Crystal structure of bis(1,10-phenanthroline-κ^2N,N')bis(2-hydroxybenzoato-$\kappa O^1;\kappa^2O^1,O^{1'}$)cadmium(II) — methanol (1:1), $Cd(C_{12}H_8N_2)_2(C_7H_5O_3)_2 \cdot CH_3OH$

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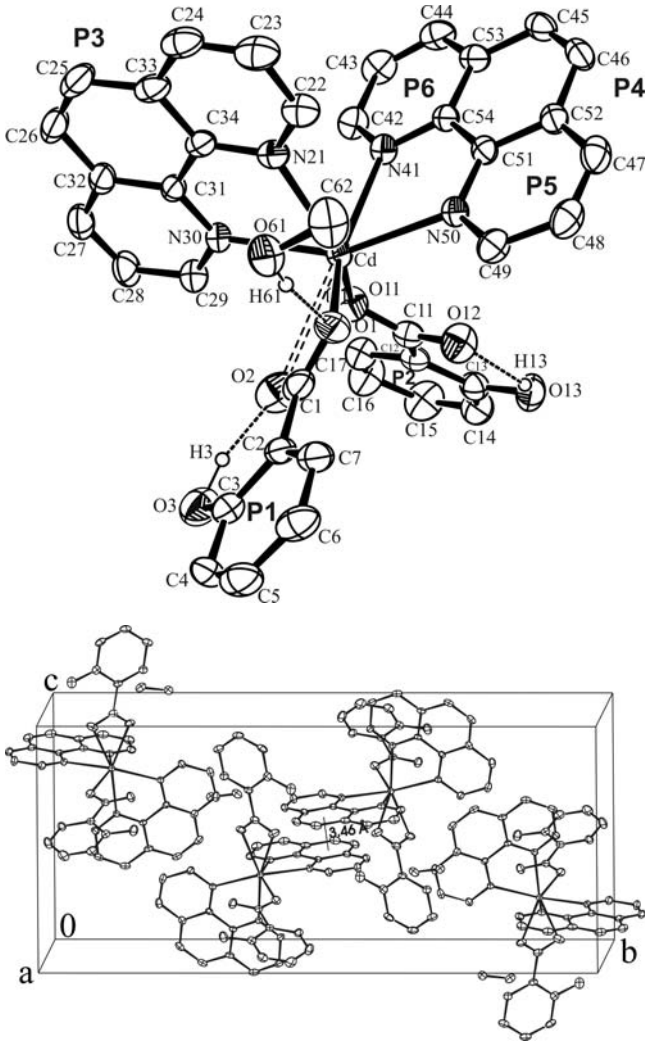

Abstract

$C_{39}H_{30}CdN_4O_7$, monoclinic, $P12_1/n1$ (no. 14), a = 10.823(5) Å, b = 26.455(9) Å, c = 11.703(6) Å, β = 92.37(4)°, V = 3348.0 Å^3, Z = 4, $R_{gt}(F)$ = 0.044, $wR_{ref}(F^2)$ = 0.129, T = 293 K.

Source of material

The cadmium(II) salicylate [$Cd^{II}(Sal)_2$] was prepared by reaction of $Cd(NO_3)_2 \cdot 4H_2O$ with NaSal after neutralizing HSal by a NaOH solution. The title compound was synthesized as follows: 1,10-phenanthroline monohydrate (0.396 g, 2 mmol) was added to a stirred solution of $Cd^{II}(Sal)_2$ (0.387 g ,1 mmol) in 20 ml of methanol at 60 °C under reflux conditions for one hour. Single crystals were obtained after 48 hours by slow evaporation of the solvent at room temperature (293 K).

Experimental details

H3 and H13 atoms involved in hydrogen bonding were first located from a difference Fourier map and then refined with the same isotropic thermal parameter. Other H atoms were inserted at calculated positions with $U_{iso}(H) = 1.2\ U_{eq}$(carrier atoms) except for hydrogen atoms of CH_3 from methanol [$U_{iso}(H) = 1.5\ U_{eq}(C)$].

Discussion

In previous works, we had reported structural characterization of ternary cadmium(II) complexes with 1,10-phenanthroline (phen) and derivatives and arylcarboxylic acids to compare the environment of the cadmium [1-4].

In the title monomeric complex, Cd(II) is six-coordinated by two phen bidendate ligands via N21 and N30 or N41 and N50 atom and two salicylate ($Hsal^-$) anionic ligands via O1 or O11 atoms (figure, top). The crystal structure is completed by a molecule of methanol. Therefore, the cadmium atom exhibits a strongly distorted octahedral environment with apical positions occupied by O11 and N21 with ∠N21–Cd–O1 = 145.0(1)°. The O1, N30, N41, N50 basis is nearly planar with a maximum deviation from the mean plane of 0.051(2) Å for N50 atom. The Cd atom lies 0.419(2) Å out of this plane. The degree of deviation from an ideal octahedron is appreciable with the bond angles ranging from 69.0(1)° to 121.5(1)°. This very irregular arrangement is imposed by the small angles of the two bidentate phen ligands [∠N21–Cd–N30 = 68.3(1)°; ∠N41–Cd–N50 = 69.0(1)°], mainly due to the rigidity of these chelate molecules. The d(Cd—N21) = 2.463(3) Å in the first phen ligand is significantly greater than d(Cd—N30) = 2.384(3), d(Cd—N41) = 2.414(3) and d(Cd—N50) = 2.394(3) Å, respectively. Each carboxylate in the single deprotonated $Hsal^-$ forms bonds in an asymmetric chelating mode with one tightly bonded carboxylato oxygen [d(Cd—O1) = 2.326(3) Å, d(Cd—O11) = 2.234(3) Å] and a second oxygen very weakly bonded [d(Cd—O2) = 2.752(4) Å, d(Cd—O12) = 3.152(4) Å]. So, the Cd environment can be described as a (6 + 1 + 1*) distorted bicapped octahedron: the O2 and O12 atoms cap the triangular faces formed by O1, O11, N30 and O11, O1, N50, respectively. The bond lengths and angles of the complexed salicylate ligands and phen are normal. The phenyl mean planes **P1** [C2-C7] and **P2** [C12-C17] [maximum deviation of 0.016(3) Å for C6] in the salicylate ligands make a dihedral an-

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gle of 80.9(1)°. The oxygen atoms O1, O2 and O3 (or O11, O12 and O13) are out of **P1** (or **P2**) with a maximum deviation of 0.306(7) Å for O1 (0.112(8) Å for O12) The phen ligands are essentially planar (maximum deviation of 0.076 (4) Å for C43) and the Cd(II) atom is displaced from the least-squares planes **P3** [N21/C22-C29/N30/C31-C34] by 0.084(3) Å and from **P4** [N41/C42-C49/N50/C51-C54] by 0.115(3) Å. The dihedral angle between planes **P3** and **P4** is 80.51(7)°. The hydroxyl H3 (or H13) atom attached to O3 (or O13) is involved in intra-molecular hydrogen bonding interaction via O2 (or O12) atom [d(O3–H3···O2) = 2.545(6) Å, ∠O3–H3···O2 = 157(4)°; d(O13–H13···O12) = 2.553(5) Å, ∠O13–H13···O12 = 139(4)°], thus contributing to planarity of the rings [O2/C1/C2/C3/O3/H3 and O12/C11/C12/C13/O13/H13] (maximum deviation of 0.077(3) Å for C1). There is an inter-molecular hydrogen bonding interaction involving the methanol molecule and the carboxylate O1 atom [d(O61–H61···O1) = 2.854(5) Å, ∠O61–H61···O1 = 165°].

Moreover, the packing is governed by π-π stacking interactions which occur between phen ligands [C25-C26/C31-C34] through inversion centre at (½01) with a centroid-to-centroid distance of 3.717(3) Å, an average spacing of 3.46 Å with an offset of 21.3° (figure, bottom). In addition, there are C–H···O interactions with d(C27–H27···O61^{i}) = 3.374(6) Å, ∠C27–H27···O61^{i} = 163°; d(C44–H44···O61^{ii}) = 3.407(6) Å, ∠C44–H44···O61^{ii} = 160° and van der Waals contacts, the shortest being d(O13···C23^{iii}) = 3.246(7) Å (symmetry codes i: 1–x,–y,2–z; ii: x,y,z–1; iii: 1+x,y,z). The crystal packing is completed by two C–H···Cg(π-ring) interactions with d(H62B···Cg1) = 2.88 Å, ∠C62–H62B···Cg1 = 152°, d(H14···Cg2^{iii}) = 2.89 Å, ∠C14–H14···Cg2^{iii} = 148°; with Cg1 and Cg2 centroid of rings **P5** (C47-C49/N50/C51-C52) and **P6** (N41/C42-C44/C53-C54), respectively.

Table 1. Data collection and handling.

Crystal:	colorless parallelepiped, size 0.28 × 0.32 × 0.35 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	7.11 cm^{-1}
Diffractometer, scan mode:	Enraf-Nonius CAD4, $\omega/2\theta$
$2\theta_{max}$:	59.98°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	19381, 9742
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 5289
$N(param)_{refined}$:	467
Programs:	SIR92 [5], SHELX-97 [6], WinGX [7], CAMERON [8], ORTEP-III [9]

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

Atom	Site	x	y	z	U_{iso}
H(3)	4*e*	0.945(4)	0.067(2)	1.103(4)	0.050(9)
H(4)	4*e*	0.9868	0.0892	1.3784	0.088
H(5)	4*e*	0.9264	0.1628	1.4601	0.092
H(6)	4*e*	0.8285	0.2250	1.3542	0.084
H(7)	4*e*	0.7769	0.2103	1.1630	0.067
H(13)	4*e*	1.133(4)	0.189(2)	0.652(4)	0.050(9)
H(14)	4*e*	1.3471	0.1256	0.5094	0.092
H(15)	4*e*	1.3451	0.0406	0.4755	0.113
H(16)	4*e*	1.1901	–0.0097	0.5422	0.108
H(17)	4*e*	1.0292	0.0263	0.6316	0.075
H(22)	4*e*	0.4547	0.1848	0.8162	0.072
H(23)	4*e*	0.2520	0.1714	0.8547	0.087
H(24)	4*e*	0.1839	0.0908	0.8831	0.083
H(25)	4*e*	0.2315	–0.0036	0.8898	0.091
H(26)	4*e*	0.3727	–0.0668	0.8838	0.085
H(27)	4*e*	0.5905	–0.0946	0.8555	0.080
H(28)	4*e*	0.7898	–0.0735	0.8186	0.080
H(29)	4*e*	0.8418	0.0102	0.7954	0.070
H(42)	4*e*	0.6617	0.0604	0.5555	0.066
H(43)	4*e*	0.5907	0.0688	0.3680	0.078
H(44)	4*e*	0.5340	0.1468	0.3001	0.076
H(45)	4*e*	0.5113	0.2411	0.3377	0.072
H(46)	4*e*	0.5459	0.3076	0.4542	0.072
H(47)	4*e*	0.6297	0.3425	0.6436	0.076
H(48)	4*e*	0.7138	0.3275	0.8219	0.078
H(49)	4*e*	0.7494	0.2450	0.8829	0.065
H(61)	4*e*	0.5919	0.1701	1.0709	0.099
H(62A)	4*e*	0.5149	0.2427	1.1320	0.125
H(62B)	4*e*	0.3900	0.2211	1.0799	0.125
H(62C)	4*e*	0.5001	0.2319	1.0004	0.125

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)	4*e*	0.73376(2)	0.125544(9)	0.79405(2)	0.0425(1)	0.0382(1)	0.0351(1)	0.0010(1)	0.00445(8)	0.0001(1)
O(1)	4*e*	0.7464(3)	0.1589(1)	0.9780(2)	0.079(2)	0.091(3)	0.044(2)	–0.016(2)	–0.013(2)	0.011(2)
C(1)	4*e*	0.8240(4)	0.1318(2)	1.0289(4)	0.057(2)	0.077(3)	0.048(2)	–0.027(2)	0.002(2)	0.003(2)
O(2)	4*e*	0.8775(4)	0.0959(2)	0.9816(3)	0.098(3)	0.111(3)	0.065(2)	–0.011(2)	0.007(2)	–0.032(2)
C(2)	4*e*	0.8542(3)	0.1416(2)	1.1533(3)	0.042(2)	0.069(3)	0.038(2)	–0.015(2)	–0.004(2)	0.006(2)
O(3)	4*e*	0.9636(4)	0.0624(2)	1.1726(4)	0.076(2)	0.075(3)	0.106(3)	0.001(2)	–0.012(2)	–0.002(2)
C(3)	4*e*	0.9197(4)	0.1053(2)	1.2180(4)	0.047(2)	0.063(3)	0.064(3)	–0.010(2)	–0.003(2)	0.004(2)
C(4)	4*e*	0.9454(4)	0.1136(2)	1.3343(4)	0.068(3)	0.095(4)	0.054(3)	–0.019(3)	–0.019(2)	0.031(3)
C(5)	4*e*	0.9096(5)	0.1576(2)	1.3825(4)	0.070(3)	0.118(5)	0.041(2)	–0.023(3)	–0.004(2)	–0.001(3)
C(6)	4*e*	0.8494(4)	0.1946(2)	1.3201(4)	0.059(3)	0.098(4)	0.053(3)	–0.015(3)	0.005(2)	–0.020(3)
C(7)	4*e*	0.8202(4)	0.1859(2)	1.2054(4)	0.048(2)	0.067(3)	0.053(2)	–0.002(2)	–0.005(2)	–0.001(2)
O(11)	4*e*	0.8987(3)	0.0923(1)	0.7134(3)	0.054(2)	0.073(2)	0.070(2)	0.009(2)	0.024(2)	0.009(2)
C(11)	4*e*	0.9852(3)	0.1214(2)	0.6897(3)	0.048(2)	0.060(3)	0.039(2)	0.006(2)	0.003(2)	–0.002(2)
O(12)	4*e*	0.9883(3)	0.1670(1)	0.7120(3)	0.081(2)	0.060(2)	0.093(3)	0.009(2)	0.016(2)	–0.015(2)
C(12)	4*e*	1.0888(3)	0.0984(2)	0.6273(3)	0.041(2)	0.063(2)	0.036(2)	0.004(2)	0.003(1)	0.001(2)
O(13)	4*e*	1.1865(3)	0.1780(2)	0.6037(4)	0.074(2)	0.068(2)	0.110(3)	–0.007(2)	0.017(2)	0.011(2)

Table 3. Continued.

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(13)	4*e*	1.1844(4)	0.1277(2)	0.5886(4)	0.053(2)	0.067(3)	0.056(2)	–0.001(2)	0.002(2)	0.010(2)
C(14)	4*e*	1.2820(4)	0.1058(2)	0.5334(5)	0.054(3)	0.098(4)	0.079(3)	–0.003(3)	0.023(2)	0.015(3)
C(15)	4*e*	1.2813(5)	0.0552(2)	0.5149(5)	0.070(3)	0.109(5)	0.105(5)	0.011(3)	0.041(3)	–0.021(4)
C(16)	4*e*	1.1880(5)	0.0251(2)	0.5532(6)	0.082(4)	0.069(3)	0.122(5)	0.008(3)	0.034(3)	–0.024(3)
C(17)	4*e*	1.0931(4)	0.0466(2)	0.6073(4)	0.059(3)	0.062(3)	0.067(3)	0.005(2)	0.014(2)	–0.007(2)
N(21)	4*e*	0.5110(3)	0.1153(1)	0.8231(3)	0.042(2)	0.062(2)	0.037(2)	0.001(1)	0.005(1)	–0.002(1)
C(22)	4*e*	0.4285(4)	0.1519(2)	0.8284(4)	0.053(2)	0.072(3)	0.054(2)	0.007(2)	0.005(2)	–0.006(2)
C(23)	4*e*	0.3062(4)	0.1442(2)	0.8509(4)	0.051(3)	0.104(4)	0.063(3)	0.013(3)	0.009(2)	–0.008(3)
C(24)	4*e*	0.2662(4)	0.0965(2)	0.8671(4)	0.043(2)	0.117(4)	0.048(2)	–0.004(3)	0.004(2)	–0.006(3)
C(25)	4*e*	0.3134(5)	0.0041(2)	0.8761(4)	0.060(3)	0.114(4)	0.053(3)	–0.047(3)	0.001(2)	0.002(3)
C(26)	4*e*	0.3974(5)	–0.0336(2)	0.8718(4)	0.079(3)	0.079(3)	0.054(3)	–0.044(3)	–0.002(2)	0.008(2)
C(27)	4*e*	0.6119(5)	–0.0609(2)	0.8443(4)	0.097(4)	0.049(2)	0.053(2)	–0.020(2)	–0.006(2)	0.006(2)
C(28)	4*e*	0.7297(5)	–0.0485(2)	0.8233(4)	0.085(3)	0.038(2)	0.077(3)	0.002(2)	0.001(3)	0.008(2)
C(29)	4*e*	0.7601(4)	0.0020(2)	0.8086(4)	0.063(3)	0.049(2)	0.063(3)	–0.003(2)	0.004(2)	0.005(2)
N(30)	4*e*	0.6783(3)	0.0388(1)	0.8124(3)	0.049(2)	0.039(2)	0.046(2)	–0.003(1)	0.004(1)	0.004(1)
C(31)	4*e*	0.5599(3)	0.0271(1)	0.8328(3)	0.048(2)	0.050(2)	0.030(2)	–0.014(2)	–0.001(1)	0.004(1)
C(32)	4*e*	0.5225(4)	–0.0232(2)	0.8493(3)	0.070(3)	0.063(3)	0.034(2)	–0.024(2)	–0.003(2)	0.004(2)
C(33)	4*e*	0.3482(4)	0.0556(2)	0.8602(3)	0.044(2)	0.093(3)	0.035(2)	–0.015(2)	0.000(2)	–0.002(2)
C(34)	4*e*	0.4716(3)	0.0673(2)	0.8395(3)	0.042(2)	0.069(3)	0.027(2)	–0.011(2)	0.002(1)	–0.001(2)
N(41)	4*e*	0.6553(3)	0.1313(1)	0.5984(2)	0.053(2)	0.042(2)	0.038(2)	–0.001(1)	0.009(1)	–0.004(1)
C(42)	4*e*	0.6412(4)	0.0925(2)	0.5281(3)	0.067(3)	0.050(2)	0.048(2)	–0.002(2)	0.008(2)	–0.013(2)
C(43)	4*e*	0.5974(4)	0.0971(2)	0.4152(4)	0.075(3)	0.078(3)	0.042(2)	–0.008(2)	0.010(2)	–0.020(2)
C(44)	4*e*	0.5647(4)	0.1432(2)	0.3751(4)	0.056(2)	0.098(4)	0.037(2)	–0.008(2)	0.002(2)	–0.004(2)
C(45)	4*e*	0.5461(4)	0.2358(2)	0.4107(4)	0.046(2)	0.085(3)	0.048(2)	0.002(2)	0.005(2)	0.027(2)
C(46)	4*e*	0.5665(4)	0.2754(2)	0.4802(4)	0.045(2)	0.064(3)	0.070(3)	0.011(2)	0.012(2)	0.031(2)
C(47)	4*e*	0.6458(4)	0.3096(2)	0.6674(4)	0.056(2)	0.043(2)	0.093(4)	0.007(2)	0.014(2)	0.004(2)
C(48)	4*e*	0.6949(4)	0.3007(2)	0.7729(4)	0.063(3)	0.043(2)	0.089(4)	–0.002(2)	0.011(2)	–0.017(2)
C(49)	4*e*	0.7174(4)	0.2507(2)	0.8090(4)	0.060(3)	0.048(2)	0.056(2)	–0.003(2)	0.004(2)	–0.011(2)
N(50)	4*e*	0.6945(3)	0.2116(1)	0.7409(2)	0.046(2)	0.040(2)	0.040(2)	0.000(1)	0.007(1)	0.000(1)
C(51)	4*e*	0.6466(3)	0.2199(1)	0.6335(3)	0.037(2)	0.046(2)	0.042(2)	0.001(1)	0.011(1)	0.007(2)
C(52)	4*e*	0.6191(3)	0.2692(2)	0.5933(4)	0.036(2)	0.048(2)	0.062(2)	0.004(2)	0.012(2)	0.011(2)
C(53)	4*e*	0.5768(3)	0.1859(2)	0.4465(3)	0.042(2)	0.075(3)	0.034(2)	–0.003(2)	0.007(1)	0.011(2)
C(54)	4*e*	0.6251(3)	0.1779(1)	0.5588(3)	0.036(2)	0.051(2)	0.032(2)	–0.002(1)	0.008(1)	0.005(1)
O(61)	4*e*	0.5211(3)	0.1723(1)	1.0927(3)	0.083(2)	0.090(3)	0.074(2)	–0.012(2)	0.004(2)	0.026(2)
C(62)	4*e*	0.4783(5)	0.2207(2)	1.0749(4)	0.115(5)	0.066(3)	0.070(3)	–0.002(3)	0.019(3)	–0.005(3)

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