# *catena*-Poly[tris(ethylenediamine-$\kappa^2 N,N'$)nickel(II) [cadmium(II)-di-$\mu$-1,2-dicyanoethylenedithiolato-$\kappa^3 S,S':S'$] monohydrate]

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**Key indicators**

Single-crystal X-ray study

$T$ = 293 K

Mean $\sigma$(C–C) = 0.013 Å

$R$ factor = 0.051

$wR$ factor = 0.083

Data-to-parameter ratio = 15.2

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The title compound, $\{[Ni(C_2H_8N_2)_3][Cd(C_4N_2S_2)_2] \cdot H_2O\}_n$, contains chains of bis(1,2-dicyanoethylenedithiolato)-cadmate(II) complex anions, tri(ethylenediamine)nickel(II) cations and uncoordinated water molecules. The Cd[II] centre is in a very distorted CdS$_6$ octahedral environment. Three bidentate ethylenediamine ligands are coordinated to the Ni[II] atom, resulting in somewhat distorted NiN$_6$ octahedra. The polymeric anionic chains, cations and water molecules are linked by hydrogen bonds into a three-dimensional framework.

## Comment

Recently we have reported a number of *d*-block metal ion complexes with ethylenediamine (en) and 1,2-dicyanoethylenedithiolate (mnt) (Fu *et al.*, 2004, 2004*a*,*b*; Wang, Fu & Wei, 2004; Wang, Fu & He, 2004), which display a plethora of interesting structures. We now report the crystal structure of the title compound, (I), which has a crystal structure distinct from those previously determined.



(I)
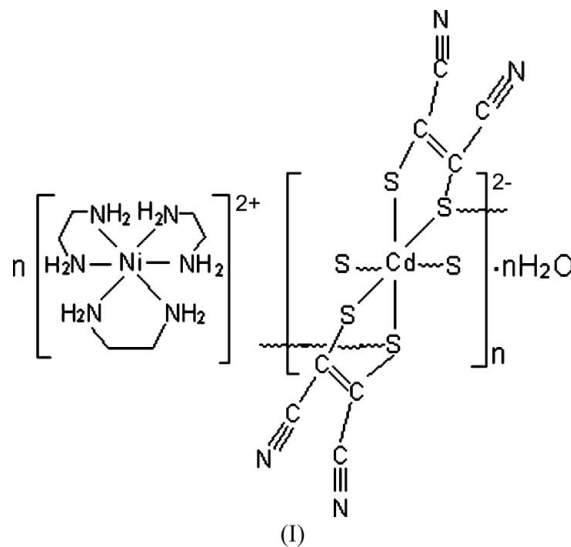
Compound (I) can be formulated as $\{[Ni(C_2H_8N_2)_3]-[Cd(C_4N_2S_2)_2] \cdot H_2O\}_n$ and consists of chains of bis($\mu_2$-1,2-dicyanoethylenedithiolato-$\kappa^3 S,S':S'$)cadmate(II) complex anions, tri(ethylenediamine-$\kappa^2 N,N'$)nickel(II) complex cations and uncoordinated water molecules (Fig. 1).

The central Ni[II] atom of the cation is in an octahedral geometry, coordinated by three bidentate en ligands *via* six N atoms. The three *trans* angles for the octahedron are 169.1 (3), 168.4 (2) and 170.7 (3)°, and the other angles range from 81.1 (3)° to 96.7 (3)°, indicating a somewhat distorted octa-
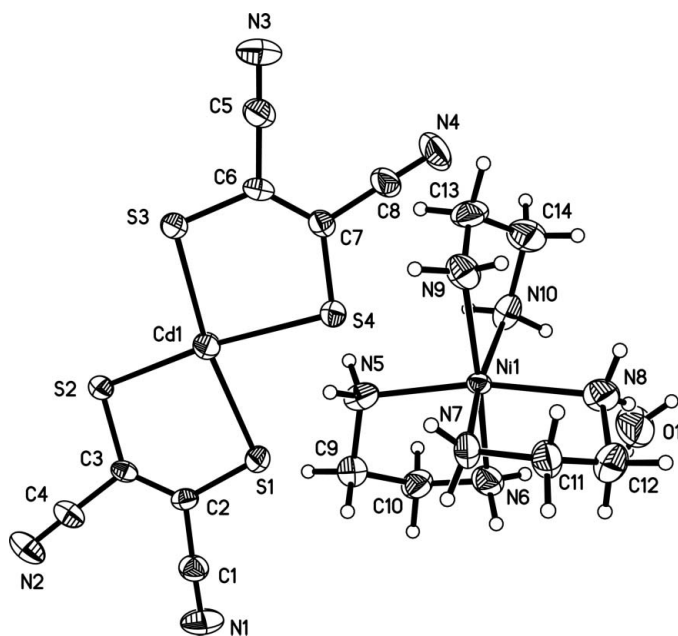
**Figure 1**
View of the asymmetric unit of (I), showing 30% probability displacement ellipsoids (arbitrary spheres for the H atoms).
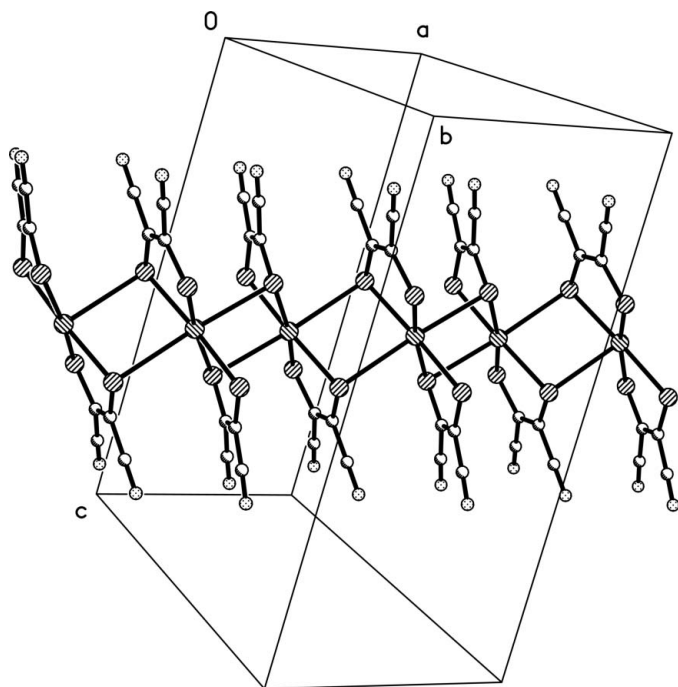


**Figure 2**
The chain-like structure for the complex anion of (I).

hedral geometry. The Ni—N distances (Table 1) are comparable to the values of 2.110 (3)–2.151 (2) Å observed in related complexes (Fu *et al.*, 2004, 2004a,b; Wang, Fu & Wei, 2004; Wang, Fu & He, 2004).

Atom Cd1 of the anionic chain is coordinated by six S atoms, of which S1–S4 are from two chelating mnt ligands and constitute the equatorial plane of the coordination octahedron [mean Cd—S = 2.589 (2) Å]. The two longer Cd—S bonds [mean Cd—S = 3.032 (3) Å; Table 1], to atoms S3$^i$ and S2$^{ii}$

[symmetry codes: (i) $1 - x, -y, 2 - z$; (ii) $2 - x, -y, 2 - z$], are from additional mnt bridging ligands and occupy the axial positions of the octahedron. The CdS$_4$ equatorial arrangement of the octahedron is not completely planar and displays a puckered shape. Dihedral angles of 17.39 (19)° between the equatorial CdS$_4$ group and the N1/C1–C4/N2 (mnt$^{2-}$) mean plane, and 26.78 (18)° between the CdS$_4$ group and the N3/C5–C8/N4 (mnt$^{2-}$) mean plane, are observed. The S—Cd—S bond angles within the equatorial coordiantion are 84.01 (7) and 82.34 (7)°

Bridging atoms S3$^i$ and S2$^{ii}$ coordinate to two neighboring Cd atoms simultaneously, and these four atoms (as –S3—Cd1—S3$^i$—Cd1$^i$–) construct an essentially planar four-membered ring. In this way each mnt divalent anion bridges two cadmium(II) ions to form a one-dimensional chain along the *a* axis, as shown in Fig. 2. The distances between neighbouring Cd atoms in the chain are 4.009 (9) and 4.139 (9) Å.

The water H atoms and the NH groups of the en ligands serve as hydrogen-bond donors (Table 2). The acceptor species include water O and mnt N and S atoms. Some of these bonds connect adjacent inversion-related chains, forming a three-dimensional network (Table 2 and Fig. 3).

## Experimental

H$_2$mnt (1.00 mmol) and NaOH (2.00 mmol) were dissolved in ethanol (20 ml). To this solution, en (1.50 mmol) and an ethanol solution (30 ml) of CdSO$_4$ (1.00 mmol) and NiSO$_4$ (0.50 mmol) were added dropwise at 313 K. The mixture was stirred for 6 h and part of the solvent was evaporated in a rotary vacuum evaporator. The resulting solution was filtered and left in air for about 20 days. Large green block-like crystals of (I) suitable for X-ray analysis were obtained. Analysis found: C 25.75, H 3.96, N 21.38, S 19.58%; calculated for C$_{14}$H$_{26}$CdN$_{10}$NiOS$_4$: C 25.88, H 4.03, N 21.55, S 19.74%.

*Crystal data*

| | |
|---|---|
| [Ni(C$_2$H$_8$N$_2$)$_3$][Cd(C$_4$N$_2$S$_2$)$_2$]·H$_2$O | $D_x = 1.749$ Mg m$^{-3}$ |
| $M_r = 649.80$ | Mo $K\alpha$ radiation |
| Monoclinic, $P2_1/n$ | Cell parameters from 1561 |
| $a = 7.5796$ (15) Å | reflections |
| $b = 19.255$ (4) Å | $\theta = 2.4$–19.6° |
| $c = 17.201$ (4) Å | $\mu = 1.99$ mm$^{-1}$ |
| $\beta = 100.509$ (4)° | $T = 293$ (2) K |
| $V = 2468.3$ (9) Å$^3$ | Block, green |
| $Z = 4$ | $0.30 \times 0.15 \times 0.12$ mm |

*Data collection*

| | |
|---|---|
| Bruker SMART CCD diffractometer | 4346 independent reflections |
| $\varphi$ and $\omega$ scans | 2220 reflections with $I > 2\sigma(I)$ |
| Absorption correction: multi-scan (*SADABS*; Bruker, 1997) | $R_{int} = 0.069$ |
| | $\theta_{max} = 25.0°$ |
| | $h = -9 \rightarrow 8$ |
| $T_{min} = 0.587$, $T_{max} = 0.796$ | $k = -22 \rightarrow 16$ |
| 12887 measured reflections | $l = -20 \rightarrow 20$ |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | H atoms treated by a mixture of independent and constrained refinement |
| $R[F^2 > 2\sigma(F^2)] = 0.051$ | |
| $wR(F^2) = 0.083$ | |
| $S = 1.00$ | $w = 1/[\sigma^2(F_o^2) + (0.0141P)^2]$ |
| 4346 reflections | where $P = (F_o^2 + 2F_c^2)/3$ |
| 286 parameters | $(\Delta/\sigma)_{max} = 0.001$ |
| | $\Delta\rho_{max} = 0.88$ e Å$^{-3}$ |
| | $\Delta\rho_{min} = -0.77$ e Å$^{-3}$ |

**Table 1**
Selected bond lengths (Å).

| Cd1—S1 | 2.555 (2) | Ni1—N5 | 2.133 (6) |
|---|---|---|---|
| Cd1—S3 | 2.558 (2) | Ni1—N9 | 2.147 (7) |
| Cd1—S2 | 2.588 (2) | Ni1—N7 | 2.149 (7) |
| Cd1—S4 | 2.657 (2) | Ni1—N10 | 2.153 (7) |
| Cd1—S3$^i$ | 2.949 (3) | Ni1—N8 | 2.156 (7) |
| Cd1—S2$^{ii}$ | 3.116 (3) | Ni1—N6 | 2.161 (6) |

Symmetry codes: (i) $-x + 1, -y, -z + 2$; (ii) $-x + 2, -y, -z + 2$.

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

| $D$—H$\cdots A$ | $D$—H | H$\cdots A$ | $D\cdots A$ | $D$—H$\cdots A$ |
|---|---|---|---|---|
| O1—H1$\cdots$O1$^{iii}$ | 0.83 (5) | 2.38 (7) | 2.847 (13) | 116 (5) |
| O1—H2$\cdots$N3$^{iv}$ | 0.84 (7) | 2.10 (8) | 2.870 (12) | 154 (8) |
| N5—H5$A\cdots$S1$^{v}$ | 0.90 | 2.57 | 3.404 (7) | 154 |
| N5—H5$B\cdots$S4 | 0.90 | 2.66 | 3.483 (7) | 153 |
| N6—H6$A\cdots$O1 | 0.90 | 2.36 | 3.209 (12) | 157 |
| N6—H6$B\cdots$N2$^{vi}$ | 0.90 | 2.34 | 3.141 (11) | 149 |
| N7—H7$A\cdots$S1$^{v}$ | 0.90 | 2.86 | 3.478 (6) | 127 |
| N7—H7$B\cdots$N4$^{vii}$ | 0.90 | 2.27 | 3.066 (11) | 147 |
| N8—H8$A\cdots$O1 | 0.90 | 2.59 | 3.410 (11) | 152 |
| N8—H8$A\cdots$N3$^{iv}$ | 0.90 | 2.59 | 3.237 (11) | 129 |
| N8—H8$B\cdots$N1$^{viii}$ | 0.90 | 2.34 | 3.189 (11) | 156 |
| N9—H9$A\cdots$S4$^{v}$ | 0.90 | 2.79 | 3.498 (8) | 136 |
| N9—H9$B\cdots$N1$^{viii}$ | 0.90 | 2.48 | 3.346 (12) | 160 |
| N10—H10$A\cdots$O1 | 0.90 | 2.49 | 3.322 (11) | 154 |

Symmetry codes: (iii) $-x + 1, -y + 1, -z + 2$; (iv) $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{3}{2}$; (v) $x - 1, y, z$; (vi) $-x + \frac{3}{2}, y + \frac{1}{2}, -z + \frac{5}{2}$; (vii) $x - \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$; (viii) $x - \frac{3}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$.

The water H atoms were found in difference maps. The O—H distances were restrained to 0.90 (1) Å and the $U_{iso}$(H) values were allowed to refine. All other H atoms were placed in idealized positions (C—H = 0.97 Å and N—H = 0.90 Å) and refined as riding on their carrier atoms with $U_{iso}$(H) = $1.2U_{eq}$(carrier).

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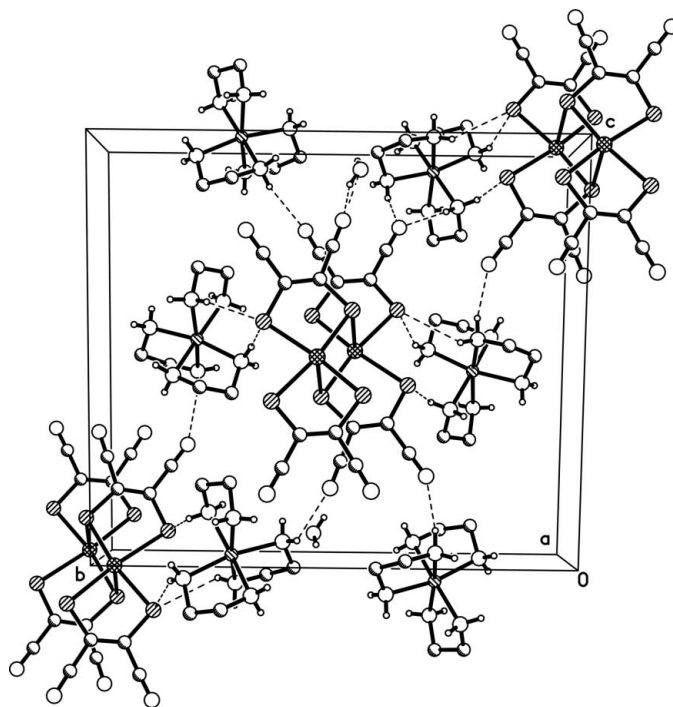


**Figure 3**
Packing diagram for (I), viewed down *a*, with hydrogen-bonded interactions indicated by dashed lines.

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