

КРАТКИЕ СООБЩЕНИЯ

UDC 548.73

CRYSTAL STRUCTURES OF TWO DINUCLEAR CADMIUM(II) COMPLEXES WITH SCHIFF BASES AS LIGANDS

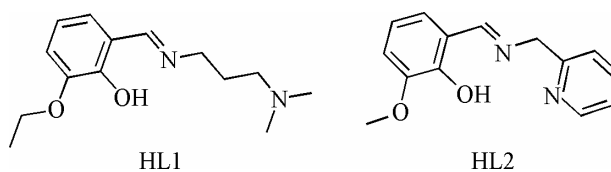
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Two new cadmium(II) complexes, $Cd_2(L1)_2(NCS)_2$ (*1*) and $Cd_2(L2)_2(NCS)_2$ (*2*), where L1 and L2 are the deprotonated forms of 2-[(3-dimethylaminopropylimino)methyl]-6-ethoxyphenol and 2-methoxy-6-[(pyridin-2-ylmethylimino)methyl]phenol, respectively, have been isolated as crystalline products and characterized by elemental analysis, IR spectroscopy, and single crystal X-ray diffraction method. Both compounds are structurally similar and are phenolate-O-bridged dinuclear cadmium(II) complexes. Each Cd(II) cation in the complexes is octahedrally coordinated. The Cd...Cd distances in (*1*) and (*2*) are 3.618(2) and 3.571(2) Å, respectively.

Keywords: Schiff base, Cd(II), dimer, isothiocyanate, phenolate.

Schiff bases are frequently used as chelating ligands due to their structural diversity and potential applications [1—3]. The thiocyanate ligands are versatile bridging groups, especially for the cadmium(II) complexes [4—6]. In this paper, two new structurally similar dinuclear cadmium(II) complexes, $Cd_2(L1)_2(NCS)_2$ (*1*) and $Cd_2(L2)_2(NCS)_2$ (*2*), where L1 and L2 are the deprotonated forms of 2-[(3-dimethylaminopropylimino)methyl]-6-ethoxyphenol (HL1) and 2-methoxy-6-[(pyridin-2-ylmethylimino)methyl]phenol (HL2), respectively, have been synthesized and structurally characterized.



Experimental. Materials and methods. Infrared spectra were recorded on a Bruker IFS-125 model FT-IR spectrometer using KBr pellets. C, H, N analyses were carried out on a Perkin-Elmer model 240 analyzer. Aldehydes and amines, purchased from Lancaster Company, and other chemicals were of analytical grade quality and were used without further purification. The Schiff bases HL1 and HL2 were synthesized according to the literature method [7].

Synthesis of (*1*). To a methanol solution (10 ml) of HL1 (25.0 mg, 0.1 mmol) and NH_4NCS (7.6 mg, 0.1 mmol) was added a methanol solution (10 ml) of $Cd(NO_3)_2 \cdot 4H_2O$ (30.8 mg, 0.1 mmol). The mixture was stirred for 3 min at room temperature to give a clear colorless solution. After keeping the solution in air for a few days, colorless block-shaped crystals of (*1*), suitable for single crystal X-ray diffraction, formed at the bottom of the vessel due to slow evaporation of the solvent. The crystals were isolated, washed three times with methanol and dried in air. Yield: 73 % based on HL1.

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Crystal data for the complexes studied

Complex	(1)	(2)
Gross formula	C ₃₀ H ₄₂ Cd ₂ N ₆ O ₄ S ₂	C ₃₀ H ₂₆ Cd ₂ N ₆ O ₄ S ₂
<i>M</i>	839.6	823.5
<i>T</i> , K	298(2)	298(2)
Crystal shape/color	Block/colorless	Block/colorless
Crystal size, mm	0.22×0.20×0.18	0.33×0.30×0.27
Crystal system, space group	Monoclinic, <i>P</i> 2 ₁ / <i>c</i>	Triclinic, <i>P</i> -1
<i>a</i> , <i>b</i> , <i>c</i> , Å	16.115(3), 12.019(2), 18.280(4)	11.971(1), 12.126(1), 13.794(2)
α , β , γ , deg.	96.03(3)	67.702(1), 84.905(1), 77.538(1)
<i>V</i> , Å ³	3521.0(12)	1808.9(3)
<i>Z</i>	4	2
<i>d</i> _c , g/cm	1.584	1.512
μ (MoK α), cm ⁻¹	1.368	1.330
Index ranges (<i>h</i> , <i>k</i> , <i>l</i>)	-20/20, -15/15, -20/20	-15/6, -15/14, -17/17
Unique reflections	7301	7886
<i>R</i> _{int}	0.030	0.032
Observed refl-s [<i>I</i> ≥ 2σ(<i>I</i>)]	5479	4773
Refined parameters	403	399
GOOF on <i>F</i> ²	1.025	1.018
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> ≥ 2σ(<i>I</i>)]*	0.043, 0.102	0.056, 0.143
<i>R</i> ₁ , <i>wR</i> ₂ (all data)*	0.062, 0.114	0.094, 0.174
Residual max/min, e/Å ³	0.94 / -0.51	1.01 / -0.66
CCDC deposition no.	761067	638060

$$* R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|, \quad wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}.$$

Analysis: Calcd. for C₃₀H₄₂Cd₂N₆O₄S₂: C 42.9, H 5.0, N 10.0 %. Found: C 42.5, H 5.2, N 9.8 %. Selected IR data (KBr pellets): 2064 (vs, ν_{NCS}), 1634 (s, $\nu_{\text{C=N}}$).

Synthesis of (2). Complex (2) was prepared in a similar method as for (1), with HL1 replaced by HL2 (24.2 mg, 0.1 mmol). Yield: 82 % based on HL2. Analysis: Calcd. for C₃₀H₂₆Cd₂N₆O₄S₂: C 43.8, H 3.2, N 10.2 %. Found: C 43.2, H 3.3, N 10.6 %. Selected IR data (KBr pellets): 2065 (vs, ν_{NCS}), 1632 (s, $\nu_{\text{C=N}}$).

X-ray crystallography. The single crystals of (1) and (2) of suitable quality were each mounted on a thin-walled glass capillary and aligned on the Bruker SMART 1000 CCD diffractometer, equipped with graphite-monochromated MoK α radiation source ($\lambda = 0.71073$ Å). The θ range for data collection was 2.03–27.00° for (1) and 1.95–27.50° for (2). All data were corrected for Lorentz and polarization effects and for absorption. The structures were solved by direct methods and refined by the least-square procedure. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. All calculations were performed using the SHELXTL-97 package [8]. The data collection and refinement parameters are summarized in Table 1. Selected bond lengths and angles are given in Table 2.

Crystallographic data for the complexes (1) and (2) have been deposited with the Cambridge Crystallographic Data Centre, CCDC reference numbers 761067 for (1) and 638060 for (2). This information may be obtained free of charge from: the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk; website: <http://www.ccdc.cam.ac.uk>).

Table 2

Selected bond lengths (Å) and angles (deg.) for the complexes

Complex (1)							
Cd1—O1	2.119(3)	Cd2—O1	2.416(3)	Cd1—O3	2.477(3)	Cd2—O2	2.484(4)
Cd1—N1	2.343(4)	Cd2—O3	2.141(3)	Cd1—N2	2.468(4)	Cd2—O4	2.736(3)
Cd1—N3	2.071(4)	Cd2—N5	2.179(5)	Cd1—N4	2.558(4)	Cd2—N6	2.124(5)
N3—Cd1—O1	150.8(2)	N6—Cd2—N5	138.5(2)	N3—Cd1—N1	120.7(2)	O3—Cd2—N5	99.7(2)
O1—Cd1—N1	86.5(2)	N6—Cd2—O1	103.6(2)	N3—Cd1—N2	87.0(2)	O3—Cd2—O1	76.2(2)
O1—Cd1—N2	104.7(2)	N5—Cd2—O1	113.4(2)	N1—Cd1—N2	89.7(2)	N6—Cd2—O2	77.4(2)
N3—Cd1—O3	79.7(2)	O3—Cd2—O2	138.5(2)	O1—Cd1—O3	75.2(2)	N5—Cd2—O2	102.8(2)
N1—Cd1—O3	158.3(2)	O1—Cd2—O2	62.9(2)	N2—Cd1—O3	83.9(2)	O1—Cd2—O4	146.2(2)
N3—Cd1—N4	86.9(2)	O2—Cd2—O4	150.8(2)	O1—Cd1—N4	87.7(2)	O3—Cd2—O4	70.3(2)
N1—Cd1—N4	80.5(2)	N5—Cd2—O4	69.3(2)	N2—Cd1—N4	163.8(2)	N6—Cd2—O4	90.2(2)
O3—Cd1—N4	109.7(2)			N6—Cd2—O3	107.0(2)		
Complex (2)							
Cd1—O2	2.236(4)	Cd2—O1	2.537(5)	Cd1—O4	2.258(4)	Cd2—O2	2.231(4)
Cd1—N1	2.319(5)	Cd2—O3	2.579(4)	Cd1—N2	2.362(5)	Cd2—O4	2.212(4)
Cd1—N3	2.321(5)	Cd2—N5	2.162(8)	Cd1—N4	2.359(5)	Cd2—N6	2.174(7)
O2—Cd1—O4	73.4(2)	N5—Cd2—O4	105.2(3)	O2—Cd1—N1	78.2(2)	N6—Cd2—O4	122.4(2)
O4—Cd1—N1	137.7(2)	N5—Cd2—O2	128.0(3)	O2—Cd1—N3	137.6(2)	N6—Cd2—O2	103.6(2)
O4—Cd1—N3	78.2(2)	O4—Cd2—O2	74.4(2)	N1—Cd1—N3	141.0(2)	N5—Cd2—O1	86.3(3)
O2—Cd1—N4	101.9(2)	N6—Cd2—O1	85.5(2)	O4—Cd1—N4	126.0(2)	O4—Cd2—O1	136.1(2)
N1—Cd1—N4	89.8(2)	O2—Cd2—O1	65.8(2)	N3—Cd1—N4	70.7(2)	N5—Cd2—O3	83.4(2)
O2—Cd1—N2	122.8(2)	N6—Cd2—O3	82.0(2)	O4—Cd1—N2	100.1(2)	O4—Cd2—O3	65.9(2)
N1—Cd1—N2	70.2(2)	O2—Cd2—O3	135.1(2)	N3—Cd1—N2	92.4(2)	O1—Cd2—O3	157.7(2)
N4—Cd1—N2	123.7(2)			N5—Cd2—N6	117.6(4)		

Results and Discussion. The reaction of the Schiff bases with cadmium nitrate and ammonium thiocyanate leads to the title cadmium(II) complexes. Even though the thiocyanate ligands are versatile

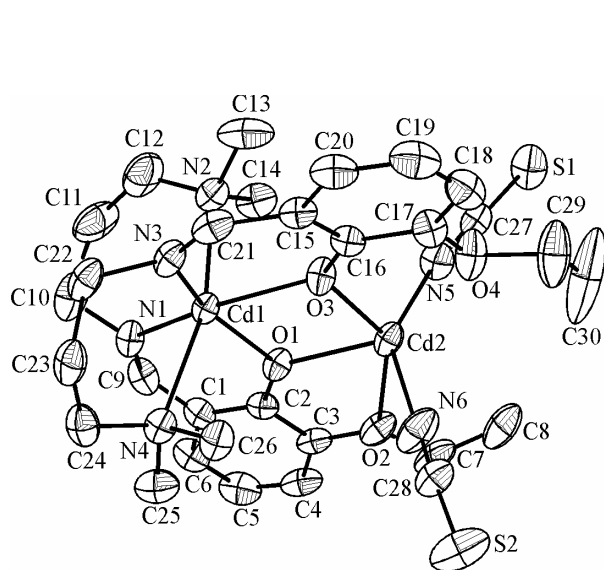


Fig. 1. Molecular structure of (1) with 30 % probability thermal ellipsoids. H atoms are omitted for clarity

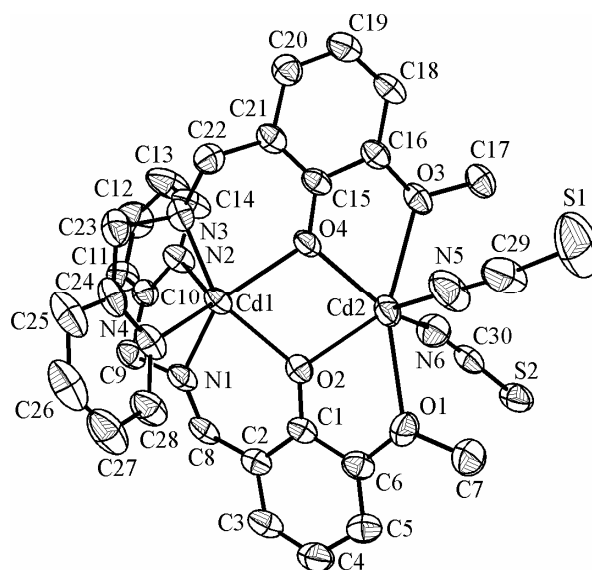


Fig. 2. Molecular structure of (2) with 30 % probability thermal ellipsoids. H atoms are omitted for clarity

bridging groups in many cadmium complexes, they act as isothiocyanate terminal ligands in the two complexes of this study. Both complexes are stable in air at room temperature and soluble in common polar solvents such as methanol, ethanol, acetonitrile, DMF and DMSO.

Figures 1 and 2 show the molecular structure of the complexes as found in the crystals studied. The two molecules are structurally similar and are phenolate-O-bridged dinuclear cadmium(II) complexes. Each Cd(II) cation is in an octahedral coordination. The Cd1 atom in (1) is surrounded by two phenolate O atoms, two imine N atoms and two amine N atoms from two L1 ligands. The donor atoms surrounding Cd1 atom in (2) are similar to those in (1), with the amine N atoms of L1 replaced by the pyridine N atoms of L2. The Cd2 atoms in both (1) and (2) are coordinated by two phenolate O atoms and two ether O atoms from two Schiff base ligands, and by two N atoms from two terminal isothiocyanate ligands. The distortion of the octahedral geometries can be observed from the bond angles. The coordination bond lengths in the two complexes are similar and comparable to those in other Schiff base cadmium(II) complexes [4–6, 9]. The Cd...Cd distances in (1) and (2) are 3.618(2) and 3.571(2) Å, respectively.

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