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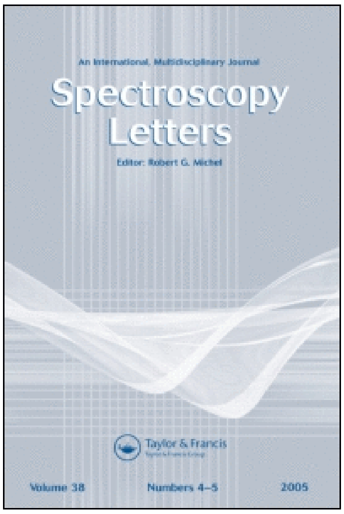

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Structure of *bis*(4-Methyl Pyridine) Cadmium Tetracyanonickelate

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SPECTROSCOPY LETTERS, 31(6), 1325-1331 (1998)

STRUCTURE OF BIS(4-METHYL PYRIDINE) CADMIUM TETRACYANONICKELATE

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ABSTRACT

The structure, $C_{16}H_{14}CdN_6Ni$, consist of corrugated polymeric networks made up of tetracyanonickelate ions coordinated to Cd. The 4-methyl pyridine molecules bound to Cd 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 positions. The crystal structure of the title compound was determined as monoclinic by single crystal X-Ray diffraction technique. The crystal parameters of this compound are as follows: monoclinic C2/m, a=18.156(2) Å, b=7.581(2) Å, c= 6.983(2) Å, β = 110.09(2)°, V = 902.6(5) $Å^3$, Z=2, Dx = 1.698 g/cm^3, F(000) = 456, λ (MoKα) = 0.71070 Å, μ = 2.121 mm^{-1}. The structure was solved by SHELXS-86 and refined by SHELXL-93. R = 0.02 for 1074 observed reflections with $I > 2\sigma(I)$.

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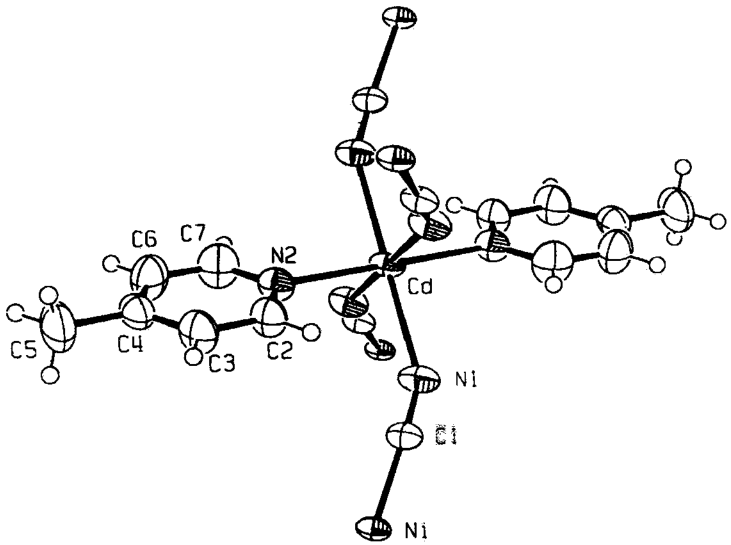

Figure-1. ORTEPII view of the molecule and atomic numbering. The displacement ellipsoids are at the %50 probability level. H atoms are shown as spheres of arbitrary size.

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COMMENT

Hofmann-type complexes with the formula $ML_2Ni(CN)_4$, where M is a divalent transition metal and L is a N-donor ligand molecule, have a structure consisting of polymeric two-dimensional networks formed $Ni(CN)_4^{2-}$ anions bridged by ML_2^{2+} cations (Akyüz et al., 1992). The Nickel atoms are surrounded by four carbon atoms of the cyanide group in a square planar environment. In this present structure Cd atoms are in an octahedral environment formed by coordination to four nitrogen atoms of the cyanide groups and the nitrogen atoms of the 4-methyl pyridine molecules. The structure determination of this complex was undertaken because of the increasing interest in Hofmann-type complexes.

The structure consists of corrugated polymeric networks made up of tetracyanonickelate ions coordinated to Cd. The nearest neighbours of Cd involve

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Table 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $C_{16}H_{14}CdN_6Ni$.

$$U_{eq} = \left(\frac{1}{3}\right)\sum_i \sum_j U_{ij} a_i a_j a_i^* a_j^*$$

Atom	x	y	z	U_{eq}
Cd	0	0	0	32(1)
Ni	0	5000	-5000	29(1)
N2	1210(2)	0	2624(5)	40(1)
N1	423(2)	2169(3)	-1793(3)	44(1)
C1	287(1)	3257(3)	-2999(3)	34(1)
C2	1248(2)	0	4555(6)	46(1)
C3	1963(3)	0	6174(6)	56(1)
C4	2654(2)	0	5814(7)	49(1)
C5	3432(3)	0	7547(12)	83(2)
C6	2609(3)	0	3813(9)	66(1)
C7	1881(3)	0	2283(7)	62(1)

Table 2. Bond lengths [Å] for $C_{16}H_{14}CdN_6Ni$

Cd - N2	2.328(3)	Cd - N2#1	2.328(3)
Cd - N1#2	2.350(2)	Cd - N1#3	2.350(2)
Cd - N1#1	2.350(2)	Cd - N1	2.350(2)
Ni - C1#4	1.863(2)	Ni - C1#5	1.863(2)
Ni - C1	1.863(2)	Ni - C1#6	1.863(2)
N2 - C7	1.319(6)	N2 - C2	1.326(5)
N1 - C1	1.143(3)	C2 - C3	1.398(6)
C2 - H2	0.93	C3 - C4	1.361(7)
C3 - H3	0.93	C4 - C6	1.371(7)
C4 - C5	1.512(6)	C5 - H5A	0.93(3)
C5 - H5B	0.90(3)	C6 - C7	1.386(7)
C6 - H6	0.93	C7 - H7	0.93

Symmetry transformations used to generate equivalent atoms:

#1 = -x, -y, -z ; #2 = x, -y, z; #3 = -x, y, -z; #4 = -x, y, -z-1; #5 = x, -y+1, z ; #6 = -x, -y+1, -z-1

Table 3. Bond angles [°] for $C_{16}H_{14}CdN_6Ni$.

N2 - Cd - N2#1	180.0	N2 - Cd - N1#2	91.53(8)
N2#1 - Cd - N1#2	88.47(8)	N2 - Cd - N1#3	88.47(8)
N2#1 - Cd - N1#3	91.53(8)	N1#2 - Cd - N1#3	180.0
N2 - Cd - N1#1	88.47(8)	N2#1 - Cd - N1#1	91.53(8)
N1#2 - Cd - N1#1	91.15(2)	N1#3 - Cd - N1#1	88.85(2)
N2 - Cd - N1	91.53(8)	N2#1 - Cd - N1	88.47(8)
N1#2 - Cd - N1	88.85(1)	N1#3 - Cd - N1	91.15(2)
N1#1 - Cd - N1	180.0	C1#4 - Ni - C1#5	180.0
C1#4 - Ni - C1	89.65(4)	C1#5 - Ni - C1	90.35(4)
C1#4 - Ni - C1#6	90.6(1)	C1#5 - Ni - C1#6	89.7(1)
C1 - Ni - C1#6	180.0	C7 - N2 - C2	117.0(4)
C7 - N2 - Cd	122.6(3)	C2 - N2 - Cd	120.4(3)
C1 - N1 - Cd	150.5(2)	N1 - C1 - Ni	176.4(2)
N2 - C2 - C3	122.2(4)	N2 - C2 - H2	118.9(2)
C3 - C2 - H2	118.9(3)	C4 - C3 - C2	120.6(4)
C4 - C3 - H3	119.7(2)	C2 - C3 - H3	119.7(3)
C3 - C4 - C6	116.9(4)	C3 - C4 - C5	121.3(5)
C6 - C4 - C5	121.8(5)	C4 - C5 - H5A	123(6)
C4 - C5 - H5B	107(6)	H5A - C5 - H5B	96(6)
C4 - C6 - C7	119.5(4)	C4 - C6 - H6	120.2(3)
C7 - C6 - H6	120.2(3)	N2 - C7 - C6	123.8(4)
N2 - C7 - H7	118.1(2)	C6 - C7 - H7	118.1(3)

Symmetry transformations used to generate equivalent atoms:

#1 = -x, -y, -z ; #2 = x, -y, z; #3 = -x, y, -z; #4 = -x, y, -z-1; #5 = x, -y+1, z ; #6 = -x, -y+1, -z-1

four cyanide N atoms and two ligands N atoms a ORTEPII (Johnson, 1974) drawing of the molecule with the atomic numbering scheme is shown in Fig. 1. The atomic coordinates and equivalent izotropic thermal parameters of non-H atoms are listed in Table. 1. Bond distances and angles are given Table. 2 and Table. 3. Cd-N1,Cd-N2 distances and N2-Cd-N1 angle are 2.350(2) Å, 2.328(3) Å, 91.53(8)°, respectively. Also Ni-C distance is 1.863(2) Å. Anisotropic displacement parameters for

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Table 4. Anisotropic displacement parameters (Å^2 x10^3) for $C_{16}H_{14}CdN_6Ni$. The anisotropic displacement factor exponent takes the form:

$$-2\pi^2 [\, h^2 a^{*2} U_{11} + \ldots + 2\, h\, k\, a^* b^* U_{12} \,].$$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cd	50(1)	22(1)	18(1)	0	5(1)	0
Ni	45(1)	20(1)	20(1)	0	10(1)	0
N(2)	48(2)	43(2)	27(1)	0	9(1)	0
N(1)	66(1)	31(1)	32(1)	4(1)	12(1)	-3(1)
C(1)	49(1)	25(1)	26(1)	-2(1)	10(1)	-3(1)
C(2)	46(2)	61(3)	27(2)	0	8(2)	0
C(3)	55(2)	74(3)	30(2)	0	4(2)	0
C(4)	46(2)	38(2)	51(2)	0	1(2)	0
C(5)	48(3)	80(4)	92(5)	0	-13(3)	0
C(6)	50(2)	84(4)	68(3)	0	27(2)	0
C(7)	64(3)	86(4)	41(2)	0	24(2)	0

Table 5. Hydrogen coordinates (x10^4)and isotropic displacement parameters (Å^2 x 10^3) for $C_{16}H_{14}CdN_6Ni$.

Atom	x	y	z	U_{eq}
H2	785(2)	0	4842(6)	55
H3	1967(3)	0	7509(6)	67
H5A	391(3)	0	733(1)	13(3)
H5B	349(5)	-1077(6)	811(1)	22(4)
H6	3064(3)	0	3486(9)	79
H7	1864(3)	0	937(7)	74

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$C_{16}H_{14}CdN_6Ni$ and hydrogen coordinates and isotropic displacement parameters are listed in Table. 4, Table. 5, respectively. 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. Similar corrugated polymeric layers are also reported in some other related compounds (Rayner, Powell, 1952; Ülkü, 1975; Büyükgüngör, Ülkü, 1987).

From the observed bond distances and angles we may conclude that the slightly distorted octahedron formed by the two ligands N atoms and the four cyanide N atoms. The two 4-methyl pyridine molecules bound two Cd in trans positions are located on both sides of the network.

EXPERIMENTAL

The crystals wre prepared using a method analogous to that used for 2-methyl pyridine tetracyanonickelate complexes (Akyüz, Dempster, Morehouse and Suzuki, 1973).

Data were corrected for Lorentz, Polarization factors. The structure was solved by direct methods using SHELXS (Sheldrick, 1990) and refined by full matrix least squares using SHELXL93 (Sheldrick, 1993). H atoms isotropically, other non-H atoms anisotropically refined.

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