5429 reflections
370 parameters
H-atom parameters not refined

$\Delta\rho_{\min} = -0.79$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Ni1—Cl1	2.507 (1)	Ni1—N2	2.070 (3)
Ni1—Cl1^{i}	2.3655 (8)	Ni1—N3	2.085 (3)
Ni1—N1	2.086 (2)	Ni1—N4	2.084 (3)
Cl1—Ni1—Cl1^{i}	87.37 (3)	Cl1^{i}—Ni1—N4	99.76 (8)
Cl1—Ni1—N1	93.16 (7)	N1—Ni1—N2	80.0 (1)
Cl1—Ni1—N2	87.98 (7)	N1—Ni1—N3	83.4 (1)
Cl1—Ni1—N3	175.38 (7)	N1—Ni1—N4	81.5 (1)
Cl1—Ni1—N4	90.76 (7)	N2—Ni1—N3	94.4 (1)
Cl1^{i}—Ni1—N1	178.66 (8)	N2—Ni1—N4	161.3 (1)
Cl1^{i}—Ni1—N2	98.81 (8)	N3—Ni1—N4	85.7 (1)
Cl1^{i}—Ni1—N3	96.15 (7)	Ni1—Cl1—Ni1^{i}	92.63 (3)

Symmetry code: (i) $-x, -1-y, -z$.

H atoms were placed in idealized positions (C—H 0.95 Å and N—H 0.97 Å), with $U_{\rm iso} = 1.2U_{\rm eq}$ of the attached atom.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1997). Program(s) used to solve structure: *PATTY* in *DIRDIF*92 (Beurskens *et al.*, 1992). Program(s) used to refine structure: *TEXSAN*. Software used to prepare material for publication: *TEXSAN*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1198). Services for accessing these data are described at the back of the journal.

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A three-dimensional host framework with small tetragonal and large hexagonal channels

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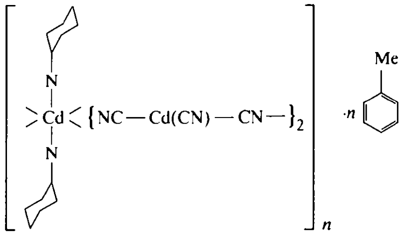
Abstract

Bis(cyclohexylamine-*N*)cadmium(II)bis{tricyanocadmate(II)}–toluene (1/1), $[Cd(C_6H_{11}NH_2)_2\{Cd(CN)_3\}_2]\cdot C_6H_5CH_3$ {or, alternatively, bis(cyclohexylamine-*N*)-hexacyanotricadmium(II) toluene solvate, $[Cd_3(CN)_6(C_6H_{13}N)_2]_n\cdot nC_7H_8$}, is a three-dimensional framework made up of octahedral and tetrahedral Cd sites (in a 1:2 ratio) bridged by cyanide groups. The octahedral Cd centers are coordinated by four cyano groups and two *trans* cyclohexylamine ligands, and the tetrahedral Cd centers are coordinated by four cyano groups. The host structure provides small tetragonal and large hexagonal channels, which are occupied, respectively, by the toluene guest molecules and the cyclohexylamine ligands coordinated to the octahedral Cd site.

Comment

Inorganic supramolecular chemistry and the construction of polymeric multi-dimensional frameworks are ideas which currently garner much interest. As part of their strategy for designing novel supramolecular systems using cyanometallate complex hosts and organic guest molecules, Iwamoto and co-workers (Iwamoto, 1991) have employed various complementary ligands, such as NH_3, H_2O, unidentate aliphatic and aromatic amines, and ambidentate α,ω-diaminoalkanes, for stabilizing multi-dimensional structures. They have obtained various types of supramolecular structures, such as one-dimensional chains, two-dimensional layers and three-dimensional networks (Iwamoto, 1996). However, cyclic amine compounds have not been reported as a complementary ligand for designing novel multi-dimensional frameworks. We therefore introduced the cyclohexylamine molecule as a complementary cyclic amine ligand in order to produce novel supramolecular structures. These structure types may eventually play roles in molecular recognition and separation-media technology. The title compound, $[Cd(C_6H_{11}NH_2)_2\{Cd(CN)_3\}_2]\cdot C_6H_5CH_3$, (I), was crystallized from an aqueous solution and to the best of our knowledge is the first example of a multi-dimensional cyanocadmate inclusion compound coordinated by cyclic amine ligands.



(I)

As shown in Figs. 1 and 2, the structure of (I) has cyanide bridges between two kinds of sites, namely octahedral and tetrahedral Cd ions in a 1:2 ratio. The Cd1 atom is coordinated octahedrally by the N atoms of four cyano groups and by two cyclohexylamine ligands in *trans* positions. The Cd2 and Cd3 atoms are each coordinated tetrahedrally by four cyano groups. The octahedral Cd center is linked to the four tetrahedral Cd atoms *via* cyanide bridging ligands. The tetrahedral Cd centers are likewise each linked to two octahedral and two tetrahedral Cd atoms.

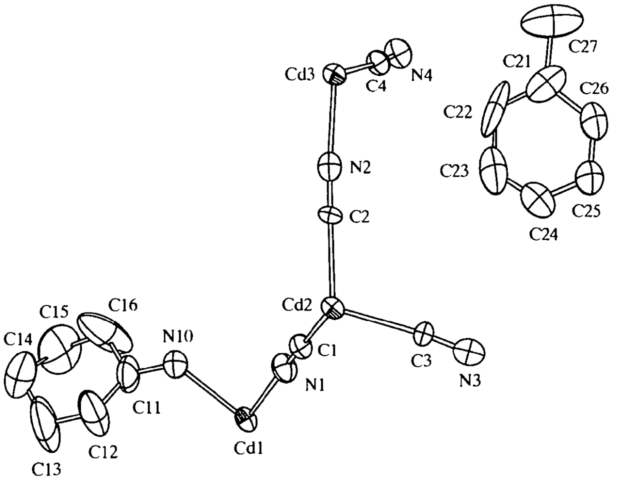


Fig. 1. The asymmetric unit of (I), with displacement ellipsoids at the 30% probability level.

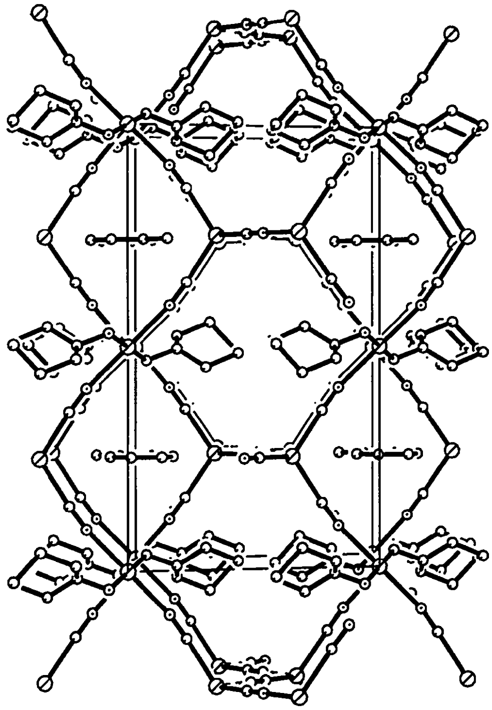


Fig. 2. Perspective view of the unit cell of (I) along the *a* axis.

The three-dimensional host framework, $[Cd(CN)_2]_n$, showing two types of channels running in the *a* direction, is illustrated in Fig. 2. One type of channel has a small tetragonal cross-section, and the other has a large hexagonal cross-section. Although several $[Cd(CN)_2]_n$ frameworks with tetragonal and hexagonal channels have been reported, the inclusion phenomena and host framework of the present clathrate is significantly different from the others. In the $[Cd(CN)_2]_n$ framework of $Cd(CN)_2\cdot\frac{1}{3}C_6H_{12}N_4$, all of the hexamethylenetetramine units are located in channels having a roughly square cross-section, and the large channels of hexagonal cross-section are vacant (Abrahams *et al.*, 1991). In $(NMe_4)[CuPt(CN)_4]$, the tetramethylammonium cations are located in hexagonal channels, and the large square channels are essentially empty (Gable *et al.*, 1990). In the $Cd(CN)_2\cdot H_2O\cdot DMF$ and $Cd(CN)_2\cdot\frac{4}{3}DMSO$ clathrates (DMF is dimethylformamide and DMSO is dimethyl sulfoxide), DMF and DMSO molecules are located in linear channels having a large elongated hexagonal cross-section, and the small rectangular channels are empty (Kim *et al.*, 1994). In contrast, both channels are occupied in the present clathrate (Fig. 2). The cyclohexylamine ligands coordinated to octahedral Cd atoms are found in the large channels of hexagonal cross-section, and the toluene guest molecules are found in the small channels of tetragonal cross-section.

The introduction of complementary ligands such as cyclohexylamine into the host structure gives rise to a change in the $[Cd(CN)_2]_n$ framework. The cyclohexylamine ligand appears to play two roles in building up the host framework, *i.e.* one is to occupy the channel space and the other is to block a coordination site of a Cd atom. Therefore, suitable combinations of the central metal ions, complementary ligands, and guest molecules lead to a variety of $[Cd(CN)_2]_n$ topological and geometrical host frameworks.

Experimental

To an aqueous solution (200 ml) containing $CdCl_2\cdot 2.5H_2O$ (2.28 g, 10 mmol) and $K_2[Cd(CN)_4]$ (2.95 g, 10 mmol) was added $C_6H_{11}NH_2$ (2.3 ml, 20 mmol). The pH of the solution was adjusted to 9 by adding 2-aminoethanol and citric acid. After the small amount of precipitate was filtered off, the aqueous solution was covered with a layer of neat toluene guest species and allowed to stand in a refrigerator at 278 K. After a few weeks, colorless crystals were obtained.

Crystal data

$[Cd_3(CN)_6(C_6H_{13}N)_2]\cdot C_7H_8$
$M_r = 783.80$
Monoclinic
$P2_1/m$
$a = 9.0494\ (12)$ Å
$b = 17.475\ (2)$ Å
$c = 10.5357\ (10)$ Å
$\beta = 106.359\ (8)^\circ$
$V = 1598.7\ (3)$ Å^3
$Z = 2$
$D_x = 1.628$ Mg m^{-3}
$D_m = 1.63$ Mg m^{-3}
D_m measured by flotation in mesitylene/bromoform

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 40 reflections
$\theta = 4.70$–12.48°
$\mu = 2.002$ mm^{-1}
$T = 293\ (2)$ K
Block
0.32 × 0.30 × 0.28 mm
Colorless

Data collection

Siemens *P*4 diffractometer
$2\theta/\omega$ scans
Absorption correction: ψ scan (Siemens, 1996*a*)
$T_{min} = 0.496$, $T_{max} = 0.571$
3740 measured reflections
2910 independent reflections
2301 reflections with $I > 2\sigma(I)$

$R_{int} = 0.031$
$\theta_{max} = 25^\circ$
$h = -1 \rightarrow 10$
$k = -20 \rightarrow 1$
$l = -12 \rightarrow 12$
3 standard reflections every 97 reflections
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.039$
$wR(F^2) = 0.105$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.621$ e Å^{-3}
$\Delta\rho_{min} = -0.558$ e Å^{-3}

$S = 1.042$
2910 reflections
186 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0487P)^2 + 1.0289P]$
where $P = (F_o^2 + 2F_c^2)/3$

Extinction correction: *SHELXL*93
Extinction coefficient: 0.0279 (11)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a^i a^j \mathbf{a}_i.\mathbf{a}_j.$$

	x	*y*	*z*	U_{eq}
Cd1	0	0	0	0.0557 (2)
Cd2	0.16794 (7)	1/4	0.34898 (5)	0.0484 (2)
Cd3	0.77230 (7)	1/4	0.66831 (5)	0.0486 (2)
C1	0.1204 (7)	0.1446 (4)	0.2312 (5)	0.0591 (14)
N1	0.0886 (7)	0.0929 (3)	0.1643 (5)	0.0728 (15)
C2	0.4089 (8)	1/4	0.4689 (7)	0.048 (2)
N2	0.5331 (9)	1/4	0.5320 (7)	0.070 (2)
C3	0.0212 (9)	1/4	0.4829 (7)	0.053 (2)
N3	−0.0628 (9)	1/4	0.5416 (8)	0.076 (2)
C4	0.8204 (7)	0.1462 (3)	0.7905 (5)	0.0576 (14)
N4	0.8559 (7)	0.0951 (3)	0.8568 (5)	0.079 (2)
N10	0.2180 (8)	0.0304 (5)	−0.0657 (6)	0.103 (2)
C11	0.2441 (12)	0.0041 (7)	−0.1859 (9)	0.142 (5)
C12	0.1576 (17)	0.0457 (7)	−0.3030 (9)	0.177 (6)
C13	0.181 (2)	0.0142 (11)	−0.4324 (12)	0.277 (14)
C14	0.350 (2)	0.0060 (12)	−0.4183 (18)	0.280 (15)
C15	0.404 (2)	−0.0569 (9)	−0.3161 (15)	0.239 (9)
C16	0.3968 (16)	−0.0256 (11)	−0.1831 (13)	0.284 (13)
C21	0.5491 (17)	1/4	1.048 (2)	0.119 (5)
C22	0.529 (3)	1/4	0.920 (3)	0.205 (13)
C23	0.371 (3)	1/4	0.8317 (17)	0.210 (12)
C24	0.2592 (19)	1/4	0.8733 (13)	0.119 (5)
C25	0.2701 (16)	1/4	0.9960 (12)	0.126 (5)
C26	0.4090 (19)	1/4	1.0820 (13)	0.139 (6)
C27	0.7085 (19)	1/4	1.148 (2)	0.211 (11)

Table 2. *Selected geometric parameters (Å, °)*

Cd1—N10	2.329 (6)	Cd2—C1	2.194 (6)
Cd1—N1	2.344 (5)	Cd3—C4	2.196 (6)
Cd1—N4^i	2.373 (5)	Cd3—N2	2.235 (8)
Cd2—C2	2.191 (7)	Cd3—N3^{ii}	2.265 (9)
Cd2—C3	2.193 (7)		
N10—Cd1—N1	85.4 (2)	C3—Cd2—C1	107.8 (2)
N10—Cd1—N4^i	90.6 (2)	C4—Cd3—N2	111.9 (2)
N1—Cd1—N4^i	89.8 (2)	C4—Cd3—N3^{ii}	106.9 (2)
C2—Cd2—C3	108.3 (3)	N2—Cd3—N3^{ii}	107.5 (3)
C2—Cd2—C1	109.3 (2)		

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

Data collection: *XSCANS* (Siemens, 1996*a*). Cell refinement: *XSCANS*. Data reduction: *SHELXTL* (Siemens, 1996*b*). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: DA1061). Services for accessing these data are described at the back of the journal.

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Aqua(1,10-phenanthroline)(L-prolinato)-copper(II) nitrate monohydrate

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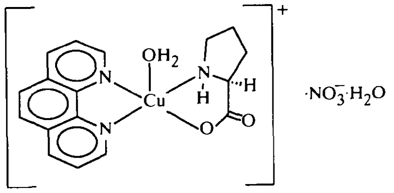
Abstract

The reaction of copper(II) nitrate hydrate with L-proline in the presence of one equivalent of 1,10-phenanthroline produces the title ternary complex, $[Cu(C_5H_8NO_2)(C_{12}H_8N_2)(H_2O)]NO_3{\cdot}H_2O$. The enantiomorphous molecules contain two square-pyramidal complex cations as a loosely associated dimer. The bidentate proline ligands differ in conformation in the cations. In one cation, L-proline α-CH and NH groups lie on the same side as coordinated water and the Cu—OH_2 distance [2.382 (3) Å] is longer than in the other cation [2.234 (4) Å], in which the α-CH and NH groups lie below the pyramid base away from coordinated water. Additionally, copper is coordinated weakly by carboxyl oxygen from a neighboring inequivalent complex *trans* to water, with the longer C═O· · ·Cu distance [3.390 (4) Å] opposite the shorter Cu—OH_2 distance, and the shorter C═O· · ·Cu distance [3.102 (4) Å] opposite the longer Cu—OH_2 distance. Uncoordinated nitrates are hydrogen bonded to both coordinated and uncoordinated waters.

Comment

The role of ternary copper(II) complexes in biological systems is well documented (Baran, 1995; Sabat, 1996). Of particular interest are systems in which both purine and pyrimidine ligands and amino acids coordinate metal ions (Garcia-Raso *et al.*, 1998; Szalda & Kistenmacher, 1977). A variety of monomeric ternary complexes between copper(II), bidentate nitrogenous ligands like 2,2′-bipyridyl and 1,10-phenanthroline, and α-amino acids have been described (Griesser & Sigel, 1970; Fischer & Sigel, 1980; Kwik *et al.*, 1980; Antolini *et al.*, 1986). The typical structure involves an *O*,*N*-bidentate amino acid coordination, square-pyramidal coordination geometry and an apical water (Antolini *et al.*, 1983, 1985). Because L-proline, among the biologically important amino acids, is an unsymmetrical secondary amine, the resulting complexes are diastereomeric. A similar situation can occur in comparable 3-hydroxy-L-proline complexes. This leads to the possibility that on crystallization, diastereomers may form separate phases.

In the present case, the ternary complex of copper(II), 1,10-phenanthroline (*o*-phen) and L-proline, (I), crystallizes in space group $P2_1$, with two complex cations in the asymmetric unit. Copper ions in each cation have distorted square-pyramidal coordination geometry with bidentate phenanthroline, *O*,*N*-bidentate proline and apical water. The vacant coordination site is blocked distantly by the proline carboxyl oxygen of a neighboring complex cation, which serves to link the complexes weakly as dimers. Coordinated water in one complex cation is on the same side of the pyramid as the proline NH group. In this orientation, the NH group (N—H 1.0 Å) forms a hydrogen bond with an uncoordinated water oxygen [N6· · ·O3*W* 2.87 (1) Å, H6*A*· · ·O3*W* 1.89 (3) Å and angle at H6*A* 166 (3)°]. In the other cation, water is on the opposite side from the proline NH group, which makes a much weaker hydrogen bond to a nitrate oxygen [N3· · ·O51^{i} 3.27 (1) Å, H3*B*· · ·O51^{i} 2.44 (3) Å and angle at H3*B* 140 (3)°; symmetry code: (i) $2-x$, $\frac{1}{2}+y$, $-z$]. The configuration at the proline nitrogen and the α-carbon is *S* in each complex cation. The pyrrolidine rings adopt different conformations in the two cations. The proline coordinated to Cu1 has the C_2–C^{γ}-*exo* conformation and that coordinated to Cu2 has the C_s–C^{δ}-*endo* conformation (IUPAC–IUB Commission on Biochemical Nomenclature, 1970; Balasubramanian *et al.*, 1971). In one of the complex cations, considerable thermal motion is noted in the pyrrolidine



(I)