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A three-dimensional network of cadmium

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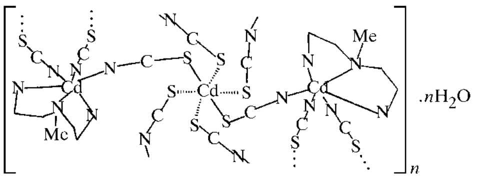
The title complex, poly[bis[*N*-(2-aminoethyl)-*N*-methyl-1,2-ethanediamine]hexa-μ-thiocyanato-tricadmium(II) monohydrate], $[Cd_3(NCS)_6(medien)_2]_n\cdot nH_2O$ [medien is *N*,*N*-bis(2-aminoethyl)methylamine, $C_5H_{16}N_3$], adopts a three-dimensional inorganic polymeric network structure. Two cadmium centres (Cd1 and Cd2) are linked to each other *via* thiocyanate bridges. The environment of the Cd1 atom involves only S atoms, making it soft, whereas the environment of the Cd2 atom involves only N atoms, making it hard.

Comment

In attempts to build molecular materials with interesting properties, such as catalysis clathration *etc*., much attention has been given to the synthesis of one-, two- and three-dimensional extended solids involving cadmium. Rigid bridged ligands are frequently employed to construct these materials (Abrahams *et al.*, 1994; Soma *et al.*, 1994; Fujita *et al.*, 1994; Yuge & Iwamoto, 1995). The ambidentate thiocyanate ion which is usually S-bonded to a soft and N-bonded to a hard metal centre can also act as a bridging bidentate ligand to satisfy the coordination number of the metal ion, although the thiocyanate anion has not been widely used in the construction of inorganic polymeric networks. In order to synthesize uncharged three-dimensional polymers where channels remain unblocked by anions and free for solvent inclusion, we have chosen cadmium(II) thiocyanate as an effective building block. Cadmium is well suited to this as its d^{10} configuration permits a wide variety of symmetries and coordination numbers. Recently, we reported the syntheses of the inorganic polymer $[Cd_3(dien)_2(\mu\text{-NCS})_6]_n\cdot nH_2O$ (dien is diethylenetriamine), (II) (Mondal *et al.*, 1999), which utilizes the full bridging potential of the anion. The structure of complex (II) is a polymeric network which contains solvent-filled channels. Channel-containing solids have been and continue to be investigated intensively because of their potential applications, *viz*. as heterogeneous catalysts and molecular sieves. As part of a continuing investigation into control over the channels, we are currently studying the corresponding cadmium compounds. In this paper, we report the structure of the title Cd^{II} complex (I), where medien [medien is *N*,*N*-bis(2-aminoethyl)methylamine] ligands replace the dien ligands of complex (II).



(I)

The structure determination of (I) reveals that the polymer has the stoichiometry $[Cd_3(\mu\text{-NCS})_6(medien)_2]\cdot H_2O$, with the occurrence of infinite Cd2—N1—C1—S1—Cd1— zigzag chains forming a three-dimensional network. Water molecules are accommodated in interstitial sites which are nearly rectangular and have a volume of 341.0 Å^3 (Spek, 1998). Each Cd1 atom is connected to six Cd2 atoms by thiocyanate bridges. Three N1 atoms, two symmetry-related N2 atoms and one N3 atom complete the CdN_6 chromophore. The geometry around the Cd1 atom is a trigonally distorted octahedron and that around the Cd2 atom is a distorted octahedron.

It should be noted that each Cd2 atom, coordinated by the N atoms of the medien ligand, is invariably linked with the hard N atom of the thiocyanate ion. In other words, the N atoms of the medien ligand 'harden' Cd2 and so the thiocyanate bonds to it preferentially through the N atom.

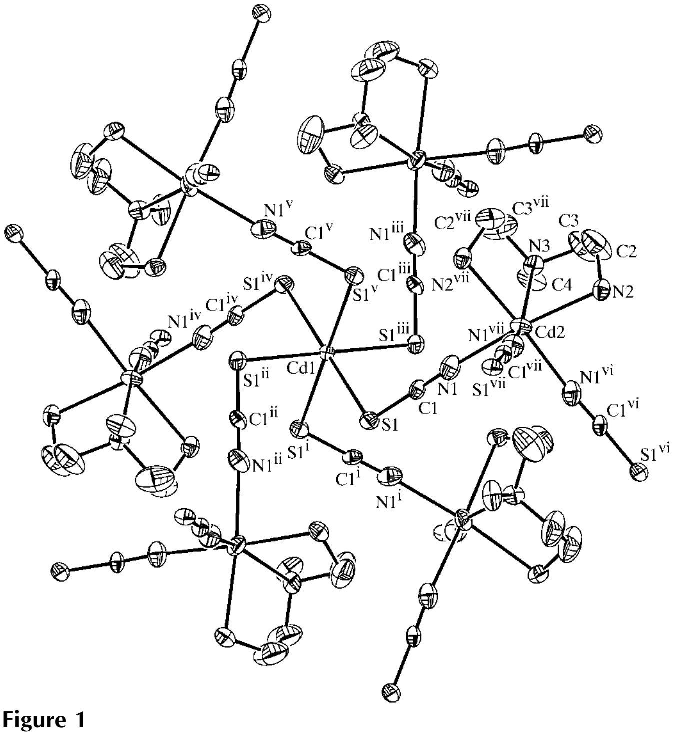


Figure 1
A *ZORTEP* (Zsolnai, 1995) view of the title complex showing the Cd1 and Cd2 octahedra (50% probability level). Only one of the three possible orientations of the medien ligand is shown.

Conversely, the soft end of each thiocyanate ion (*i.e.* the S atom) is cordinated to Cd1 making it 'soft'. Thus, the thiocyanate S atoms are clubbed together around Cd1. Each Cd ion is coordinated by N- or S-donor atoms only, and both hard and soft metal centres are generated in the same compound. There are six branches emanating from the Cd1 centre. In each branch, Cd2 is connected to Cd1 *via* thiocyanate bridges. Every such Cd2 atom produces two other branches which are connected *via* a thiocyanate bridge to two other Cd1 atoms, each of which in turn produces five other branchings. The sequence in one branch can be written as Cd1—S1—C1—N1—Cd2—N1—C1^{vi}—S1^{vi}—Cd1^{vi} [symmetry code: (vi) $1 - x$, $z - \frac{1}{2}$, $\frac{3}{2} - x$]. The Cd2—N and Cd1—S distances are comparable to corresponding values in analogous octahedrally coordinated Cd complexes. The thiocyanate ligands are almost linear [177.7 (10)°]. Other bond distances and angles in the ligand are close to expected values.

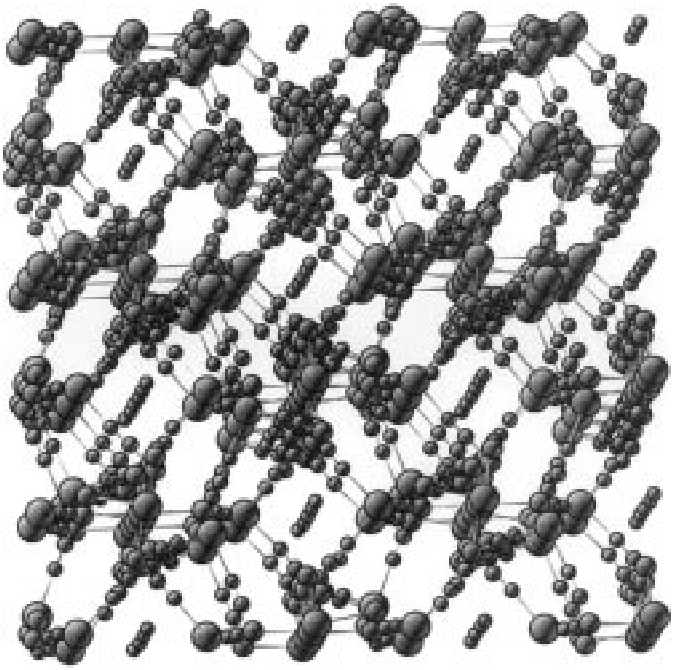


Figure 2
A view of $[Cd_3(\mu\text{-}NCS)_6(medien)_2]\cdot H_2O$ showing the water-molecule-filled channels. For clarity, the medien ligand has been omitted.

Experimental

Bis(2-aminoethyl)methylamine (2 mmol) in methanol was added dropwise with stirring to $Cd(NCS)_2$ (3 mmol) dissolved in methanol (10 ml). A sticky oily layer separated at the bottom of the container. The supernatant solution was filtered and the filtrate was kept in a $CaCl_2$ desiccator for a few days at ~300 K giving the title polymer as shining transparent crystals in 34% isolated yield. Elemental analyses supported the unusual stoichiometry of the compound.

Crystal data

$[Cd_3(NCS)_6(C_5H_{16}N_3)_2]\cdot H_2O$
$M_r = 938.10$
Cubic, $Pa\overline{3}$
$a = 15.0766$ (9) Å
$V = 3427.0$ (4) Å^3
$Z = 4$
$D_x = 1.818$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 27 reflections
$\theta = 5.06$–12.48°
$\mu = 2.241$ mm^{-1}
$T = 293$ (2) K
Octahedron, colourless
0.64 × 0.48 × 0.46 mm

Data collection

Siemens *P*4 diffractometer
ω scans
Absorption correction: by integration (North *et al.*, 1968)
$T_{min} = 0.450$, $T_{max} = 0.498$
4244 measured reflections
1010 independent reflections
902 reflections with $I > 2\sigma(I)$
$R_{int} = 0.038$
$\theta_{max} = 24.98°$
$h = -1 \rightarrow 17$
$k = -1 \rightarrow 17$
$l = -1 \rightarrow 17$
3 standard reflections every 97 reflections intensity decay: 3.43%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.044$
$wR(F^2) = 0.129$
$S = 1.037$
1067 reflections
78 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0279P)^2 + 3.3796P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = -0.036$
$\Delta\rho_{max} = 0.73$ e Å^{-3}
$\Delta\rho_{min} = -0.66$ e Å^{-3}
Extinction correction: *SHELXL*93
Extinction coefficient: 0.0046 (5)

Since the site symmetry of Cd2 is 3, three sites of coordinating thiocyanate N1 atoms are accordingly related by symmetry. The primary N atoms, N2 and the secondary N3 atoms are in general positions, there being three symmetry-related sites for each of them. These six sites (3+3) were envisaged to be occupied by three groups of two N2 atoms with two-thirds occupancy and one N3 atom with one-third occupancy leading to a threefold disorder about the [111] direction. Although the geometry of this model looked reasonable at the isotropic level of refinement, the *R*1 value of ~0.25 was too high and there were many peaks in the difference map which could not be incorporated in the model. A twin model was then proposed such that the crystal is composed of two twin domains with the reciprocal lattices of these two components being coincident: $I(hkl) = (1-\alpha)I(hkl) + \alpha I(hk\bar{l})$. In *SHELXL*93 (Sheldrick, 1993), this is incorporated into the least-squares refinement by the twin matrix ($010/100/00\bar{1}$). Application of this twin law in the isotropic refinement resulted in a drastic drop in the *R*1 factor to 0.118. Anisotropic refinement was carried out for all non-H atoms, except for the disordered water O atom, with *DFIX* constraints for the C—N and C—C distances of the medien ligand and *EADP* constraints for the

Table 1
Selected geometric parameters (Å, °).

Cd1—S1	2.715 (2)	N1—Cd2	2.293 (10)
S1—C1	1.634 (9)	Cd2—N3	2.203 (17)
C1—N1	1.148 (12)	Cd2—N2	2.492 (12)
S1^{i}—Cd1—S1	88.03 (10)	N3—Cd2—N1	108.3 (5)
S1—Cd1—S1^{ii}	180.0	N1^{iv}—Cd2—N1	93.8 (3)
S1—Cd1—S1^{iii}	91.97 (10)	N3—Cd2—N2	75.7 (6)
C1—S1—Cd1	101.2 (3)	N1^{iv}—Cd2—N2	84.4 (4)
N1—C1—S1	177.7 (10)	N1—Cd2—N2	174.6 (4)
C1—N1—Cd2	172.8 (9)	N2^{iv}—Cd2—N2	100.3 (4)

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

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C2 and C3 atoms. The water H atoms were located from a difference synthesis but their positions were not refined. Other H atoms were allowed to ride on their attached C or N atoms. At convergence, the value for the *BASF*(α) parameter was 0.4883.

Data collection: *XSCANS* (Siemens, 1995); cell refinement: *XSCANS*; data reduction: *SHELXTL* (Sheldrick, 1995); program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985); program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993); molecular graphics: *ZORTEP* (Zsolnai, 1995); software used to prepare material for publication: *SHELXL*93.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1256). Services for accessing these data are described at the back of the journal.

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