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catena-Poly[[bis[μ-2,4-dichloro-6-(2-pyridylmethyliminomethyl)phenolato]dicadmium(II)]-di-μ-thiocyanato]

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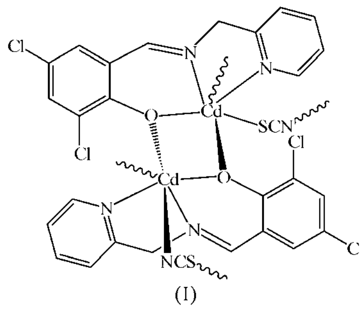
The title complex, $[Cd_2(C_{13}H_9Cl_2N_2O)_2(NCS)_2]_n$, is a novel thiocyanate-bridged polynuclear cadmium(II) compound. The Cd^{II} atom is six-coordinated in a distorted octahedral configuration, with one O and two N atoms of one Schiff base molecule and one terminal S atom of a bridging thiocyanate ligand defining the equatorial plane, and one terminal N atom of another bridging thiocyanate ligand and one O atom of another Schiff base molecule occupying axial positions. Adjacent inversion-related [2,4-dichloro-6-(2-pyridylmethyliminomethyl)phenolato]cadmium(II) moieties utilize bridging phenolate and thiocyanate groups to form polymeric 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 (You, 2005*b*; Adams, Clunas, Fenton, Gregson *et al.*, 2002; Tiron *et al.*, 2003). Cadmium(II) coordination polymers feature 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); most of these compounds 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).

Our work is aimed at obtaining multidimensional polymetallic complexes. On the basis of the above considerations, we designed and synthesized a tridentate ligand containing a phenolate O atom, *viz.* 2,4-dichloro-6-(2-pyridylmethyliminomethyl)phenol (DPMP), with the potential to coordinate through three donor atoms (You & Zhu, 2005*b*). Thiocyanate ions readily bridge different metal ions through the terminal donor atoms, forming polynuclear complexes (Kuang *et al.*, 2001). The novel polynuclear title structure, (I), formed by the reaction of the DPMP ligand, ammonium thiocyanate and cadmium(II) acetate, is reported here.



(I)

Complex (I) is a phenolate- and thiocyanate-bridged polynuclear cadmium(II) compound (Fig. 1). In the crystal structure, the smallest repeat unit contains two Cd(DPMP) moieties and two bridging thiocyanate anions related by crystallographic centres of symmetry. Each Cd^{II} atom is six-coordinate in a distorted octahedral configuration, with one O and two N atoms from one Schiff base ligand and one terminal S atom of a bridging thiocyanate ligand defining the equatorial plane. A terminal N atom of another bridging thiocyanate ligand and one O atom of another Schiff base ligand occupy the axial positions. The angles subtended at the Cd^{II} atom confirm the distorted octahedral coordination (Table 1). It is interesting that the tridentate Schiff base also acts as a bridging ligand, through the phenolate O atom. This behaviour has been observed in the dinuclear nickel(II) compound (μ_2-acetato-*O*,*O*′){μ_2-2-*N*-ethyl-[2-(dimethylamino)ethylaminomethyl)]-6-(2-pyridylmethyliminomethyl)-4-methylphenol-

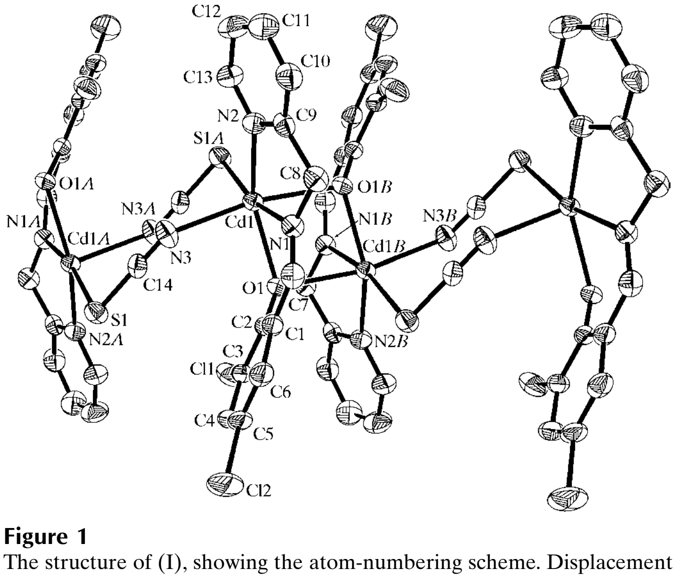


Figure 1
The structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. Atoms labelled with the suffixes *A* and *B* are related by the symmetry operations $(1 - x, -y, 1 - z)$ and $(1 - x, 1 - y, 1 - z)$, respectively.

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ato}(μ_2-isothiocyanato)isothiocyanatomethanoldinickel (BADHEU; Adams, Clunas, Fenton & Spey, 2002). In complexes containing phenolate O atoms that are not acting as a bridging group, the Schiff base ligands are nearly coplanar (You, 2005*a*,*b*,*c*). However, the Schiff base ligand is severely distorted in (I), with a dihedral angle between the pyridine and phenol rings of 43.5 (2)°, promoted by the coordination of the bridging phenolate O atom to another metal ion. The same pattern can be observed in a similar phenolate O-bridged structure, bis{[μ_2-*N*-(benzene-2-thiolato)salicylaldiminato-$\kappa^4 O,O,S,N$](1,10-phenanthroline-$\kappa^2 N,N'$)cadmium(II)} (WIGRUZ; Labisbal *et al.*, 1994). The thiocyanate anion here acts as a bridging ligand by coordinating to symmetry-related cadmium(II) ions *via* the terminal N and S atoms.

The bond lengths subtended at atom Cd1 are comparable to those observed in other Schiff base–cadmium(II) complexes (You & Zhu, 2005*a*) and WIGRUZ, but much longer, as expected for the greater atomic radii, in than the corresponding nickel(II) structure BADHEU [*e.g.* Ni1—O1 = 2.001 (2) Å]. The bridging thiocyanate group is nearly linear and shows bent coordination modes with the metal atoms, as observed in BADHEU. The N1—Cd1—N2 bond angle of the Cd1/N1/C8/C9/N2 chelate ring is much smaller than 90°, as expected for a five-membered chelate ring; this ring approximates to an envelope conformation, with atom N1 as the flap (Spek, 2003). Atom O1 lies out of the C1–C6 benzene ring, by 0.112 (2) Å in the direction of the Cd1^{i} atom [symmetry code: (i) $1 - x, 1 - y, 1 - z$], as might be expected from its bridging coordination to the Cd1^{i} ion. The same pattern is observed in WIGRUZ, where atom O1 deviates from the benzene ring by 0.015 (2) Å.

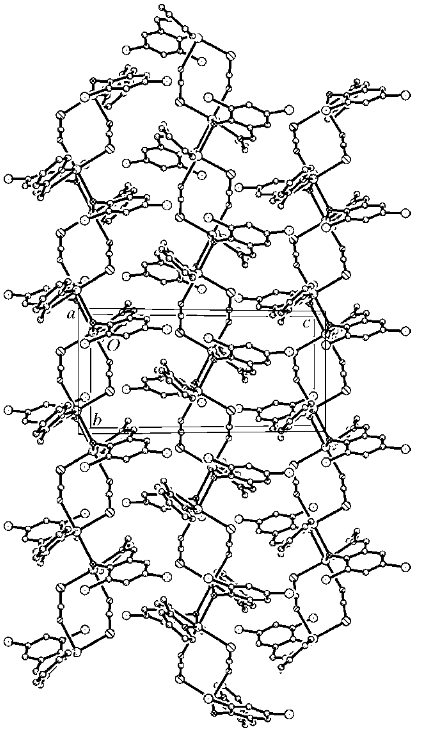

Figure 2
The crystal packing of (I), viewed along the *a* axis.

In the crystal structure of (I), the bis(DPMP)dicadmium(II) moieties are linked by the bridging thiocyanate ligands into polymeric chains with backbones of the type [–Cd—(N—C—S)$_2$—Cd—O$_2$]$_n$ running along the *b* axis (Fig. 2). There are weak but significant interactions, such as C8—H8*B*···N3 and C10—H10···π bonding to the C1–C6 ring (Table 2), which complement the main binding of the polymeric chain.

Experimental

3,5-Dichlorosalicylaldehyde (0.1 mmol, 19.1 mg) and 2-aminomethylpyridine (0.1 mmol, 10.8 mg) were dissolved in MeOH (10 ml). The mixture was stirred at room temperature for 10 min to give a clear yellow solution. To this solution was added an aqueous solution (2 ml) of NH_4NCS (0.1 mmol, 7.6 mg) and an MeOH solution (3 ml) of $Cd(CH_3COO)_2 \cdot 4H_2O$ (0.1 mmol, 30.3 mg), with stirring. The mixture was stirred for another 10 min at room temperature. After the filtrate had been kept in air for 13 d, colourless block-shaped crystals had formed at the bottom of the vessel.

Crystal data

$[Cd_2(C_{13}H_9Cl_2N_2O)_2(NCS)_2]$
$M_r = 450.60$
Monoclinic, $P2_1/c$
$a = 13.131$ (1) Å
$b = 7.829$ (1) Å
$c = 16.911$ (2) Å
$\beta = 111.903$ (1)°
$V = 1613.0$ (3) Å^3
$Z = 4$

$D_x = 1.855$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5699 reflections
$\theta = 2.5$–27.5°
$\mu = 1.82$ mm^{-1}
$T = 298$ (2) K
Block, colourless
0.20 × 0.20 × 0.12 mm

Data collection

Bruker SMART CCD area-detector diffractometer
ω scan
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.713$, $T_{\max} = 0.812$
13342 measured reflections

3640 independent reflections
3085 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.022$
$\theta_{\max} = 27.5°$
$h = -17 \rightarrow 17$
$k = -10 \rightarrow 9$
$l = -21 \rightarrow 21$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.028$
$wR(F^2) = 0.071$
$S = 1.04$
3640 reflections
199 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0365P)^2 + 0.562P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.64$ e Å^{-3}
$\Delta\rho_{\min} = -0.46$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cd1—O1	2.269 (2)	Cd1—O1^{i}	2.381 (2)
Cd1—N1	2.328 (2)	Cd1—S1^{ii}	2.5916 (9)
Cd1—N2	2.334 (2)	N1—C7	1.271 (4)
Cd1—N3	2.345 (3)	N1—C8	1.441 (4)
O1—Cd1—N1	76.82 (7)	N3—Cd1—O1^{i}	169.37 (8)
O1—Cd1—N2	148.29 (8)	O1—Cd1—S1^{ii}	113.42 (5)
N1—Cd1—N2	71.72 (8)	N1—Cd1—S1^{ii}	168.00 (6)
O1—Cd1—N3	87.28 (9)	N2—Cd1—S1^{ii}	97.47 (6)
N1—Cd1—N3	94.16 (8)	N3—Cd1—S1^{ii}	92.62 (6)
N2—Cd1—N3	98.77 (9)	O1^{i}—Cd1—S1^{ii}	92.14 (5)
O1—Cd1—O1^{i}	82.11 (6)	C14—S1—Cd1^{ii}	96.15 (9)
N1—Cd1—O1^{i}	82.88 (7)	C14—N3—Cd1	139.5 (2)
N2—Cd1—O1^{i}	90.02 (7)	N3—C14—S1	177.2 (2)

Symmetry codes: (i) $-x + 1, -y + 1, -z + 1$; (ii) $-x + 1, -y, -z + 1$.

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

*Cg*5 is the centroid of the C1–C6 ring.

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C8—H8$B\cdots$N3$^{\rm iii}$	0.97	2.61	3.566 (2)	168
C10—H10$\cdots Cg5^{\rm i}$	0.93	2.86	3.736 (2)	157

Symmetry codes: (i) $-x+1, -y+1, -z+1$; (iii) $-x+1, y+\frac{1}{2}, -z+\frac{3}{2}$.

All H atoms were placed in geometrically idealized positions and allowed to ride on their parent atoms, with C—H distances of 0.93–0.97 Å and with $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C).

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: GA1113). Services for accessing these data are described at the back of the journal.

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