

Polymeric μ -cyano-dicyanonickel-ate(II)- μ -cyano-*trans*-bis[*N*-(2-hydroxyethyl)ethylenediamine]cadmium(II)

Ahmet Karadağ,^a Hümeysra Paşaoğlu,^{b*} Gökhan Kaştaş^b
and Orhan Büyükgüngör^b

^aDepartment of Chemistry, Faculty of Science, Gaziosmanpaşa University, 60250 Tokat, Turkey, and ^bDepartment of Physics, Faculty of Arts and Sciences, Ondokuz Mayıs University, 55139 Kurupelit Samsun, Turkey
Correspondence e-mail: hpaşa@omu.edu.tr

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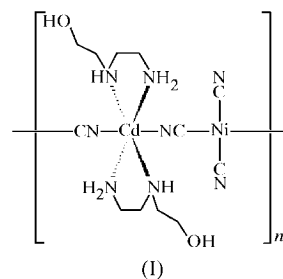
The title compound, *catena*-poly[[μ -cyano-1:2 κ^2 C:*N*-dicyano-1 κ^2 C-*trans*-bis[*N*-(2-hydroxyethyl)ethane-1,2-diamine-2 κ^2 -*N,N'*]cadmium(II)nickel(II)]- μ -cyano-1:2' κ^2 C:*N*], [CdNi(CN)₄(C₄H₁₂N₂O)₂], consists of alternating square-planar Ni(CN)₄ fragments, formally dianionic, and Cd(hydet-en)₂ moieties [hydet-en is *N*-(2-hydroxyethyl)ethylenediamine], with the two bridging cyanide ligands in a mutually *trans* disposition at the Ni atom and *cis* at the Cd atom. The resulting one-dimensional zigzag chain structure has the Ni atom on an inversion center, while the distorted octahedron centered on the Cd atom lies on a twofold axis. The polymer chains are connected into undulating sheets by weak interchain N—H···N, N—H···O and O—H···N hydrogen bonds, which are also present between successive sheets.

Comment

The chemistry of cyanide-bridged homo- and heteronuclear polymers involving transition metals is of current interest as these coordination polymers may have interesting properties and applications, for example, in adsorption or ion exchange, or as non-linear optical and magnetic materials. Such polymers may possess interesting one-, two- or three-dimensional topologies, including helical, diamondoid and honeycomb, T-shaped, and ladder (Goher *et al.*, 2003; Kumar & Goldberg, 1998; Lin *et al.*, 1998). For example, tetracyanonickelates are suitable model compounds for magnetic studies at low temperatures, as they may bridge paramagnetic ions partially coordinated with amine ligands and thus form molecular one-, two- and three-dimensional structures (Smékal *et al.*, 2001, 2003). In addition, a series of polymeric cyanide-bridged cadmium and nickel compounds include organic molecules in a host–guest type of relationship (Zhang *et al.*, 2000).

The crystal engineering of coordination polymers is usually achieved by the reaction of metal ions with bi- or multidentate

ligands containing O-atom donors or mixed N/O-atom donors (Xia *et al.*, 2004). In general, the construction of one-dimensional systems containing cyanide complex anions as bridging species is achieved by the so-called 'brick-and-mortar' method (Willet *et al.*, 1993; Kahn, 1993). The Cd^{II} ion is well suited for construction of such materials, as its electronic configuration and size permit a wide variety of geometries and coordination numbers (Banerjee *et al.*, 2003). In the present study, we have used a mixed N/O-atom donor ligand, namely *N*-(2-hydroxyethyl)ethylenediamine (hydet-en), to prepare a compound exhibiting a one-dimensional structure. The hydet-en ligand, which has three donor sites, has been the subject of few studies (Yılmaz *et al.*, 2002; Karadağ *et al.*, 2004), and its coordination behavior, therefore, is not well characterized. In this context, we have synthesized a Cd^{II}–Ni^{II} coordination polymer, *viz.* the title complex, (I), and determined its crystal structure.



In the literature, the expression '2,2-*TT*-type chain' is used for a one-dimensional structure with two bridging cyanide groups in both the cation and the anion, and with both bridges in relative *trans* positions in their respective coordination polyhedra (Černák *et al.*, 2002). In accordance with this definition, the title complex can be said to be of the 2,2-*CT* type. Cadmium complexes usually exhibit 2,2-*TT* (linear chain) topologies in one-dimensional systems. To our knowledge, there are only a few examples of zigzag chain structures and there is no known cadmium coordination polymer exhibiting a 2,2-*CT*-type zigzag chain in a one-dimensional system.

Complex (I) has a cyanide-bridged polymeric structure in which the Ni^{II} ion is coordinated by four cyanide ligands (two cyano groups are terminal, while two cyano groups coordinated in a *trans* fashion about the Ni atom constitute the bridges) in a square-planar arrangement. The Cd^{II} ion is six-coordinated by four N atoms of the two chelating hydet-en ligands and two N atoms of the bridging cyanide ligands (Fig. 1). The cyanide groups act as ambidentate ligands, bridging the Cd^{II} and Ni^{II} centers and thus forming chains. The amine ligand acts as a bidentate N-atom donor ligand and the ethanol group is not involved in coordination; this behavior was also observed in the Cu and Cd complexes of saccharin with the hydet-en ligand (Yılmaz *et al.*, 2002) and in the cyanide-bridged Zn^{II}–Ni^{II} complex (Karadağ *et al.*, 2004). Selected bond lengths and angles for (I) are given in Table 1. While the Ni1–C1–N1 angle [178.95 (14)°] is essentially linear, the Cd1–N1–C1 angle [167.30 (12) Å] deviates from linearity. This deviation is greater than those observed in related structures (Zhan *et al.*, 2000; Mukherjee *et al.*, 2001; Smékal *et al.*, 2003; Černák *et al.*, 2001). The Ni1–C2–N2

angle [178.53 (12)°] is effectively linear, as expected. The Cd—N bond lengths are longer than those in the Zn—Ni complex, as expected, but are in the same range as those found for the Cd complex of saccharin with the hydret-en ligand. The C1—Ni1, C2—Ni1, C1—N1 and C2—N2 bond distances of the square-planar Ni coordination environment in (I) are comparable to those in related cyanide-bridged tetracyanonickelates (Zhan *et al.*, 2000; Smékal *et al.*, 2001, 2003; Mukherjee *et al.*, 2001).

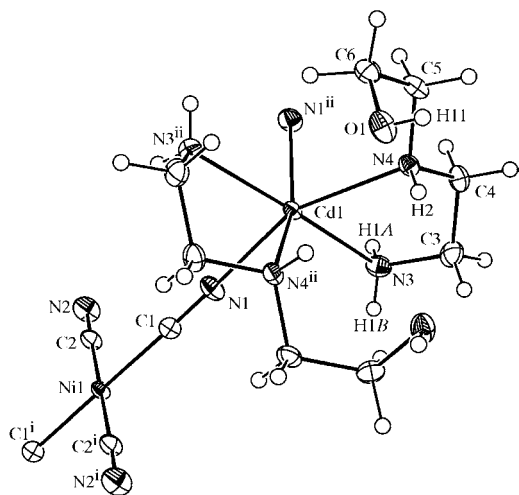


Figure 1
The molecular structure of (I), showing the atom-labeling scheme and displacement ellipsoids at the 50% probability level. [Symmetry code: (i) $-x, 1 - y, 2 - z$; (ii) $-x, y, \frac{3}{2} - z$.]

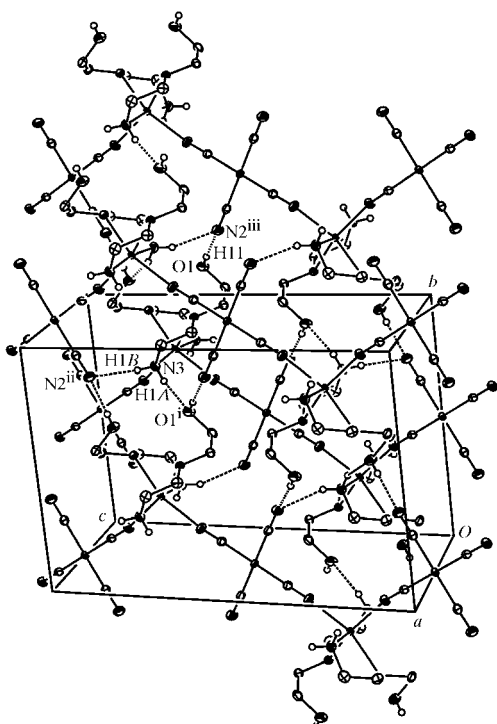


Figure 2
The zigzag chain structure of (I), with intra- and interchain interactions indicated by dashed lines.

In the extended structure, the NH, NH₂ and OH groups of the hydret-en ligand are involved in interchain hydrogen bonding; the polymer chains are connected by interchain N3—H1A···O1($x + \frac{1}{2}, y - \frac{1}{2}, z$), N3—H1B···N2($x + \frac{1}{2}, y + \frac{1}{2}, z$) and O1—H11···N2($-x, y + 1, -z + \frac{3}{2}$) interactions (Fig. 2). These interactions are also effective in forming a layered structure, and the geometry of the interactions is given in Table 2. The intrachain Cd1···Cd1($-x, -y + 1, -z + 1$) distance is 10.5839 (8) Å, whereas the shortest interchain distance is 7.5083 (6) Å for Cd1···Cd1($x + \frac{1}{2}, y - \frac{1}{2}, z$).

Experimental

Cadmium sulfate (CdSO₄· $\frac{8}{3}$ H₂O, Aldrich), nickel sulfate hexahydrate (NiSO₄·6H₂O, Panreac), potassium cyanide (KCN, Merck) and *N*-(2-hydroxyethyl)ethylenediamine (C₄H₁₂N₂O, Aldrich) were used as received, and the dihydrate of potassium tetracyanonickelate(II) {K₂[Ni(CN)₄]·2H₂O} was recrystallized as described by Fernelius (1946). To an aqueous solution (40 ml) of CdSO₄· $\frac{8}{3}$ H₂O (1 mmol, 0.256 g) was added an aqueous solution (20 ml) of K₂[Ni(CN)₄]·2H₂O (1 mmol, 0.241 g). The cream-colored precipitate that formed after 5 min of stirring was dissolved by pouring the mixture into a bulb containing *N*-(2-hydroxyethyl)ethylenediamine (0.208 g, 2 mmol). The resultant light-yellow solution was filtered to remove any solid impurities and left to crystallize at room temperature. Several days of standing led to the growth of light-yellow crystals suitable for X-ray analysis.

Crystal data

[CdNi(CN)₄(C₄H₁₂N₂O)₂]
M_r = 483.50
 Monoclinic, *C*2/*c*
a = 10.0637 (5) Å
b = 11.1455 (8) Å
c = 17.5089 (9) Å
 β = 103.046 (4)°
V = 1913.20 (19) Å³
Z = 4

D_x = 1.679 Mg m⁻³
 Mo Kα radiation
 Cell parameters from 26 673 reflections
 θ = 2.4–28.9°
 μ = 2.12 mm⁻¹
T = 293 (2) K
 Prism, light yellow
 0.58 × 0.40 × 0.14 mm

Data collection

Stoe IPDS-II diffractometer
 ω scans
 Absorption correction: by integration (*X-RED32*; Stoe & Cie, 2002)
T_{min} = 0.376, *T_{max}* = 0.744
 14 985 measured reflections

2457 independent reflections
 2292 reflections with *I* > 2σ(*I*)
R_{int} = 0.059
 θ_{max} = 28.7°
h = -13 → 13
k = -14 → 14
l = -23 → 23

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.016
wR(*F*²) = 0.036
S = 1.05
 2457 reflections
 159 parameters
 All H-atom parameters refined

w = 1/[σ²(*F_o*²) + (0.0096*P*)² + 1.3234*P*]
 where *P* = (*F_o*² + 2*F_c*²)/3
 (Δ/σ)_{max} = 0.020
 Δρ_{max} = 0.30 e Å⁻³
 Δρ_{min} = -0.79 e Å⁻³

Table 1
Selected geometric parameters (Å, °).

C1—N1	1.1459 (17)	N1—Cd1	2.3198 (12)
C1—Ni1	1.8595 (13)	N3—Cd1	2.3726 (13)
C2—N2	1.146 (2)	N4—Cd1	2.3905 (11)
C2—Ni1	1.8680 (15)		
N1—C1—Ni1	178.95 (14)	C1—Ni1—C2	89.62 (6)
N2—C2—Ni1	178.53 (12)	N1—Cd1—N3	86.16 (5)
C1—N1—Cd1	167.30 (12)	N1—Cd1—N4	157.96 (5)

Table 2

Hydrogen-bonding geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$N3-H1A\cdots O1^{iii}$	0.83 (2)	2.30 (2)	3.0276 (17)	146 (2)
$N3-H1B\cdots N2^{iv}$	0.82 (2)	2.59 (2)	3.303 (2)	145.4 (19)
$O1-H11\cdots N2^v$	0.75 (2)	2.09 (2)	2.8328 (18)	173 (2)

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

All H atoms were located in a difference Fourier map, and their coordinates and $U_{iso}(H)$ values were refined freely [$O-H = 0.75$ (2) Å, $N-H = 0.82$ (2)– 0.862 (19) Å and $C-H = 0.948$ (19)– 1.00 (2) Å].

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA*; data reduction: *X-RED32* (Stoe & Cie, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA1079). Services for accessing these data are described at the back of the journal.

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