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A novel thiocyanate-bridged dinuclear cadmium(II) complex: di-μ-thiocyanato-bis((methanol){4-nitro-2-[2-(dimethylamino)ethyliminomethyl]phenolato}cadmium(II))

Zhong-Lu You[a]* and Hai-Liang Zhu[b]

[a]Department of Chemistry and Chemical Engineering, Liaoning Normal University, Dalian 116029, People's Republic of China, and [b]Institute of Functional Biomolecules, State Key Laboratory of Pharmaceutical Biotechnology, Nanjing University, Nanjing 210093, People's Republic of China
Correspondence e-mail: youzhonglu@yahoo.com.cn

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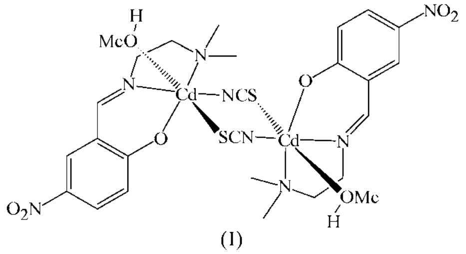
The title complex, $[Cd_2(C_{11}H_{14}N_3O_3)_2(NCS)_2(CH_4O)_2]$, is an interesting thiocyanate-bridged dinuclear cadmium(II) compound. It is located on a crystallographic inversion center. The Cd^{II} atom is six-coordinated in an octahedral configuration by one O and two N atoms of one Schiff base ligand and by the terminal N atom of a bridging thiocyanate ligand, defining the basal plane, and by the terminal S atom of another bridging thiocyanate ligand and by the O atom of a coordinated methanol molecule, occupying the axial positions. The molecules are linked through intermolecular O—H···O hydrogen bonds, forming chains running along the *b* axis.

Comment

Metal-organic complexes containing bridging ligands are of current interest because of their interesting molecular topologies and crystal-packing motifs, as well as the fact that they may be designed with specific functionalities (Batten & Robson, 1998; Abourahma *et al.*, 2002; Konar *et al.*, 2002). In addition to being robust and thermally stable, some possess photoluminescent properties, a feature that has contributed to d^{10} metal polynuclear complexes being investigated in the search for new materials (Weidenbruch *et al.*, 1989; Kunkely & Vogler, 1990; Bertoncello *et al.*, 1992). Most of the Cd^{II} coordination polymers featuring interesting supramolecular structures, such as one-dimensional helical ribbons or molecular zippers, two-dimensional molecular square or triangular grids, and interpenetrating/non-interpenetrating three-dimensional networks (Dai *et al.*, 2002; Chen *et al.*, 2003; Luo *et al.*, 2003), possess photoluminescent properties (Xiong *et al.*, 2000; Wang *et al.*, 2003).

Owing to the versatile coordination modes of the ambidentate thiocyanate ligand, this pseudohalide ligand has become one of the most extensively studied building blocks in multidimensional complexes (Sailaja *et al.*, 2003; Dey *et al.*, 2004). Thiocyanate complexes of various dimensionalities have been obtained (Zurowska *et al.*, 2002; Zhang *et al.*, 2003; You, 2005*a*). A major obstacle to a more comprehensive study of such thiocyanate-based polymeric coordination complexes is the lack of rational synthetic procedures, since with the present knowledge it is hardly possible to determine which coordination mode will be adopted by the thiocyanate ligand and whether the sought-after alternating chain structure will finally be formed (Tercero *et al.*, 2002; Ribas *et al.*, 1999; Liu *et al.*, 2003).

Our work is aimed at obtaining multidimensional polymetallic complexes. On the basis of the above considerations, we designed and synthesized a tridentate ligand, 4-nitro-2-[2-(dimethylamino)ethyliminomethyl]phenol (NDAP). We chose to use NDAP as a ligand because it could adopt an almost fixed coordination mode through the three donor atoms (You, 2005*b*; Yue *et al.*, 2005). The second ligand, *viz*. thiocyanate, is a well known bridging group. It readily bridges different metal ions through the terminal donor atoms, forming polynuclear complexes (Kuang *et al.*, 2001). Cd^{II} is a good candidate for octahedral coordination geometry. We report here the structure of the dinuclear title compound, (I), formed by the reaction of the NDAP ligand, ammonium thiocyanate and Cd^{II} acetate.



(I)

Complex (I) (Fig. 1) contains two Cd(NDAP) units connected to each other by two bridging thiocyanate anions. The Cd^{II} atom is in an octahedral coordination environment and is six-coordinated by one O and two N atoms of one Schiff base ligand and by the terminal N atom of a bridging thiocyanate ligand, defining the basal plane, and by the terminal S atom of another bridging thiocyanate ligand and by the O

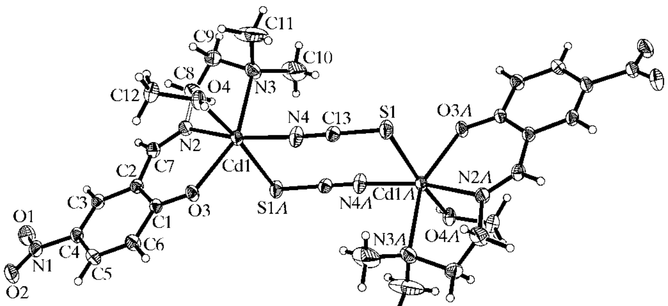


Figure 1
The structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. Atoms labeled with the suffix *A* are at the symmetry position $(1 - x, 1 - y, 1 - z)$. Only the major component of the disordered C9/N3/C10/C11 moiety is shown.

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atom of a coordinated methanol molecule, occupying the axial positions. The Schiff base ligand acts as a tridentate ligand and ligates to the metal *via* three O- and N-donor atoms. The thiocyanate anion acts as a bridging ligand and ligates to two different but symmetry-related Cd^{II} atoms *via* the terminal N and S atoms.

The three *trans* angles at the Cd^{II} atom lie in the range 151.7 (3)–170.90 (4)° (Table 1). The other angles subtended at the Cd^{II} atom range from 74.5 (3) to 109.81 (7)°, indicating a somewhat distorted octahedral geometry. The bond lengths subtended at atom Cd1 are comparable to those observed in other Schiff base–cadmium(II) complexes (You *et al.*, 2004) and, as expected, the bond involving amine atom N3 [2.419 (13) Å] is longer than that involving imine atom N2 [2.296 (2) Å] (Mondal *et al.*, 2001). The Cd1—S1^{i} bond [symmetry code: (i) $1-x, 1-y, 1-z$] is much longer than the other bonds, indicating that the Cd—S bond is not very strong. The bridging thiocyanate group is nearly linear and shows bent coordination modes with the metal atoms [N4—C13—S1 = 179.3 (2)°, Cd1—N4—C13 = 160.4 (2)° and Cd1^{i}—S1—C13 = 100.71 (8)°]. The N2—Cd1—N3(or N3′) bond angle [mean 75.3 (3)°] of the five-membered chelate ring is much smaller than 90°, a result of the strain created by the five-membered chelate rings Cd1/N2/C8/C9/N3 and Cd1/N2/C8′/C9′/N3′.

The C7═N2 bond length [1.280 (3) Å] conforms to the normal value for a double bond, while the C8—N2 bond length [1.458 (3) Å] conforms to the normal value for a single bond. The O1/N1/O2 plane and the C1–C6 benzene ring are not coplanar, having a dihedral angle of 14.7 (3)°.

In the crystal structure, the molecules are linked by intermolecular O—H···O hydrogen bonds, forming chains running along the *b* axis (Table 2 and Fig. 2).

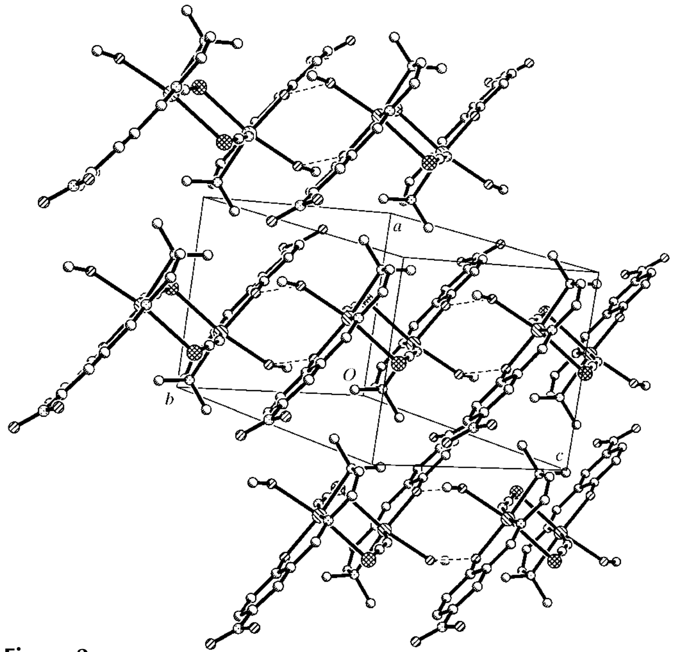

Figure 2
The crystal packing of (I). Dashed lines indicate the intermolecular O—H···O hydrogen bonds.

Experimental

5-Nitrosalicylaldehyde (0.1 mmol, 16.7 mg) and *N*,*N*-dimethylethane-1,2-diamine (0.1 mmol, 8.8 mg) were dissolved in MeOH (10 ml). The mixture was stirred at room temperature for 10 min to give a yellow solution. To this solution was added an MeOH solution (5 ml) of $Cd(CH_3COO)_2\cdot 4H_2O$ (0.1 mmol, 30.3 mg), with stirring. The resulting mixture was stirred for another 10 min at room temperature. After keeping the filtrate in air for 3 d, colorless block-shaped crystals were formed.

Crystal data

$[Cd_2(C_{11}H_{14}N_3O_3)_2(NCS)_2(CH_4O)_2]$
$M_r = 877.55$
Triclinic, $P\overline{1}$
$a = 8.286$ (1) Å
$b = 8.946$ (1) Å
$c = 11.971$ (2) Å
$\alpha = 110.019$ (2)°
$\beta = 92.705$ (2)°
$\gamma = 91.482$ (2)°
$V = 832.0$ (2) Å^3
$Z = 1$
$D_x = 1.751$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5707 reflections
$\theta = 2.4$–28.3°
$\mu = 1.46$ mm^{-1}
$T = 298$ (2) K
Block, colorless
0.32 × 0.21 × 0.11 mm

Data collection

Bruker SMART CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.652$, $T_{max} = 0.856$
7155 measured reflections
3686 independent reflections
3559 reflections with $I > 2\sigma(I)$
$R_{int} = 0.016$
$\theta_{max} = 27.5$°
$h = -10 \rightarrow 10$
$k = -11 \rightarrow 11$
$l = -15 \rightarrow 15$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.025$
$wR(F^2) = 0.062$
$S = 1.10$
3686 reflections
253 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.034P)^2 + 0.1681P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.34$ e Å^{-3}
$\Delta\rho_{min} = -0.55$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cd1—N4	2.244 (2)	Cd1—N3	2.419 (13)
Cd1—O3	2.250 (2)	Cd1—S1^{i}	2.7527 (8)
Cd1—N2	2.296 (2)	N2—C7	1.280 (3)
Cd1—O4	2.378 (2)	N2—C8	1.458 (3)
N4—Cd1—O3	109.81 (7)	N2—Cd1—N3	74.5 (3)
N4—Cd1—N2	168.91 (7)	O4—Cd1—N3	85.14 (18)
O3—Cd1—N2	81.28 (6)	N4—Cd1—S1^{i}	91.83 (6)
N4—Cd1—O4	85.89 (6)	O3—Cd1—S1^{i}	89.50 (4)
O3—Cd1—O4	83.00 (6)	N2—Cd1—S1^{i}	88.20 (5)
N2—Cd1—O4	95.72 (6)	O4—Cd1—S1^{i}	170.90 (4)
N4—Cd1—N3	94.8 (3)	N3—Cd1—S1^{i}	103.85 (17)
O3—Cd1—N3	151.7 (3)		

Symmetry code: (i) $-x+1, -y+1, -z+1$.

Table 2
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O4—H4···O3^{ii}	0.89 (1)	1.80 (1)	2.685 (2)	174 (3)

Symmetry code: (ii) $-x+1, -y, -z+1$.

Atom H4 was located in a difference Fourier map and refined isotropically, with the O—H distance restrained to 0.88 (1) Å. The other H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms, with C—H distances in the range 0.93–0.97 Å, and with U_{iso}(H) values of 1.2 or 1.5 times U_{eq}(C). The C9/N3/C10/C11 unit is disordered over two distinct sites, with occupancies of 0.535 (5) and 0.465 (5).

Data collection: *SMART* (Bruker, 1998); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1998); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997*a*); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997*a*); molecular graphics: *SHELXTL* (Sheldrick, 1997*b*); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1859). Services for accessing these data are described at the back of the journal.

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