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Double and Triple Interpenetrations of the Three-Dimensional Frameworks [Cd(mea)(daptn){Ni(CN)$_4$}] and [Cd(mea)(dahxn){Ni(CN)$_4$}].H$_2$O (mea = 2-Aminoethanol, daptn = 1,5-Diaminopentane, dahxn = 1,6-Diaminohexane)

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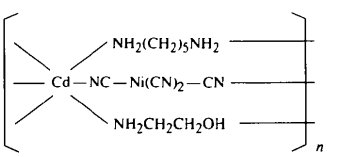
Abstract

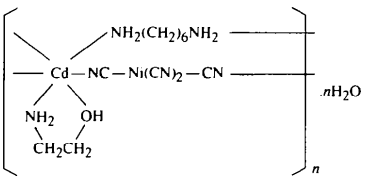
catena-Poly[cadmium-[μ-(2-aminoethanol-*N*:*O*)-μ-[μ-cyano-1κ*N*:2κ*C*-[*trans*-bis(cyano-*C*)nickel(II)]-μ-cyano-1κ*N*:2κ*C*]-μ-(1,5-diaminopentane-*N*:*N*′)]], [Cd{Ni(CN)$_4$}(C$_2$H$_7$NO)(C$_5$H$_{14}$N$_2$)], (1), has a three-dimensional structural unit composed of a distorted Cd-cornered rectangular box edged by *catena*-μ-1,5-diaminopentane, *catena*-μ-2-aminoethanol and *catena*-μ-*trans*-NC—Ni(CN)$_2$—CN- bridges. The void space in one of the frameworks is filled with another framework to give a doubly interpenetrating framework structure. *catena*-Poly[[(2-aminoethanol-*N*,*O*)cadmium]-[μ-[μ-cyano-1κ*N*:2κ*C*-[*trans*-bis(cyano-*C*)nickel(II)]-μ-cyano-1κ*N*:2κ*C*]-μ-(1,6-diaminohexane-*N*:*N*′)] monohydrate], [Cd{Ni(CN)$_4$}(C$_2$H$_7$NO)(C$_6$H$_{16}$N$_2$)].H$_2$O, (2), contains 2-aminoethanol ligands chelated to Cd, which decreases the number of *catena*-μ-bridges about the Cd^{2+} ion to four, two each of *catena*-μ-1,6-diaminohexane and *catena*-μ-*trans*-NC—Ni(CN)$_2$—CN-, giving a distorted adamantoid unit. The void space is occupied by two other frameworks and a water molecule to give a triply interpenetrating framework.

Comment

The three-dimensional (3D) host frameworks of the Hofmann-diam type clathrates [Cd(diam)Ni(CN)$_4$].*x*G [diam = NH$_2$(CH$_2$)$_n$NH$_2$, *n* = 2–9, *x* = 0.5–2, *G* = aromatic guest species; Iwamoto, 1984, 1991] have topologies identical to the two-dimensional (2D) networks of [Cd(CN—Ni$_{1/4}$)$_4$]$_n$ spanned by one-dimensional (1D) [-Cd—diam-]$_n$ linkages. Without enclathration of any aromatic guests, topologically variegated series of the complexes CdNi(CN)$_4$.2diam.*x*H$_2$O (*n* = 2–7 and 9, *x* = 0, 1 or 2; Yuge, Mamada, Asai, Nishikiori & Iwamoto, 1995) have been obtained from aqueous solutions containing CdCl$_2$, K$_2$[Ni(CN)$_4$], NH$_2$(CH$_2$)$_2$OH (mea) and the relevant diamine. Their various structures have been shown to comprise single 1D chains (*n* = 2), triple 1D chains (*n* = 5), double 1D chains (*n* = 6), 2D networks (*n* = 3, 4), 3D frameworks (*n* = 9) and fourfold interpenetrating 3D frameworks (*n* = 7). Among them, [Cd(daptn)$_2$Ni(CN)$_4$].H$_2$O [(1′), daptn = 1,5-diaminopentane] has a 1D chain structure of Cd atoms triply spanned by two *catena*-μ-daptn ligands and a *catena*-μ-*cis*-NC—Ni(CN)$_2$—CN- entity. [Cd(H$_2$O)$_2$(dahxn)$_2$][Ni(CN)$_4$] [(2′), dahxn = 1,6-diaminohexane)] consists of discrete [Ni(CN)$_4$]$^{2-}$ anions and cationic 1D chains with a double span of *catena*-μ-dahxn ligands between the *trans*-[Cd(H$_2$O)$_2$]$^{2+}$ units. Under preparation conditions similar to those for (1′) and (2′), the mea complexes [Cd(mea)(daptn){Ni(CN)$_4$}], (1), and [Cd(mea)(dahxn){Ni(CN)$_4$}].H$_2$O, (2), have been obtained.



(1)



(2)

Compounds (1) and (2) both crystallize in the space group *C*2/*c*. The mea moiety acts as a bridging ligand in (1), but as a chelating ligand in (2). The N and O atoms

of the mea ligand are crystallographically equivalent; this atom is denoted ON. *ORTEP*II (Johnson, 1976) drawings of the asymmetric units of (1) and (2), along with the atomic labelling schemes used, are shown in Figs. 1 and 2.

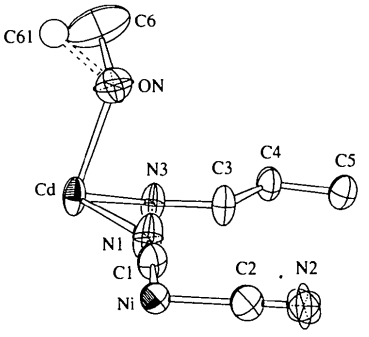


Fig. 1. The asymmetric unit of [Cd(mea)(daptn){Ni(CN)$_4$}], (1), showing the atomic labelling. Displacement ellipsoids are drawn at the 50% probability level; H atoms are omitted for the sake of clarity.

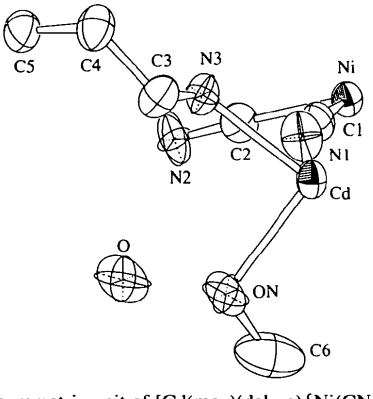


Fig. 2. The asymmetric unit of [Cd(mea)(dahxn){Ni(CN)$_4$}].H$_2$O, (2), showing the atomic labelling. Displacement ellipsoids are drawn at the 50% probability level; H atoms are omitted for the sake of clarity.

The [Ni(CN)$_4$] moieties are located on inversion centres and behave as *catena*-μ-*trans*-NC—Ni(CN)$_2$—CN- ligands linking Cd atoms in both (1) and (2). The 1D chain of [-Cd—NC—Ni(CN)$_2$—CN-]$_n$ runs along the [010] direction with a repeating Cd···Cd distance of 10.197 Å in (1). The mea and the daptn ligands also behave as *catena*-μ-bridging ligands to extend the 1D chains of [-Cd—mea-]$_n$ and [-Cd—daptn-]$_n$. The Cd···Cd distances are 7.367 Å along the [101] and 11.573 Å along the [10$\bar{1}$] directions, respectively. The centres of both the mea and daptn bridges lie on twofold axes. Eight Cd atoms form a distorted rectangular box edged by four Cd—NC—Ni(CN)$_2$—CN—Cd, four Cd—mea—Cd and four Cd—daptn—Cd bridges (Fig. 3). The void space inside one framework is interpenetrated by another without covalent bonds. However, a hydrogen bond is formed between the ON end of the mea ligand in one framework and the unbridged N atom N2 of the [Ni(CN)$_4$] group in the other with a N2···ON distance of 2.951 (10) Å. A large value of U_{eq} for C6 and a peak (*ca* 0.5 e Å^{-3}) found nearby in a Fourier difference map suggested the presence of positional disorder, which was treated by the introduction of a second atom, C61. C61 was treated isotropically and the site-occupancy factors of the two atoms were refined. The skeletal conformation of daptn is all-*trans* but that of mea is *trans-gauche-trans* for Cd—ON—C6—C6^i—ON^i—Cd^i or all-*trans* for Cd—ON—C61—C61^i—ON^i—Cd^i.

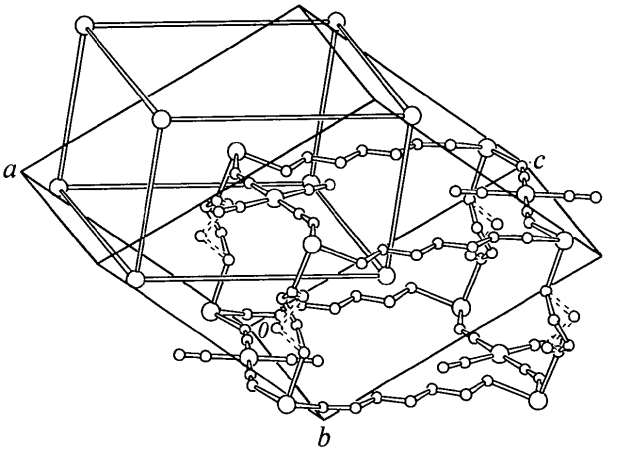


Fig. 3. Doubly interpenetrating 3D framework of [Cd(mea)(daptn)-{Ni(CN)$_4$}], (1). One distorted rectangular box is represented with all non-H atoms, and the other is drawn with a ball-and-stick model; Cd atoms are represented as balls and mea, daptn and Ni(CN)$_4$ units as sticks.

In (2), the 1D chain of [-Cd—NC—Ni(CN)$_2$—CN-]$_n$ runs along the [201] direction with a repeating Cd···Cd distance of 10.584 Å. The Cd atom on the twofold axis is chelated by the mea ligand. It extends the *catena*-μ linkages of the [-Cd—dahxn-]$_n$ from the *cis* positions to give a zigzag 1D chain running along the [10$\bar{1}$] direction with a Cd···Cd distance of 12.141 Å. A distorted adamantoid skeleton is built of ten Cd atoms with six Cd—NC—Ni(CN)$_2$—CN—Cd and six Cd—dahxn—Cd bridges (Fig. 4). The cage accommodates a water molecule and the chelate ring of the mea ligand. Two other cages interpenetrate each cage to give a triply interpenetrating 3D lattice structure. Hydrogen-bond formation is observed between the water molecule and atom N3 of the NH$_2$ group of dahxn, between the water molecule and atom N2 of the unbridged CN group and between the atom ON of mea and N2 [O···N3 3.090 (8), O···N2 3.038 (6), ON···N2 2.911 (8) Å]. The skeletal conformation of dahxn is *trans-gauche-*(*trans*)$_3$-*gauche-trans*.

The doubly and triply interpenetrating 3D lattice structures of [Cd(4,4′-bipyridine)$_2${Ag(CN)$_2$}$_2$] and [Cd(pyrazine){Ag$_2$(CN)$_3$}{Ag(CN)$_2$}] previously

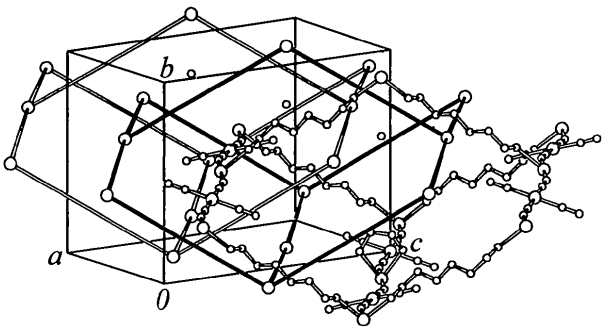


Fig. 4. Triply interpenetrating 3D framework of [Cd(mea)(dahxn)-{Ni(CN)$_4$}].H$_2$O, (2). One distorted adamantoid cage is represented with all non-H atoms, and the others are drawn with a ball-and-stick model; Cd atoms are represented as balls and daptn and Ni(CN)$_4$ units as sticks.

reported by us (Soma, Yuge & Iwamoto, 1994) are built of rigid bridging moieties without any hydrogen bonds. In contrast, the structures of (1) and (2) described here, which contain flexible skeletons of diamine and mea ligands, are supported by hydrogen bonds.

Experimental

The mother solutions were prepared by procedures already described (Yuge, Mamada, Asai, Nishikiori & Iwamoto, 1995). The title compounds could be crystallized by keeping the solutions in a refrigerator at *ca* 278 K for a few months after the crystallization of (1′) or (2′) (see *Comment*), or by preparing solutions containing Cd^{2+}, $[Ni(CN)_4]^{2-}$ and the relevant diamine in the molar ratio of 1:1:x (where $x < 1$). Densities were measured by flotation in mesitylene/bromoform.

Compound (1)

Crystal data

[Cd{Ni(CN)$_4$}(C$_2$H$_7$NO)-(C$_5$H$_{14}$N$_2$)]
M_r = 438.44
Monoclinic
$C2/c$
a = 13.479 (5) Å
b = 10.197 (3) Å
c = 13.954 (5) Å
β = 115.06 (2)°
V = 1737.4 (9) Å^3
Z = 4
D_x = 1.68 Mg m^{-3}
D_m = 1.67 (1) Mg m^{-3}

Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 25 reflections
θ = 17.02–17.37°
μ = 2.318 mm^{-1}
T = 293 K
Prism
0.30 × 0.20 × 0.18 mm
Yellow

Data collection

Rigaku AFC-5*S* diffractometer
$\omega/2\theta$ scans
Absorption correction: none
3087 measured reflections
2050 independent reflections
1474 observed reflections [$F > 4\sigma(F)$]
R_{int} = 0.010
θ_{max} = 30.00°
$h = 0 \rightarrow 18$
$k = 0 \rightarrow 14$
$l = -19 \rightarrow 17$
3 standard reflections monitored every 150 reflections
intensity decay: 1.0%

Refinement

Refinement on F
R = 0.0379
wR = 0.0529
S = 1.359
1474 reflections
132 parameters
All H-atom parameters refined except for H8, H9, H10, H11, H81, H91, H101 and H111, for which no parameters were refined
$w = 1/[\sigma^2(F_o) + 0.0008F_o^2]$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.85 e Å^{-3}
$\Delta\rho_{min}$ = −0.89 e Å^{-3}
Extinction correction: none
Atomic scattering factors from *SHELX76* (Sheldrick, 1976) (C, H, N, ON) and *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B) (Cd, Ni)

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

U_{iso} for C61; $U_{eq} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$ for all other atoms.

	x	y	z	U_{eq}/U_{iso}
Cd	1/4	1/4	0	0.0379 (2)
Ni	1/4	3/4	0	0.0366 (3)
ON	0.3847 (5)	0.2350 (5)	0.1776 (4)	0.076 (2)
N1	0.2192 (4)	0.4662 (4)	0.0393 (4)	0.057 (2)
N2	0.1401 (5)	0.8392 (5)	0.1365 (4)	0.073 (3)
N3	0.1239 (5)	0.1609 (5)	0.0529 (5)	0.044 (2)
C1	0.2292 (4)	0.5749 (5)	0.0254 (4)	0.041 (2)
C2	0.1824 (5)	0.8054 (5)	0.0852 (4)	0.047 (2)
C3	0.0902 (5)	0.2384 (5)	0.1243 (4)	0.042 (2)
C4	0.0428 (5)	0.1557 (5)	0.1845 (4)	0.038 (2)
C5	0	0.2385 (7)	1/4	0.039 (2)
C6†	0.4401 (9)	0.1164 (8)	0.2280 (15)	0.100 (7)
C61‡	0.472 (2)	0.124 (3)	0.180 (2)	0.034 (9)

† Site occupancy 0.80 (3). ‡ Site occupancy 0.20 (3).

Table 2. *Selected geometric parameters (Å, °) for (1)*

Cd—N1	2.351 (4)	C3—C4	1.509 (7)
Cd—N3	2.308 (4)	C4—C5	1.527 (6)
Cd—ON	2.377 (5)	ON—C6	1.439 (9)
Ni—C1	1.865 (5)	ON—C61	1.63 (3)
Ni—C2	1.867 (6)	C6—C6^i	1.47 (2)
C1—N1	1.142 (6)	C61—C61^i	1.78 (5)
C2—N2	1.140 (7)	N2···ON^{iii}	2.951 (10)
N3—C3	1.485 (6)		
N1—Cd—N3	93.9 (2)	Ni—C1—N1	177.3 (5)
N1—Cd—ON	87.1 (2)	Ni—C2—N2	179.3 (6)
N3—Cd—ON	89.0 (2)	N3—C3—C4	113.4 (4)
C1—Ni—C2	90.9 (2)	C3—C4—C5	112.4 (4)
Cd—N1—C1	145.6 (4)	C4—C5—C4^{ii}	112.8 (6)
Cd—N3—C3	118.8 (3)	ON—C6—C6^i	117.1 (9)
Cd—ON—C6	125.0 (7)	ON—C61—C61^i	89 (2)
Cd—ON—C61	107.0 (9)		

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

Compound (2)

Crystal data

[Cd{Ni(CN)$_4$}(C$_2$H$_7$NO)-(C$_6$H$_{16}$N$_2$)].H$_2$O
M_r = 470.48
Monoclinic
$C2/c$

Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 25 reflections
θ = 16.04–17.21°

a = 9.247 (2) Å
b = 13.434 (6) Å
c = 16.367 (3) Å
β = 105.60 (2)°
V = 1958 (1) Å^3
Z = 4
D_x = 1.60 Mg m^{-3}
D_m = 1.59 (1) Mg m^{-3}

μ = 2.066 mm^{-1}
T = 293 K
Plate
0.20 × 0.20 × 0.15 mm
Yellow

Data collection

Rigaku AFC-5*S* diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (North, Phillips & Mathews, 1968)
T_{min} = 0.87, T_{max} = 1.00
3217 measured reflections
2565 independent reflections
1997 observed reflections [$F > 4\sigma(F)$]

R_{int} = 0.018
θ_{max} = 30.00°
$h = 0 \rightarrow 12$
$k = 0 \rightarrow 18$
$l = -23 \rightarrow 22$
3 standard reflections monitored every 150 reflections
intensity decay: 1.3%

Refinement

Refinement on F
R = 0.0431
wR = 0.0443
S = 1.172
1997 reflections
157 parameters
All H-atom parameters refined except for H9 and H10, for which only coordinates were refined
$w = 1/[\sigma^2(F_o) + 0.0003F_o^2]$
$(\Delta/\sigma)_{max}$ = 0.001

$\Delta\rho_{max}$ = 0.81 e Å^{-3}
$\Delta\rho_{min}$ = −0.79 e Å^{-3}
Extinction correction: none
Atomic scattering factors from *SHELX*76 (Sheldrick, 1976) (C, H, N, O, ON) and *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B) (Cd, Ni)

Table 3. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for (2)*

$U_{eq} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq}
Cd	0	0.51843 (4)	1/4	0.0310 (2)
Ni	1/2	1/2	1/2	0.0287 (3)
O	1/2	0.3133 (6)	1/4	0.076 (4)
ON	0.0521 (5)	0.3778 (4)	0.1765 (4)	0.058 (2)
N1	0.2439 (5)	0.5193 (4)	0.3420 (3)	0.051 (2)
N2	0.7006 (5)	0.4357 (4)	0.3921 (3)	0.058 (2)
N3	0.0895 (6)	0.6249 (4)	0.1669 (3)	0.043 (2)
C1	0.3423 (5)	0.5130 (3)	0.4019 (3)	0.035 (1)
C2	0.6271 (5)	0.4615 (3)	0.4340 (3)	0.038 (2)
C3	0.0011 (7)	0.6501 (4)	0.0802 (4)	0.046 (2)
C4	0.0685 (7)	0.7324 (4)	0.0387 (4)	0.048 (2)
C5	0.2166 (8)	0.7077 (4)	0.0202 (4)	0.047 (2)
C6	0.0635 (9)	0.2905 (5)	0.2302 (7)	0.087 (4)

Table 4. *Selected geometric parameters (Å, °) for (2)*

Cd—N1	2.352 (4)	C3—C4	1.517 (7)
Cd—N3	2.277 (5)	C4—C5	1.516 (8)
Cd—ON	2.359 (5)	C5—C5^i	1.526 (9)
Ni—C1	1.865 (5)	ON—C6	1.452 (10)
Ni—C2	1.870 (5)	C6—C6^{ii}	1.486 (15)
C1—N1	1.146 (6)	O···N2^{iii}	3.038 (6)
C2—N2	1.142 (6)	O···N3^{iv}	3.090 (8)
N3—C3	1.474 (7)	N2···ON^{iii}	2.911 (8)
N1—Cd—N3	86.5 (2)	Ni—C1—N1	178.6 (4)
N1—Cd—ON	92.2 (2)	Ni—C2—N2	177.5 (4)
N3—Cd—ON	92.4 (2)	N3—C3—C4	114.3 (5)
C1—Ni—C2	89.8 (2)	C3—C4—C5	115.6 (5)
Cd—N1—C1	161.9 (4)	C4—C5—C5^i	114.6 (5)
Cd—N3—C3	121.5 (4)	ON—C6—C6^{ii}	109.1 (6)
Cd—ON—C6	109.3 (5)		

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

All calculations were carried out on a HITAC M-680H computer at the Institute for Molecular Science, Okazaki.

For both compounds, data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988); cell refinement: *MSC/AFC Diffractometer Control Software*; program(s) used to solve structures: *SHELX*76 (Sheldrick, 1976); program(s) used to refine structures: *SHELX*76; molecular graphics: *ORTEP*II (Johnson, 1976).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1281). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1996). C**52**, 578–581

$[\{(C_5Me_4H)Fe(C_5Me_4)CH_2C_5H_4\}_2Fe]^{2+}.[C_2(CN)_4]^-.[C_3(CN)_5]^-$

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Abstract

The structure of the organometallic charge-transfer salt 1,1′-bis[(octamethylferroceniumyl)methyl]ferrocene tet-