The two-dimensional coordination polymer poly[[bis(3-methylpyridine)-cadmium(II)]-tetra-μ-cyano-nickel(II)]

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The title complex, $[CdNi(CN)_4(C_6H_7N)_2]_n$, adopts a slightly distorted octahedral geometry around the Cd centre. Four cyanide N atoms occupy the equatorial coordination sites around the Cd centre. The structure consists of corrugated and cyanide-bridged polymeric networks made up of tetracyano-nickelate ions coordinated to cadmium, with the Ni ion coordinated by four cyanide ligands in a square-planar arrangement. The Cd and Ni atoms occupy special positions of $2/m$ site symmetry. The 3-methylpyridine group, except for two methyl H atoms, lies on a crystallographic mirror plane. The 3-methylpyridine molecules, bound to cadmium in *trans* positions, are located on both sides of the network. The bonding in the networks occurs because of a departure of the Ni—C—N—Cd sequence of atoms from linearity at the C and N atoms.

Comment

Hofmann-type complexes with the formula $ML_2Ni(CN)_4$, where M is a divalent transition metal and L is an N-donor ligand molecule, have a structure consisting of polymeric two-dimensional networks formed by $[Ni(CN)_4]^{2-}$ anions bridged by $[ML_2]^{2+}$ cations. Metal coordination polymers with one- and two-dimensional structures are of current interest due to their possible relevance to materials science (Yaghi *et al.*, 1996). There is still much to be explored in the crystal engineering of Hofmann-type and analogous structures that are built up by CN linkages between square-planar or tetrahedral tetracyanometallate(II) complexes on the one hand, and octahedral metal(II) complexes ligated with complementary ligands on the other (Iwamoto *et al.*, 1984). Against this background, we present here the crystal structure of the title compound, (I).

The molecule of (I) adopts a slightly distorted octahedral geometry around the Cd centre (Fig. 1). The equatorial and axial coordination sites are occupied by four N atoms of the bridging cyano groups and two N atoms of the two chelating 3-methylpyridine ligands, respectively. The structure consists of corrugated and cyanide-bridged polymeric networks made up of tetracyanonickelate ions coordinated to cadmium, where the Ni ion is coordinated by four cyanide ligands in a square-planar arrangement. In this arrangement, two of the cyanide groups are terminal, while the other two, coordinated *trans* about the Ni atom, constitute the bridges. The bonding in the networks occurs because of a departure of the Ni—C—N—Cd sequence of atoms from linearity at the C and N positions. The Ni1—C7—N2 and C7—N2—Cd bond angles are 177.2 (2) and 163.5 (2)°, respectively.

(I)
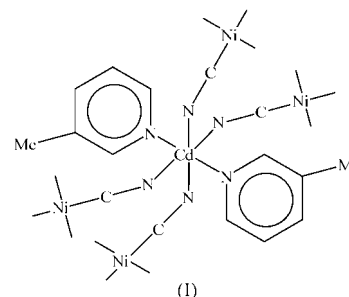
The Cd and Ni atoms of (I) lie at $(0, 0, 0)$ and $(0, \frac{1}{2}, -\frac{1}{2})$, respectively, on sites with $2/m$ symmetry. The non-H atoms of the 3-methylpyridine moiety lie on a mirror plane, chosen as that at $y = 0$. The [–Cd–{*trans*-NC–Ni(CN)$_2$–CN–}] bridges run along the face diagonals of the bc plane, sharing the Cd atoms to form layers (Figs. 2 and 3). The distance between any two adjacent layers is $a/2$ (approximately 8.255 Å). Similar corrugated polymeric layers are also reported in some related compounds (Erdönmez *et al.*, 1998). The C—N and Ni—C bond distances of the square-planar Ni coordination environment are comparable with those in related Ni(CN)$_4$ complexes (Karadağ *et al.*, 2004; Yuge & Iwamoto, 1995; Yuge *et al.*, 1996; Woodward *et al.*, 2001).

The 3-methylpyridine ligands, bound to the Cd atom in *trans* positions, are located on both sides of the network and the whole 3-methylpyridine moiety, except for two H atoms of the methyl group, lies on a crystallographic mirror plane. By
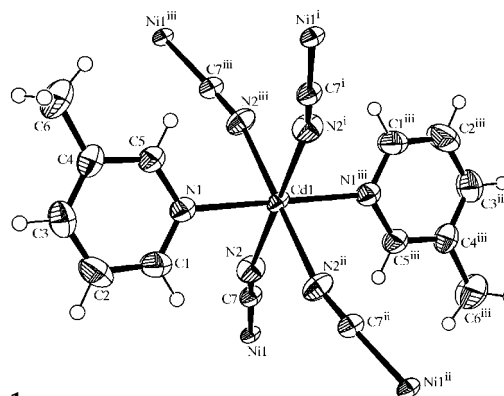

Figure 1
A drawing of the molecule of (I), showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary size. [Symmetry codes: (i) $-x, -y, -z$; (ii) $x, -y, z$; (iii) $-x, y, -z$.]
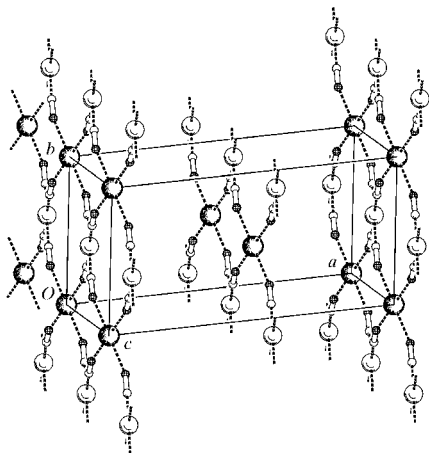
Figure 2
Part of the crystal structure of (I), showing the formation of layers parallel to (100). For the sake of clarity, the 3-methylpyridine rings and their H atoms have been omitted.
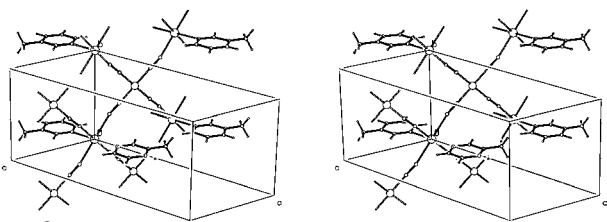

Figure 3
Stereoview of the molecular packing in (I).

translation, the 3-methylpyridine aromatic rings stack in the b direction. The stacking is an offset face-to-face π–π interaction. The distance between ring centroids is 3.7789 (7) Å and the interplanar spacing is $b/2$.

Experimental

Crystals of (I) were obtained by adding 3-methylpyridine (slightly more than 2 mmol) to an ammoniated solution containing $K_2Ni(CN)_4$ (1 mmol) and $CdCl_2$ (1 mmol) at pH 9.5. The synthesis and characterization by IR spectroscopy have been described previously in Akyüz *et al.* (1994).

Crystal data

$[CdNi(CN)_4(C_6H_7N)_2]$	$D_x = 1.730$ Mg m^{-3}
$M_r = 461.44$	Mo $K\alpha$ radiation
Monoclinic, $C2/m$	Cell parameters from 25
$a = 16.5198$ (16) Å	reflections
$b = 7.3512$ (7) Å	$\theta = 10.6$–$18.7°$
$c = 7.6309$ (6) Å	$\mu = 2.27$ mm^{-1}
$\beta = 107.060$ (10)$°$	$T = 293$ (2) K
$V = 885.92$ (14) Å^3	Prismatic, orange
$Z = 2$	$0.42 \times 0.36 \times 0.24$ mm

Data collection

Enraf-Nonius CAD-4	$R_{int} = 0.025$
diffractometer	$\theta_{max} = 26.3°$
$\omega/2\theta$ scans	$h = -20 \rightarrow 20$
Absorption correction: ψ scan	$k = 0 \rightarrow 9$
(North *et al.*, 1968)	$l = -9 \rightarrow 9$
$T_{min} = 0.427$, $T_{max} = 0.580$	3 standard reflections
1793 measured reflections	frequency: 120 min
972 independent reflections	intensity decay: 2.5%
937 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0623P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.028$	$+ 0.7317P]$
$wR(F^2) = 0.084$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.07$	$(\Delta/\sigma)_{max} < 0.001$
972 reflections	$\Delta\rho_{max} = 1.40$ e Å^{-3}
73 parameters	$\Delta\rho_{min} = -0.60$ e Å^{-3}
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

Cd1—N1	2.322 (3)	N2—C7	1.146 (3)
Ni1—C7	1.863 (2)		
N1—Cd1—N2	91.87 (8)	C1—N1—Cd1	120.7 (3)
N2—Cd1—N2^i	86.18 (12)	C5—N1—Cd1	121.4 (2)

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

H atoms were treated as riding atoms, with aromatic and methyl C—H distances in the range 0.93–0.96 Å, and with $U_{iso}(H) = 1.5U_{eq}(C)$. The methyl H atoms on C6 were not well defined in difference map plots and no great confidence should be placed in the reported coordinates of these atoms.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1993); cell refinement: *CAD-4 EXPRESS*; data reduction: *MolEN* (Fair, 1990); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

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