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Structure of *catena*-Poly[tri-μ-cyano-(ammine)(4-chloropyridine)cadmium-μ-cyano-nickel]

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Abstract. $[CdNi(CN)_4(C_5H_4ClN)(NH_3)]$, $M_r = 405{\cdot}76$, orthorhombic, $Ima2$, $a = 12{\cdot}490\ (3)$, $b = 14{\cdot}238\ (8)$, $c = 7{\cdot}705\ (5)$ Å, $V = 1370\ (2)$ Å^3, $Z = 4$, $D_m = 1{\cdot}95$, $D_x = 1{\cdot}97$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}7107$ Å, $\mu = 31$ cm^{-1}, $F(000) = 784$, $T = 293\ (3)$ K, $R = 0{\cdot}036$ for 604 unique observed reflections. The structure consists of corrugated polymeric networks made up of tetracyanonickelate ions coordinated to Cd. The 4-chloropyridine and the ammonia molecules bound to Cd in *trans* positions are located on both sides of the network. The corrugated effect occurs because of a departure of the Ni—C—N—Cd sequence of atoms from linearity at the C and N positions.

Introduction. This structure determination is part of a series of studies on the Hofmann-type pyridine complexes, $M(C_5H_5N)_2Ni(CN)_4$ where M is a metal of the first transition series. Our previous X-ray investigation of a single crystal of $Cd(C_5H_5N)_2Ni(CN)_4$ (Ülkü, 1975) and the studies of the powder samples of the analogous compounds with M = Mn, Zn, Ni, Co, Fe and Cu (Morehouse, Aytaç & Ülkü, 1977) showed its complex nature, which has frequently been confused in the literature with an analogue of the Hofmann benzene clathrate, $Ni(NH_3)_2Ni(CN)_4.2(C_6H_6)$ (Kondo & Kubo, 1957; Nakajima, Bhatnagar & Cole, 1962; Powell, 1964; Jacobs, 1970). In the search for new Hofmann pyridine complexes new compounds with different pyridine derivatives were prepared. Among nine analogous complexes only $Cd(NH_3)(Cl\text{-}C_5H_4N)\text{-}Ni(CN)_4$ could be obtained in the form of single crystals. Determination of the crystal structure of the title compound containing a pyridine derivative has been undertaken to permit a comparison of its structure with that of Hofmann pyridine complexes.

Experimental. The preparation of the pyridine complexes with M = Ni and Cd is described elsewhere (Hofmann & Küspert, 1897; Ülkü, 1975). Yellow prismatic crystals of the title compound were obtained by the same general procedure, using pyridine derivatives instead of pyridine itself at the appropriate step of the synthesis. Preliminary precession and Weissenberg photographs showed that the crystals are orthorhombic. The unit-cell dimensions were determined by least-squares refinement of 18 reflections with $20 < 2\theta < 60°$ on a diffractometer using Zr-filtered Mo radiation. The density of the sample was determined by flotation technique ($CCl_4/CHBr_3$). The observed systematic absences indicated two possible space groups: $Ima2$ and $I2/m\ 2/m\ 2/a$. Comparisons of the general and special positions of the two space groups with the number of different atoms in the unit cell and calculations of the intensity statistics (Woolfson, 1970) excluded the latter space group. $Ima2$ proved to be the correct choice also in later stages of structure determination.

Integrated intensity data were collected on a manual GE-XRD7 three-circle diffractometer using a θ–2θ scan technique and Mo $K\alpha$ radiation. Scan speed was 2° min^{-1}. For monochromatization a combination of Zr filter and a pulse-height discriminator was used. Calculated scan widths for the three ranges of 2θ, 0–20, 20–40, 40–60°, were 1·50, 1·60, 1·70°, respectively. Background counts were measured over the scan width by shifting the ω angle about 2°. A crystal having the dimensions 0·2 × 0·2 × 0·25 mm was oriented so that the c axis coincided with the φ axis of the instrument. Three standard reflections were checked every 50 measurements to ensure the alignment of the crystal but no discrepancy was observed. 1115 reflections were measured, 604 unique with $I > 3\sigma(I)$ were used in refinement ($0 \leq h \leq 16$, $0 \leq k \leq 20$, $0 \leq l \leq 10$, max. $\sin\theta/\lambda = 0{\cdot}7$ Å^{-1}). Lorentz–polarization corrections but no absorption corrections were applied. For Mo $K\alpha$ μR is *ca* 0·31; the maximum variation in $|F_o|$ ascribed to absorption would then be 1·5%.

A comparison of the space group $Ima2$ equipoints with the number of different atoms in the unit cell

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suggested the following positions for the atoms: Cd and Cl in ($\frac{1}{4}$, y, z; $\frac{3}{4}$, $\bar{y}$, z), Ni in (0,0,z; $\frac{1}{2}$,0,z). The coordinates of these three heavy atoms were deduced from a three-dimensional origin-removed Patterson synthesis. Heavy-atom phases and observed structure amplitudes were used to calculate the three-dimensional electron-density maps. Successive difference-map calculations revealed the positions of all non-H atoms. For goniostat settings, data reduction and Fourier calculations the *NRC* crystallographic programs (Ahmed, 1970) were used.

Table 1. *Atomic coordinates and equivalent isotropic thermal parameters, with e.s.d.'s in parentheses*

	x	y	z	B_{eq}*(Å^2)
Cd	0·250	0·1058 (1)	0·715 (1)	3·9 (2)
Ni	0	0	0·223 (2)	3·1 (3)
Cl	0·250	−0·3746 (4)	0·718 (5)	19 (1)
N(1)	0·115 (5)	0·110 (2)	0·503 (4)	3 (2)
N(2)	0·121 (5)	0·092 (3)	0·940 (5)	8 (3)
N(3)	0·250	−0·059 (1)	0·716 (7)	8 (2)
N(4)	0·250	0·265 (1)	0·709 (8)	8 (4)
C(1)	0·075 (5)	0·060 (3)	0·374 (4)	3 (2)
C(2)	0·067 (5)	0·070 (3)	0·028 (3)	2 (2)
C(3)	0·157 (1)	−0·108 (1)	0·717 (9)	10 (2)
C(4)	0·154 (2)	−0·204 (1)	0·726 (7)	12 (3)
C(5)	0·250	−0·251 (2)	0·70 (2)	9 (4)
H(C3)†	0·082	−0·068	0·708	
H(C4)†	0·081	−0·247	0·722	

* $B_{eq} = (B_{11} + B_{22} + B_{33})/3 = 8\pi^2 U_{eq}$.

† H atoms were given a fixed isotropic temperature factor of 3·0 Å^2.

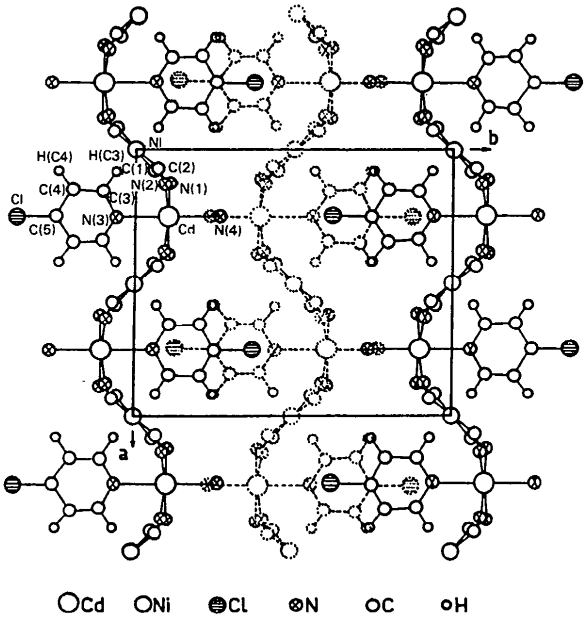

Fig. 1. A projection of the structure along the c axis and the numbering of the atoms. The dotted parts are shifted by c/2.

The refinement was carried out using the *ORFLS* program (Busing, Martin & Levy, 1970) on a B-6800 computer. Isotropic full-matrix least-squares refinement converged at $R = 0·07$. Unit weight was given to each reflection. Scattering factors were those listed in *International Tables for X-ray Crystallography* (1974). A difference density map computed after the isotropic refinement did not show clearly electron density for H atoms in the expected positions. Since the difference Fourier synthesis contained some error peaks also, H atoms of the pyridine ring were set 1·08 Å from their neighbouring C atoms. The calculated coordinates of the four H atoms at these positions were not treated as variables in the subsequent refinement. For these atoms the isotropic thermal parameter was taken as $B = 3·0$ Å^2 and kept fixed. The introduction of the fixed H atoms and the assignment of the anisotropic thermal coefficients to non-H atoms converged at $R = 0·036$ [$wR = 0·059$, $w = 1/\sigma^2(I)$] with 89 variable parameters, $\sum w(\Delta F)^2$ minimized. Max. Δ/σ was 0·84 for z coordinate of N(2). Final atomic coordinates and equivalent isotropic temperature factors are listed in Table 1.*

Discussion. The structure as viewed down the z axis is shown in Fig. 1. It consists of corrugated polymeric networks made up of tetracyanonickelate ions coordinated to Cd. The nearest neighbours of Cd involve four cyanide N atoms and the N of a 4-chloropyridine (Fig. 2). The average distance from the Cd atom to these five neighbours is 2·35 Å. A sixth N belonging to an ammonia group at 2·27 Å completes a slightly distorted

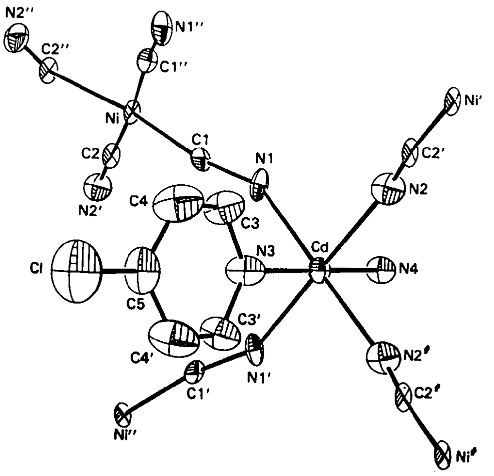

Fig. 2. Arrangement of the Cd neighbourhood.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43356 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Bond lengths* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

Cd–N(1)	2·35 (5)	N(2)–C(2)	1·01 (7)
Cd–N(2)	2·38 (5)	N(3)–C(3)	1·36 (2)
Cd–N(3)	2·34 (2)	C(3)–C(4)	1·38 (3)
Cd–N(4)	2·27 (2)	C(4)–C(5)	1·39 (3)
Ni–C(1)	1·73 (5)	C(5)–Cl	1·76 (3)
Ni–C(2)	1·99 (4)	C(3)–H(C3)	1·09 (2)
N(1)–C(1)	1·32 (6)	C(4)–H(C4)	1·09 (2)
N(1)–Cd–N(1^i)	92 (2)	C(1)–Ni–C(1^i)	95 (3)
N(1)–Cd–N(2)	91 (2)	C(1)–Ni–C(2)	92 (2)
N(2)–Cd–N(2^i)	85 (2)	C(2)–Ni–C(2^i)	82 (3)
N(1)–Cd–N(4)	88 (1)	C(3)–N(3)–C(3^i)	118 (2)
N(2)–Cd–N(4)	95 (1)	N(3)–C(3)–C(4)	122 (1)
N(1)–Cd–N(3)	92 (1)	C(3)–C(4)–C(5)	117 (2)
N(2)–Cd–N(3)	85 (1)	C(4)–C(5)–C(4^i)	120 (4)

Symmetry code: (i) $\frac{1}{2} - x, y, z$.

octahedron. The 4-chloropyridine and the ammonia molecules bound to Cd in *trans* positions are located on both sides of the network. The ligands of one network fit into the spaces of the other, so that the layers are arranged as closely as possible. The plane of the four cyanide C atoms surrounding Ni at an average distance of 1·86 Å is tilted so that its normal makes an angle of 46° to the *a* axis. The bending 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 observed in some other related compounds (Rayner & Powell, 1952; Ülkü, 1975). This compound has a structure closely related to but distinct from that of the 'Hofmann pyridine complexes' with the general formula $M(C_5H_5N)_2Ni(CN)_4$ (Ülkü, 1975; Morehouse *et al.*, 1977) as far as the unit-cell symmetry is concerned. As can be seen from Table 2 the bond distances and angles which were calculated from the final coordinates using the *ORFFE*3 program (Busing, Martin & Levy, 1971) generally agree with those observed in related compounds. Because of some differences in the bond lengths and angles within the pyridine ring from their ideal values, the ligand appears slightly distorted.

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cis-Dicarbonylbis[(2-phenylazo)phenyl]ruthenium(II)

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Abstract. $[Ru(C_{12}H_9N_2)_2(CO)_2]$, $[\overline{Ru\{C_6H_4N}{=}NC_6H_5\}_2(CO)_2]$, $M_r = 519{\cdot}5$, monoclinic, $P2_1/c$, $a = 9{\cdot}987\,(1)$, $b = 13{\cdot}891\,(1)$, $c = 17{\cdot}242\,(3)$ Å, $\beta = 101{\cdot}58\,(2)°$, $V = 2345\,(2)$ Å^3, $Z = 4$, $D_m = 1{\cdot}49\,(1)$, $D_x = 1{\cdot}472$ Mg m^{-3}, $\lambda(\text{Mo } K\bar{\alpha}) = 0{\cdot}7107$ Å, $\mu = 0{\cdot}656$ mm^{-1}, $F(000) = 1048$, $T = 295\,(2)$ K, $R = 0{\cdot}056$ for 3259 observed reflections. The distorted octahedral environment about the Ru atom consists of two cyclometallated azobenzene ligands and two mutually *cis* carbonyl ligands. The donor atoms are arranged such that the N atoms are respectively *trans* to a carbonyl ligand and an aryl C atom.

Introduction. The title compound, $C_{26}H_{18}N_4O_2Ru$, was isolated as a minor product from the reaction of $Ru_3(CO)_{12}$ and azobenzene in refluxing *n*-octane; the