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**Bis(1,2-di-4-pyridylethane-*N:N'*)-
cadmium(II) tetracyanonickelate(II)
m-Xylene Solvate**

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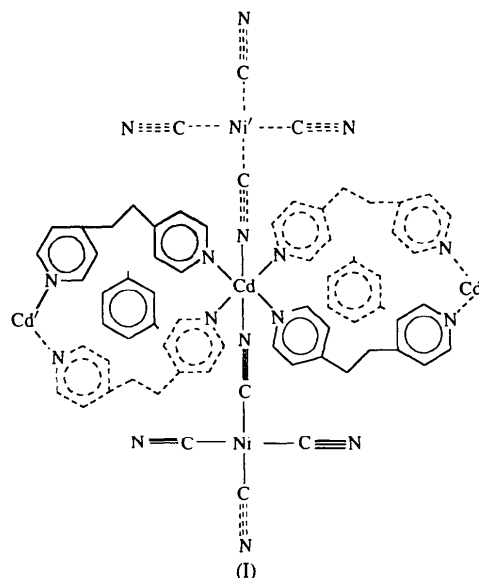
Abstract

The title compound, bis(1,2-di-4-pyridylethane-*N:N'*)-cadmium(II) tetracyanonickelate(II) di-*m*-xylene solvate, $[\text{Cd}(\text{C}_{12}\text{H}_{12}\text{N}_2)_2][\text{Ni}(\text{CN})_4] \cdot 2\text{C}_8\text{H}_{10}$, is represented by the general Hofmann-type clathrate formula $\text{Cd}(\text{Ligand})_2\text{Ni}(\text{CN})_4 \cdot 2\text{Guest}$, where *Ligand* is 1,2-di-4-pyridylethane ($\text{C}_{12}\text{H}_{12}\text{N}_2$) and *Guest* is *m*-xylene (C_8H_{10}). It was seen that the structure of the title compound is of a new type and quite different from that of the Hofmann-type clathrates.

Comment

The title structure, (I), differs from that of the Hofmann-type clathrate. In the well known Hofmann-type clathrate, *Ligand* is either bidentate (having two donor atoms) or a monodentate pair (having one donor atom each) and results in a three-dimensional metal complex host structure accommodating the aromatic *Guest* molecule. Cd atoms are in an octahedral environment formed by coordination to four N atoms of the cyanide groups and two N atoms of the ligand molecules. However, in the new type of host structure presented here, each Cd atom is coordinated octahedrally

by four N atoms of the ligand molecules and two N atoms of the cyanide groups. The other two cyanide groups of the $\text{Ni}(\text{CN})_4$ moiety have free nitrogen ends.



Of the six N atoms coordinating the Cd atom, two are from the cyanide groups, with a Cd—N3 distance of 2.320 (4) Å, and four are from pyridyl rings, with distances Cd—N2 2.422 (5) and Cd—N1 2.345 (5) Å (Fig. 1). The Ni atom is coordinated to the four C atoms of the cyanide groups in a square plane, with distances Ni—C13 1.852 (5) and Ni—C14 1.874 (7) Å. In the cyanide groups, the C—N distances are 1.139 (7) (C13—N3) and 1.150 (8) Å (C14—N4), with angles Cd—N3—C13 164.2 (5), Ni—C14—N4 179.1 (5) and Ni—C13—N3 178.2 (6)°. In the pyridyl rings, the distances N1—

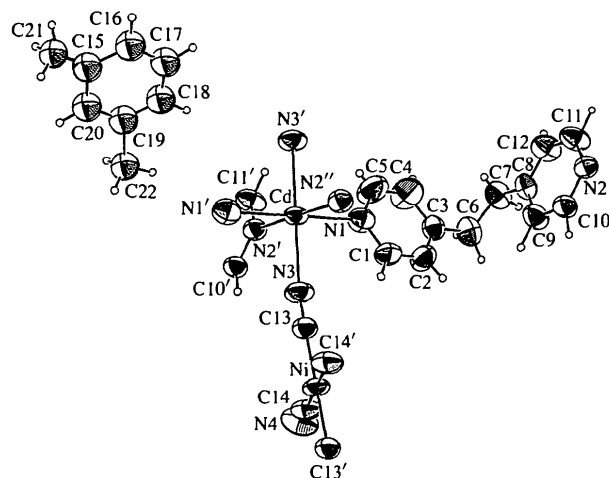


Fig. 1. A perspective view of the molecular structure of the title complex with the atom-numbering scheme. The displacement ellipsoids are plotted at the 50% probability level and the displacement parameters of the *Guest* atoms were fixed at 5 Å² for clarity.

C1 1.329 (7), N1—C5 1.343 (7), C5—C5 1.341 (9) and C11—C12 1.38 (1) Å are observed. The dipyriddyethane molecule is not planar, the dihedral angle between the pyridyl rings being 86.1 (2)°. The bond distances and angles of the host atoms are similar to those observed for the Hofmann-type clathrates (Hasegawa & Iwamoto, 1988; Kuroda & Sasaki, 1974).

In the *m*-xylene solvate molecule, the displacement parameters of the C21 and C22 atoms were very large. The distance between the C21 and C15 atoms is very short for a single C_{sp²}—C_{sp³} bond length and so was restrained to be 1.34 (2) Å. As a result, the bond lengths, angles and displacement parameters of the *Guest* molecule are not reasonable, probably as a result of disorder, as is generally seen for *Guest* molecules. The disorder is caused by the repulsive force of the walls formed by the host atoms (Hashimoto, Kytazawa, Hasegawa & Iwamoto, 1991; Yuge & Iwamoto, 1992; Hasegawa & Iwamoto, 1988; Nishikiori & Iwamoto, 1983).

Absorption correction:
empirical *via* ψ scan
(North, Phillips &
Mathews, 1968)
 $T_{\min} = 0.8554$, $T_{\max} =$
0.9981
5291 measured reflections
5142 independent reflections

$\theta_{\max} = 30.37^\circ$
 $h = -14 \rightarrow 13$
 $k = 0 \rightarrow 13$
 $l = 0 \rightarrow 25$
3 standard reflections
frequency: 120 min
intensity decay: 2.3%

Refinement

Refinement on F^2
 $R(F) = 0.0542$
 $wR(F^2) = 0.1189$
 $S = 1.495$
3782 reflections
298 parameters
All H-atom parameters
refined
 $w = 1/[\sigma^2(F_o^2) + (0.0258P)^2$
 $+ 4.9089P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.770 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.611 \text{ e } \text{Å}^{-3}$
Extinction correction: none
Atomic scattering factors
from *International Tables*
for *Crystallography* (1992),
Vol. C, Tables 4.2.6.8 and
6.1.1.4)

Experimental

Citric acid, cadmium chloride dihydrate, sodium hydroxide and all other chemicals used were employed without further purification. Potassium tetracyanonickelate hydrate, K₂Ni(CN)₄.H₂O, was prepared by conventional methods using potassium cyanide and nickel(II) chloride hexahydrate. CdCl₂.2H₂O (0.5 mmol) and K₂Ni(CN)₄.H₂O (0.5 mmol) were dissolved in 50 ml of H₂O. 1,2-Di-4-pyridylethane (C₁₂H₁₂N₂) was dissolved in 25 ml of acetone. The two solutions were mixed to form a creamy suspension. Citric acid and NaOH were then added and the mixture stirred vigorously. After filtration, a golden yellow solution was obtained. About 40 ml of the filtrate was transferred to a vial and neat *m*-xylene (20 ml) was placed over the solution. The vial was left at ambient temperature for approximately one month. Single crystals were formed at both the interface and bottom of the solution. The density D_m was measured by flotation in CCl₄/C₇H₈ solution.

Crystal data

[Cd(C₁₂H₁₂N₂)₂][Ni(CN)₄].-
2C₈H₁₀
 $M_r = 855.98$
Monoclinic
 $P2_1/c$
 $a = 10.510 (1) \text{ Å}$
 $b = 10.438 (1) \text{ Å}$
 $c = 19.012 (2) \text{ Å}$
 $\beta = 103.552 (7)^\circ$
 $V = 2027.6 (3) \text{ Å}^3$
 $Z = 2$
 $D_x = 1.402 \text{ Mg m}^{-3}$
 $D_m = 1.420 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation
 $\lambda = 0.71073 \text{ Å}$
Cell parameters from 24
reflections
 $\theta = 7-21^\circ$
 $\mu = 1.030 \text{ mm}^{-1}$
 $T = 293 (2) \text{ K}$
Prismatic
 $0.60 \times 0.32 \times 0.12 \text{ mm}$
Golden yellow

Data collection

Enraf-Nonius CAD-4
diffractometer
 $\omega/2\theta$ scans
2563 observed reflections
 $[I > 2\sigma(I)]$
 $R_{\text{int}} = 0.0182$

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

	x	y	z	U_{eq}
Cd	0	0	0	0.0395 (2)
Ni	-1/2	0	0	0.0404 (2)
N1	0.0735 (4)	-0.1606 (5)	0.0862 (3)	0.042 (1)
N2	0.0478 (5)	0.1639 (5)	0.0926 (3)	0.048 (1)
N3	-0.2108 (4)	-0.0222 (5)	0.0163 (3)	0.050 (1)
N4	-0.4684 (6)	-0.1150 (7)	0.1491 (3)	0.077 (2)
C1	-0.0091 (6)	-0.2405 (7)	0.1070 (4)	0.049 (2)
C2	0.0285 (6)	-0.3340 (6)	0.1589 (4)	0.052 (2)
C3	0.1585 (6)	-0.3500 (5)	0.1925 (3)	0.044 (1)
C4	0.2433 (6)	-0.2677 (8)	0.1697 (4)	0.058 (2)
C5	0.1999 (6)	-0.1774 (7)	0.1197 (4)	0.058 (2)
C6	0.2095 (8)	-0.4431 (8)	0.2521 (4)	0.057 (2)
C7	0.1207 (8)	0.4470 (7)	0.2616 (4)	0.057 (2)
C8	0.0937 (6)	0.3508 (6)	0.2016 (3)	0.050 (2)
C9	-0.0295 (7)	0.3138 (7)	0.1655 (4)	0.060 (2)
C10	-0.0484 (6)	0.2234 (7)	0.1131 (4)	0.055 (2)
C11	0.1674 (8)	0.200 (1)	0.1248 (5)	0.085 (3)
C12	0.1930 (8)	0.2899 (9)	0.1798 (5)	0.082 (3)
C13	-0.3210 (5)	-0.0157 (6)	0.0105 (3)	0.040 (3)
C14	-0.4814 (5)	-0.0716 (7)	0.0922 (4)	0.051 (2)
C15	0.386 (1)	-0.494 (2)	-0.1615 (6)	0.118 (3)
C16	0.431 (1)	-0.371 (2)	-0.1642 (9)	0.143 (5)
C17	0.425 (2)	-0.300 (1)	-0.108 (1)	0.157 (6)
C18	0.379 (1)	-0.344 (1)	-0.051 (1)	0.155 (6)
C19	0.335 (1)	-0.466 (1)	-0.0501 (7)	0.114 (3)
C20	0.3378 (9)	-0.544 (1)	-0.1044 (6)	0.109 (3)
C21	0.386 (2)	-0.570 (2)	-0.218 (1)	0.31 (3)
C22	0.716 (1)	0.512 (2)	-0.0142 (7)	0.195 (9)

Table 2. Selected geometric parameters (Å, °)

Cd—N1	2.345 (5)	C5—C4	1.341 (9)
Cd—N2	2.422 (5)	C6—C7	1.52 (1)
Cd—N3	2.320 (4)	C7—C8	1.496 (9)
Ni—C13	1.852 (5)	C8—C9	1.372 (9)
Ni—C14	1.874 (7)	C8—C12	1.37 (1)
N1—C1	1.329 (7)	C9—C10	1.352 (9)
N1—C5	1.343 (7)	C12—C11	1.38 (1)
N2—C10	1.321 (8)	C15—C16	1.38 (2)
N2—C11	1.318 (9)	C15—C20	1.40 (1)
N3—C13	1.139 (7)	C15—C21	1.34 (2)
N4—C14	1.150 (8)	C17—C16	1.32 (2)
C1—C2	1.378 (9)	C18—C17	1.35 (2)

C2—C3	1.375 (8)	C19—C18	1.36 (2)
C3—C6	1.495 (9)	C19—C22 ⁱⁱ	1.53 (2)
C4—C3	1.378 (9)	C20—C19	1.32 (1)
N1—Cd—N2	91.1 (2)	C9—C8—C7	124.0 (7)
N1—C1—C2	124.1 (6)	C10—N2—Cd	120.3 (4)
N2—C10—C9	123.7 (6)	C10—C9—C8	121.6 (7)
N2—C11—C12	122.7 (8)	C11—N2—Cd	123.6 (5)
N3—C13—Ni	178.2 (6)	C11—N2—C10	116.2 (7)
N3—Cd—N1	90.2 (2)	C12—C8—C7	121.4 (7)
N3—Cd—N2	90.9 (2)	C12—C8—C9	114.5 (7)
N4—C14—Ni	179.1 (5)	C13—Ni—C14	89.0 (2)
C1—N1—Cd	121.7 (4)	C13—N3—Cd	164.2 (5)
C1—N1—C5	114.7 (6)	C16—C15—C20	124.5 (7)
C2—C3—C4	115.1 (6)	C16—C17—C18	123.4 (9)
C2—C3—C6	124.9 (6)	C17—C16—C15	114.3 (8)
C3—C2—C1	120.3 (6)	C17—C18—C19	121.1 (9)
C3—C6—C7 ⁱ	117.4 (6)	C18—C19—C22 ⁱⁱ	119.7 (8)
C4—C3—C6	120.0 (6)	C19—C20—C15	116.8 (7)
C4—C5—N1	124.3 (7)	C20—C19—C18	119.8 (8)
C5—N1—Cd	123.5 (4)	C20—C19—C22 ⁱⁱ	120.5 (8)
C5—C4—C3	121.5 (6)	C21—C15—C16	117.4 (9)
C8—C7—C6 ⁱⁱⁱ	115.4 (6)	C21—C15—C20	118.0 (9)
C8—C12—C11	121.2 (7)		
N1—C1—C2—C3	-0.5 (9)	C1—C2—C3—C6	176.5 (7)
N1—C5—C4—C3	-1.8 (9)	C4—C3—C6—C7 ⁱ	-164.3 (7)
Cd—N1—C1—C2	-178.0 (5)	C5—C4—C3—C6	-175.6 (7)
Cd—N1—C5—C4	179.1 (6)	C6 ⁱⁱⁱ —C7—C8—C9	-126.8 (8)
Cd—N2—C11—C12	-177.1 (8)	C7—C8—C9—C10	-177.9 (7)
Cd—N2—C10—C9	178.5 (6)	C7—C8—C12—C11	179.3 (9)

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

Data collection and cell refinement were performed using CAD-4-PC software (Enraf-Nonius, 1993). *MolEN* (Fair, 1990) was used for data reduction. Absorption coefficients were taken from *International Tables for Crystallography* (1992, Vol. C, Table 4.2.4.2). The structure was solved by Patterson heavy-atom methods using *SHELXS86* (Sheldrick, 1990), which revealed the positions of the Cd and Ni atoms. Refinement was carried out by full-matrix least-squares methods using *MolEN* (Fair, 1990). H atoms, except those of the *Guest* molecule, were located from difference Fourier maps and refined isotropically. The H atoms of the *Guest* molecule were placed geometrically and refined by the riding method. The C15—C21 bond length was restrained to have a reasonable value. Positional disorder of the *Guest* atoms was not found. Molecular graphics were prepared using *ORTEPII* (Johnson, 1976) and the material for publication was prepared with *SHELXL93* (Sheldrick, 1993).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and torsion angles have been deposited with the IUCr (Reference: KA1143). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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trans-Tetraaquabis(*N,N',N''*-tricyanomelamine)cobalt(II) Hexahydrate

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Abstract

The crystal structure of *trans*-tetraaquabis[1,3,5-triazine-2,4,6-tricarbodiimidato(1-)-*N*]cobalt(II) hexahydrate, $[\text{Co}(\text{C}_6\text{H}_2\text{N}_9)_2(\text{H}_2\text{O})_4] \cdot 6\text{H}_2\text{O}$, shows the cobalt(II) metal ion to be octahedrally coordinated by two *trans* doubly-protonated tricyanomelamine ligands and four water molecules. Hydrogen bonding between ligands yields a two-dimensional sheet structure.

Comment

Recent work has demonstrated that new extended networks may be constructed by linking metal centres through rod-like or slab-like ligands (Robson *et al.*, 1992). The trianion of tricyanomelamine, tcmel^{3-} , is a robust unit which is expected to offer a rich coordination chemistry given the number and variety of potential donor sites. Accordingly, the ligand was considered an ideal candidate for the construction of metal–ligand polymers. As part of a preliminary investigation of the ligand and its coordination chemistry, a cobalt(II) complex of the doubly-protonated ligand, H_2tcmel^- , was isolated as the 1:2 complex $[\text{Co}^{\text{II}}(\text{H}_2\text{tcmel})_2(\text{H}_2\text{O})_4] \cdot 6\text{H}_2\text{O}$, (I).