

Construction of a unique three-dimensional array with cadmium(II)†

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The complex $[\text{Cd}_3(\text{dien})_2(\text{NCS})_6]_n \cdot n\text{H}_2\text{O}$ (dien = diethylenetriamine) is prepared and characterised by X-ray diffraction studies, which show a new type of three-dimensional polymeric structure having cadmium centres which are linked to each other *via* NCS bridges in such a way that two types of Cd environment (one involving only N-donor atoms and the other only S-donor atoms) are produced.

In search of molecular based 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.¹⁻⁴ Rigid bridged ligands are frequently employed to construct these materials. 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.^{5,6} In order to synthesise uncharged three-dimensional polymers⁷ 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 for this as its d^{10} configuration permits a wide variety of geometries and coordination numbers. By utilising fully the bridging potential of the thiocyanate anion we have synthesised an inorganic coordination polymer with a $\text{Cd}(\text{NCS})_2:\text{dien}$ ratio of 3:2 (dien = diethylenetriamine). Single crystal X-ray structure analysis reveals that it is a new type of 3-D network which contains solvent filled channels. Channels containing solids have been and continue to be intensively investigated because of their actual and potential applications, for example as heterogeneous catalysts and molecular sieves. Another striking feature of the molecule is that the cadmium(II) ions which are linked to each other (*via* thiocyanate bridge) are alternatively hard (having only N-donor atoms) and soft (having only S-donor atoms) centres.

The ligand (diethylenetriamine) (2 mmol) in methanol (5 cm^3) was added dropwise with stirring to $\text{Cd}(\text{NCS})_2$ (3 mmol) dissolved in methanol (10 cm^3). 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 $\approx 30^\circ\text{C}$ giving the polymer as shining transparent crystals in $\approx 34\%$ isolated yield. Elemental analysis supports the unusual stoichiometry of the compound.

The structure determination‡ reveals that the polymer has stoichiometry $\text{Cd}_3(\text{dien})_2(\text{NCS})_6 \cdot \text{H}_2\text{O}$ having a three-dimensional infinite chain forming a large spherical molecule in which water molecules (Ow) are accommodated in interstitial positions which have a nearly rectangular shape of van der Waals dimensions $14.26 \times 3.30 \text{ \AA}$. The nearest atom to Ow is N1 [$\text{Ow} \cdots \text{N1} 4.090(6) \text{ \AA}$]. A ZORTEP view with atom

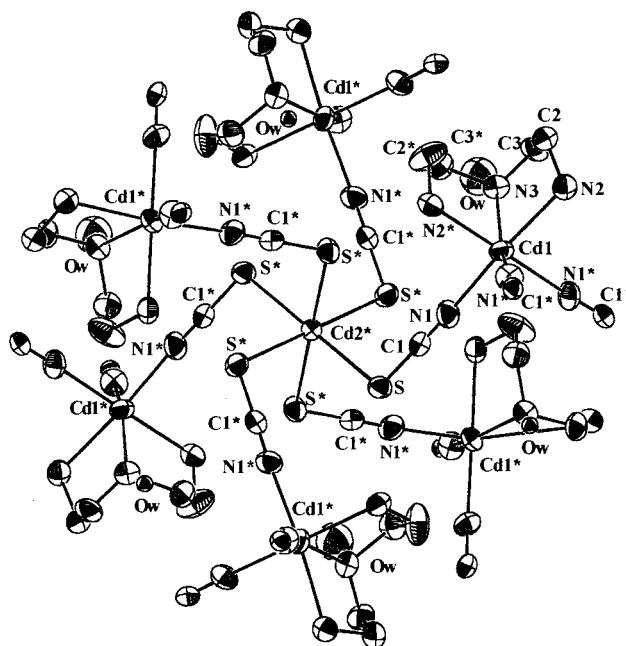


Fig. 1 ZORTEP¹⁴ plot of the complex showing the extended structure of Cd1 and Cd2 octahedra. Selected bond distances (Å) and angles (°): Cd1–N1 2.287(6), Cd1–N3 2.31(2), Cd1–N2 2.453(8), N1–C1 1.140(8), C1–S⁽ⁱ⁾ 1.646(8), Cd2–S 2.711(2), N1–Cd1–N1⁽ⁱⁱ⁾ 92.4(2), N1–Cd1–N3 103.7(5), N1–Cd1–N2 82.7(3), N3–Cd1–N2 70.6(5), C1–N1–Cd1 176.6(6), N1–C1–S⁽ⁱ⁾ 179.8(5), S⁽ⁱⁱⁱ⁾–Cd2–S^(iv) 92.62(6), S⁽ⁱⁱⁱ⁾–Cd2–S 87.38(6), S^(v)–Cd2–S 180.0. Symmetry transformations to generate equivalent atoms: (i) $y - 1/2, -z + 1/2, x$; (ii) y, z, x ; (iii) $-y + 1, -z + 1, -x + 1$; (iv) $-z + 1, -x + 1, -y + 1$; (v) $-x + 1, -y + 1, -z + 1$.

numbering scheme is shown in Fig. 1. Every cadmium atom Cd2, surrounded by six sulfur atoms, is linked to six other cadmium atoms Cd1 by thiocyanato bridges. Since the site symmetry of Cd1 is 3, its three sites of coordinating N1 atoms, are accordingly, related by symmetry. The primary nitrogen atoms N2 and the secondary nitrogen atom N3 of the tridentate dien ligand are also related by the same symmetry 3. As both N2 and N3 are in general positions, there are 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 and one N3 atom with occupancy 2/3 for N2 atoms and 1/3 for N3 leading to a three-fold disorder about the [111] direction. Thus three N1 atoms, two symmetry related N2 atoms and one N3 atom complete the CdN_6 chromophore. The geometry around the cadmium atom Cd2 is trigonally distorted octahedral and around Cd1 is distorted octahedral. The extended structure is represented in Fig. 2. It is noted that each cadmium atom Cd1,

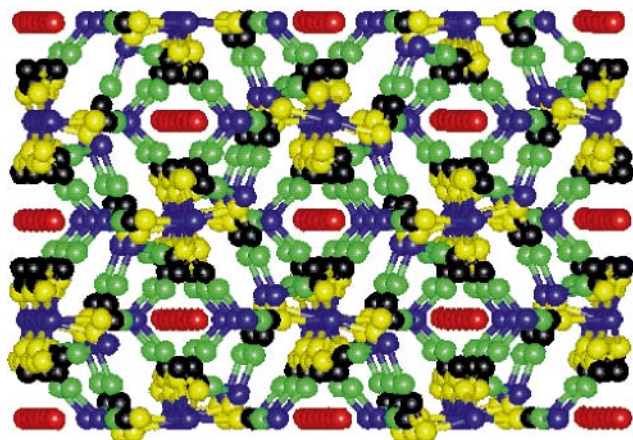


Fig. 2 View of the polymeric array formed by $[\text{Cd}_3(\text{dien})_2(\text{NCS})_6]_n \cdot n\text{H}_2\text{O}$ illustrating the water molecule (red) filled channel (Cd—blue; S—yellow; C—black; N—green; for clarity dien is not shown).

which is coordinated by the N atoms of the dien ligand, is invariably linked with the hard atom N of the thiocyanate ion. In other words the N-atoms of the dien ligand “harden” Cd1, and so the thiocyanate bonds to it preferentially through the N-atom. Conversely the soft end of each thiocyanate ion (S-atom) is coordinated to Cd2 making it “soft”. Thus all the S-atoms of the thiocyanate ion are clubbed together around Cd2. The NCS bridging between the Cd centres is quite common in Cd–amine complexes.^{8–11} The usual feature of these structures is that each Cd ion is coordinated by both N and S atoms. In the present compound, generation of two types of Cd environment, one involving only N-donor atoms and the other only S-donor atoms, is rather unique. There are six branches emanating from the centre Cd2. In each branch Cd2 is connected to Cd1 *via* NCS bridges. Every such Cd1 produces two other branches which are connected *via* NCS bridges to two other Cd2, each of which in turn produces five other branchings. The sequence in one branch can be written as Cd2–S–C1–N1–Cd1–N1*–C1*–S*–Cd2*. The Cd–N (2.287 Å for Cd–N1, 2.453 Å for Cd–N2 and 2.31 Å for Cd–N3) and Cd–S (2.711 Å) distances are comparable to corresponding values of other analogous octahedrally coordinated Cd complexes.^{12,13} The thiocyanate ligands are almost linear (179.8°). Other bond distances and angles in the ligand are close to expected values.

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Notes and references

† *Supplementary data available*: two views of the polymeric array formed by $[\text{Cd}_3(\text{dien})_2(\text{NCS})_6]_n \cdot n\text{H}_2\text{O}$ including the disordered ligand. For direct electronic access see <http://www.rsc.org/suppdata/dt/1999/9/>, otherwise available from BLDSC (No. SUP 57459, 4 pp.) or the RSC Library. See Instructions for Authors, 1999, Issue 1 (<http://www.rsc.org/dalton>).

‡ Crystal data for $[\text{Cd}_3(\text{dien})_2(\text{NCS})_6]_n \cdot n\text{H}_2\text{O}$: cubic, space group $Pa\bar{3}$, $a = b = c = 14.871(4)$ Å, $V = 3288.7(3)$ Å³, $Z = 4$, $\rho_{\text{calc}} = 1.838$ Mg m⁻³, $\rho_{\text{m}} = 1.842$ Mg m⁻³, $\mu(\text{Mo-K}\alpha) = 2.333$ mm⁻¹, $T = 295(2)$ K, no. of measured and independent reflections 2260 and 725, no. of reflections included in the refinement 725, σ limits $I \geq 2\sigma(I)$, no. of parameters 71, $R1 = 0.0360$, $wR2 = 0.0874$, refined against F^2 . CCDC reference number 186/1252. See <http://www.rsc.org/suppdata/dt/1999/9/> for crystallographic files in .cif format.

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