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Poly[deca-μ_2-cyanido-dicyanido-bis(μ_2-ethylenediamine)bis(ethylenediamine)tricadmium(II)dicobalt(III)]: a two-dimensional coordination polymer

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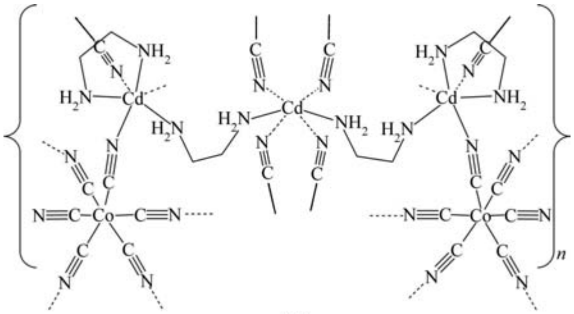
The title coordination polymer, $[\mathrm{Cd_3Co_2(CN)_{12}(C_2H_8N_2)_4}]_n$, has an infinite two-dimensional network structure. The asymmetric unit is composed of two crystallographically independent Cd$^{\mathrm{II}}$ atoms, one of which is located on a twofold rotation axis. There are two independent ethylenediamine (en) ligands, one of which bis-chelates to the Cd atom that sits in a general position, while the other bridges this Cd atom to that sitting on the twofold axis. The Cd atom located on the twofold rotation axis is linked to four equivalent Co$^{\mathrm{III}}$ atoms *via* cyanide bridges, while the Cd atom that sits in a general position is connected to three equivalent Co$^{\mathrm{III}}$ atoms *via* cyanide bridges. In this way, a series of trinuclear, tetranuclear and pentanuclear macrocycles are linked to form a two-dimensional network structure lying parallel to the *bc* plane. In the crystal structure, these two-dimensional networks are linked *via* N—H$\cdots$N hydrogen bonds involving an en NH$_2$ H atom and a cyanide N atom, leading to the formation of a three-dimensional structure. This coordination polymer is only the second example involving a cyanometallate where the en ligand is present in both chelating and bridging coordination modes.

Comment

Interest in the construction of multinuclear or polymeric complexes involving metal cyanides has been driven by application-oriented concepts, such as the design and synthesis of molecular magnets, light-emitting devices and zeolite-like materials, and also by the advantages of using cyanometallates as building blocks (Cernák *et al.*, 2002; Ohba & Okawa, 2000; Stasicka & Wasielewska, 1997; Verdaguer *et al.*, 1999; Yanai *et al.*, 2007). The dimensionality of the structures formed can be tuned to some extent by using blocking ligands, mainly of the amine type, occupying several coordination sites of the central atom of the complex cation. Using this approach a large number of coordination polymers based on cyanide complexes have been synthesized and structurally and magnetically characterized (Chen *et al.*, 2005; Liu *et al.*, 2006; Ostrovsky *et al.*, 2007).

Transition metal complexes of the ligand ethylenediamine (en) subsequently complexed with metallocyanides have been used extensively to form coordination polymers. A search of such compounds in the Cambridge Structural Database (CSD; Version 5.29, November 2008 update; Allen, 2002) revealed over 170 structures with en in its chelated form, many being coordination polymers, but only nine entries where en is present in the bridging coordination mode. There was only one example (CSD refcode HEGCEB; Yuge & Iwamoto, 1994) where en is present in both chelating and bridging modes: an infinite three-dimensional structure involving Cd^{2+}/en/[Ni(CN)$_4$]$^{2-}$, namely *catena*-[hexakis(μ_2-cyano)(μ_2-ethylenediamino)dicyanobis(ethylenediamine)dicadmium(II)dinickel(II) tetraphenol clathrate]. We have investigated the Cd^{2+}/en/[Co(CN)$_6$]$^{3-}$ system and present here the crystal structure of the title compound, (I), a two-dimensional coordination polymer in which en is again present in both chelating and bridging modes.



(I)

The asymmetric unit of complex (I) is illustrated in Fig. 1, and geometrical parameters are available in the archived CIF.

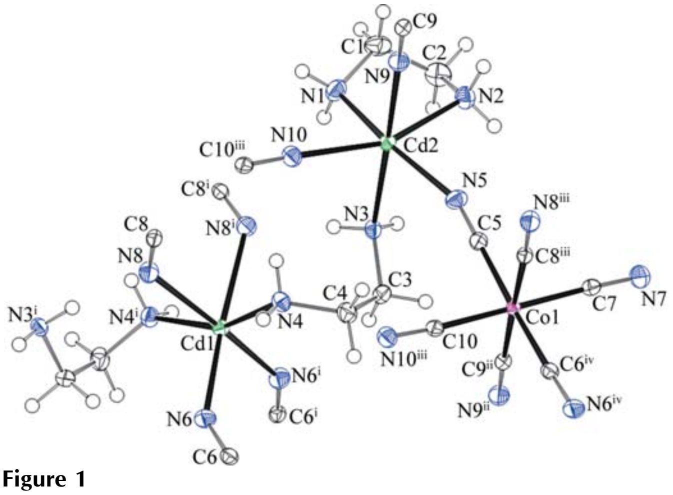


Figure 1
The asymmetric unit of compound (I), showing the atom-numbering scheme and displacement ellipsoids drawn at the 50% probability level. [Symmetry codes: (i) $-x, y, -z + \frac{1}{2}$; (ii) $x, y + 1, z$; (iii) $-x, -y + 1, -z$; (iv) $-x, -y + 2, -z$.]

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The structure is an infinte two-dimensional network consisting of a series of trinuclear, tetranuclear and pentanuclear macrocycles linked to form a two-dimensional network lying parallel to the *bc* plane (Fig. 2). The various en ligands are both bridging and chelating. There are two crystallographically independent Cd^{II} atoms, Cd1 and Cd2. Atom Cd1 sits on a twofold rotation axis and exhibits a distorted octahedral $[CdN_6]^{2+}$ coordination, involving four N-bonded cyanide groups and two N atoms of bridging en ligands. Atom Cd2 also exhibits a distorted octahedral coordination geometry, involving one chelating en ligand, three N-bonded bridging cyanide groups, and one N atom from a bridging en ligand that links it to atom Cd1.

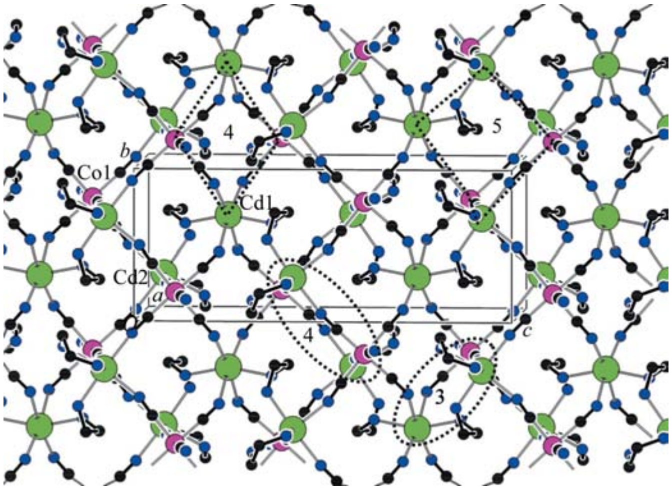

Figure 2
A view down the *a* axis of the crystal packing of compound (I), showing the various trinuclear, tetranuclear and pentanuclear macrocyles that are linked to form the two-dimensional network (H atoms have been omitted for clarity).

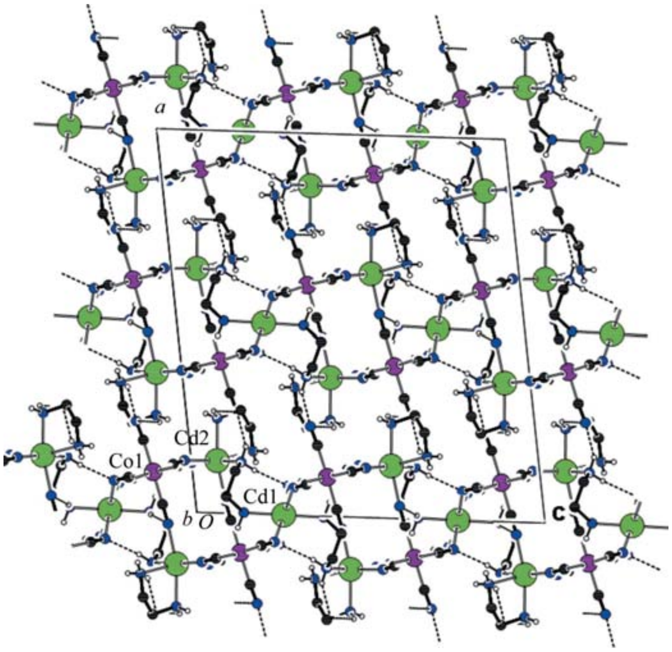

Figure 3
A view down the *b* axis of the crystal structure of compound (I), showing the intra- and inter-polymer N—H···N hydrogen bonds as dashed lines (see Table 1 for details; H atoms not involved in hydrogen bonding have been omitted for clarity).

The amine Cd—N bond distances are in the range 2.3013 (14)–2.4069 (15) Å, while the cyanide Cd—N bond distances vary from 2.2997 (15) to 2.4728 (15) Å, similar to the same distances in HEGCEB. The N—Cd—N angles range from 78.29 (5) to 108.77 (5)° and from 158.32 (5) to 172.66 (5)° about atom Cd1, and from 73.78 (5) to 106.43 (5)° and from 159.01 (5) to 174.57 (5)° about atom Cd2. Again these values are similar to those observed in HEGCEB. Some of the Cd—N≡C bonds are bent, the smallest angle being 133.94 (13)° for the Cd1—N8≡C8 bonds. Such deviations from linearity are frequent for this type of structure; for example, a value of only 128.64 (15)° has been observed in a cadmium(II)–ethylenediamine–hexacyanoferrate(III) complex (Maľarová *et al.*, 2003). The Co^{II} atom of the $[Co(CN)_6]^{3-}$ anion has a relatively regular octahedral coordination. Five cyanide groups exhibit bridging character, while the sixth, C7≡N7, is terminal, and this N atom is involved in hydrogen bonding (Table 1). It is worth noting that in the IR spectrum three absorption bands are present in the 2000–2200 cm^{-1} region; these can be assigned to the presence of terminal (2120 cm^{-1}, weak) and bridging (2137 and 2158 cm^{-1}, strong) cyanide groups (Nakamoto, 1997).

In the crystal structure of (I) there are intra- and inter-polymer N—H···N hydrogen bonds involving the N3 amino group and cyanide atoms N7 and N8 (Table 1). As can be seen in Fig. 3, the inter-polymer N3—H3*A*···N7$(-x+\frac{1}{2}, -y+\frac{3}{2}, -z)$ hydrogen bonds link the two-dimensional networks to form a three-dimensional structure.

Experimental

Complex (I) was obtained by adding an aqueous solution (30 ml) of $CdCl_2{\cdot}2H_2O$ (1 mmol, 0.219 g) to ethylenediamine (en) (1 mmol, 0.07 ml) with stirring. $K_3[Co(CN)_6]_3{\cdot}H_2O$ (0.5 mmol, 0.165 g) was then added dropwise and the mixture was stirred for 30 min. To aid crystallization, $NaClO_4$ (1 mmol, 0.12 g) was added with stirring and heating for a few minutes. The resulting solution was filtered and the filtrate placed undisturbed in the dark. After several days, a small quantity of orange crystals, suitable for X-ray analysis, were obtained.

Crystal data

$[Cd_3Co_2(CN)_{12}(C_2H_8N_2)_4]$
$M_r = 1007.72$
Monoclinic, $C2/c$
$a = 21.7002$ (11) Å
$b = 7.7859$ (5) Å
$c = 19.6450$ (9) Å
$\beta = 97.770$ (4)°
$V = 3288.7$ (3) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 2.94$ mm^{-1}
$T = 173$ (2) K
0.42 × 0.33 × 0.21 mm

Data collection

Stoe IPDS-II diffractometer
Absorption correction: multi-scan (*MULscanABS* in *PLATON*; Spek, 2003)
$T_{min} = 0.440$, $T_{max} = 0.540$
19479 measured reflections
4410 independent reflections
4101 reflections with $I > 2\sigma(I)$
$R_{int} = 0.023$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.018$	205 parameters
$wR(F^2) = 0.044$	H-atom parameters constrained
$S = 1.11$	$\Delta\rho_{\max} = 0.56$ e Å^{-3}
4410 reflections	$\Delta\rho_{\min} = -0.60$ e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N3—H3A···N7^{v}	0.92	2.14	2.960 (2)	147
N3—H3B···N8^{i}	0.92	2.15	3.066 (2)	172

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

H atoms were included in calculated positions and treated as riding [N—H = 0.92 Å and C—H = 0.99 Å, with $U_{\rm iso}$(H) = $1.2U_{\rm eq}$(N,C)].

Data collection: *X-AREA* (Stoe & Cie, 2005); cell refinement: *X-AREA*; data reduction: *X-RED32* (Stoe & Cie, 2005); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA3180). Services for accessing these data are described at the back of the journal.

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