	0.032(6)	0.036(6)	0.025(5)	–0.005(5)	0.005(5)	–0.020(5)
C(1)	2*i*	0.410(1)	0.275(1)	0.460(1)	0.030(7)	0.050(9)	0.037(7)	–0.004(6)	–0.006(6)	–0.033(7)
C(2)	2*i*	0.366(1)	0.355(1)	0.367(1)	0.044(9)	0.07(1)	0.052(9)	0.002(8)	–0.016(7)	–0.045(9)
C(3)	2*i*	0.411(1)	0.460(1)	0.319(1)	0.05(1)	0.06(1)	0.036(8)	0.012(8)	–0.010(7)	–0.026(8)
C(4)	2*i*	0.543(1)	0.397(1)	0.450(1)	0.036(7)	0.034(8)	0.022(6)	0.000(6)	–0.002(5)	–0.014(6)
C(5)	2*i*	0.649(1)	0.414(1)	0.4924(9)	0.040(7)	0.021(7)	0.018(6)	–0.002(6)	0.000(5)	–0.012(5)
C(6)	2*i*	0.788(1)	0.524(1)	0.487(1)	0.043(9)	0.034(8)	0.043(8)	–0.027(7)	0.005(7)	–0.015(7)
C(7)	2*i*	0.845(1)	0.441(1)	0.567(1)	0.049(9)	0.05(1)	0.034(8)	–0.007(8)	–0.015(7)	–0.017(7)
C(8)	2*i*	0.800(1)	0.340(1)	0.611(1)	0.049(9)	0.028(8)	0.033(7)	0.001(7)	–0.019(6)	–0.012(6)
C(9)	2*i*	0.405(1)	0.262(1)	0.777(1)	0.049(9)	0.026(7)	0.036(7)	0.008(6)	–0.010(6)	–0.018(6)
C(10)	2*i*	0.352(1)	0.277(1)	0.863(1)	0.040(8)	0.044(9)	0.049(9)	0.007(7)	0.006(7)	–0.025(8)
C(11)	2*i*	0.409(1)	0.220(1)	0.959(1)	0.07(1)	0.07(1)	0.040(9)	0.011(9)	–0.003(8)	–0.041(9)
C(12)	2*i*	0.545(1)	0.148(1)	0.886(1)	0.036(7)	0.039(8)	0.024(6)	0.002(6)	–0.006(5)	–0.018(6)
C(13)	2*i*	0.659(1)	0.083(1)	0.8938(9)	0.047(8)	0.021(7)	0.014(6)	0.010(6)	–0.008(5)	–0.004(5)
C(14)	2*i*	0.813(1)	–0.022(1)	0.992(1)	0.052(9)	0.06(1)	0.021(7)	0.026(8)	–0.019(6)	–0.015(7)
C(15)	2*i*	0.868(1)	–0.024(1)	0.901(1)	0.039(8)	0.046(9)	0.033(7)	0.021(7)	–0.005(6)	–0.017(7)
C(16)	2*i*	0.810(1)	0.033(1)	0.807(1)	0.036(8)	0.037(8)	0.028(7)	0.009(6)	–0.002(6)	–0.017(6)
C(17)	2*i*	0.404(1)	–0.025(1)	0.765(1)	0.030(8)	0.07(1)	0.034(8)	0.000(7)	0.002(6)	–0.034(8)
C(18)	2*i*	0.353(1)	–0.120(1)	0.782(1)	0.05(1)	0.06(1)	0.05(1)	–0.023(8)	0.008(8)	–0.016(9)
C(19)	2*i*	0.396(1)	–0.165(1)	0.722(1)	0.043(9)	0.041(9)	0.06(1)	–0.019(7)	0.008(8)	–0.025(8)
C(20)	2*i*	0.543(1)	–0.038(1)	0.643(1)	0.036(7)	0.020(7)	0.033(7)	–0.002(6)	–0.010(6)	–0.014(6)
C(21)	2*i*	0.655(1)	0.003(1)	0.5707(9)	0.033(7)	0.022(7)	0.016(6)	0.002(5)	0.001(5)	–0.007(5)
C(22)	2*i*	0.810(1)	–0.011(1)	0.462(1)	0.047(9)	0.07(1)	0.06(1)	–0.008(8)	0.007(8)	–0.048(9)
C(23)	2*i*	0.859(1)	0.077(1)	0.448(1)	0.06(1)	0.06(1)	0.05(1)	–0.004(9)	0.018(8)	–0.042(9)
C(24)	2*i*	0.801(1)	0.129(1)	0.503(1)	0.038(8)	0.037(8)	0.036(7)	–0.013(7)	0.008(6)	–0.016(7)
I(1)	2*i*	1.01902(9)	0.35789(9)	0.36388(8)	0.0476(6)	0.0513(6)	0.0432(5)	–0.0125(5)	–0.0058(4)	–0.0234(5)
I(2)	2*i*	0.81764(8)	0.42196(8)	0.22398(7)	0.0445(5)	0.0397(5)	0.0355(5)	–0.0027(4)	–0.0002(4)	–0.0207(4)
I(3)	2*i*	0.62031(9)	0.47897(9)	0.08435(8)	0.0526(6)	0.0588(7)	0.0472(6)	0.0062(5)	–0.0124(5)	–0.0288(5)
I(4)	2*i*	–0.12063(9)	0.83083(8)	0.29656(7)	0.0621(6)	0.0373(5)	0.0278(5)	–0.0002(5)	–0.0020(4)	–0.0164(4)
I(5)	2*i*	0.02308(9)	0.73040(8)	0.15853(7)	0.0617(7)	0.0368(5)	0.0334(5)	0.0038(5)	–0.0175(4)	–0.0135(4)
I(6)	2*i*	0.1786(1)	0.63867(9)	0.05504(8)	0.0739(8)	0.0504(7)	0.0401(6)	0.0018(6)	–0.0034(5)	–0.0208(5)
O(1)	2*i*	0.256(2)	0.189(1)	0.204(1)	0.11(1)	0.09(1)	0.071(9)	0.02(1)	–0.024(9)	–0.037(9)
O(2)	2*i*	0.074(1)	0.146(1)	0.254(1)	0.14(1)	0.07(1)	0.10(1)	–0.039(9)	0.10(1)	–0.053(9)
N(13)	2*i*	0.152(2)	0.209(1)	0.197(1)	0.09(1)	0.06(1)	0.035(8)	0.01(1)	0.028(8)	–0.018(7)
C(25)	2*i*	0.119(2)	0.317(2)	0.110(1)	0.09(1)	0.08(1)	0.05(1)	0.01(1)	0.01(1)	–0.04(1)

Acknowledgment. This work was supported by Priority Research Centers Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (grant no. 2010-0029626).

References

1. Ramalakshmi, D.; Rajender Reddy, K.; Padmavathy, D.; Rajasekharan, M. V.; Arulsamy, N.; Hodgson, D. J.: Polyiodides of transition metal trischelate cations: syntheses, structures, and spectral and electrical conductivity studies of $[Mn(phen)_3](I_3)_2$ and $[Mn(bpy)_3](I_3)_{1.5}(I_8)_{0.25}$. Inorg. Chim. Acta **284** (1999) 158-166.
2. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. **A64** (2008) 112-122.
3. Farrugia, L. J.: ORTEP-3 for Windows - a version of ORTEP-III with a Graphical User Interface (GUI) J. Appl. Crystallogr. **30** (1997) 565.
4. Spek, A. L.: Single-crystal structure validation with the program PLATON. J. Appl. Crystallogr. **36** (2003) 7-13.