to form a distorted trigonal bipyramid around the central Bi atom. However, from the two additional short intramolecular Bi—O(2) and Bi—O(5) distances [mean 2·806 (4) Å; sum of the van der Waals radii presumably > 3·60 Å], the polyhedron around Bi appears to be a distorted pentagonal bipyramid, in which the four O(carboxylate) and C(21) atoms are in the equatorial and C(11) and C(31) are in the apical positions. This interpretation gains justification by considering the opening of the angle C(11)—Bi(1)—C(31) to 148·23 (2)° to allow the positioning of O(2) and O(5). A value of 120° would be expected in a regular trigonal bipyramid. The structure is very similar to that found in trimethylbis[2-thenoato(1−)]antimony (Preut, Domagala & Huber, 1987) and triphenylbis[2-thenoato(1−)]antimony (Domagala, Huber & Preut, unpublished).

The distances Bi(1)—O(1) and Bi(1)—O(4) are appreciably greater than the value of 2·075 Å, which was estimated for a Bi—O single bond (March & Ferguson, 1975). In $Ph_3BiClOx$ (Ox = 8-quinolinolate), a Bi—O bond length of 2·175 Å was determined and the bond was assumed to be covalent (Barton, Charpiot, Dau, Motherwell, Pascard & Pichon, 1984). It therefore may be speculated that the bond between Bi and the carboxylate ligand has an appreciable ionic character. The bond distances and angles of the furan ring are essentially the same as found in solid 2-furancarboxylic acid (Hudson, 1962). Coordination of O(furan) to Bi can be excluded. Intermolecular distances smaller than the sum of the van der Waals radii do not exist.

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# Structure of *catena*-Poly[tri-$\mu$-cyano-(ammine)(2-amino-3-methylpyridine)cadmium-$\mu$-cyano-nickel]

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**Abstract.** $[CdNi(CN)_4(C_6H_8N_2)(NH_3)]$, $M_r = 400{\cdot}1$, orthorhombic, $Pna2_1$, $a = 13{\cdot}535$ (1), $b = 13{\cdot}607$ (1), $c = 7{\cdot}645$ (1) Å, $V = 1407{\cdot}99$ Å$^3$, $Z = 4$, $D_m = 1{\cdot}875$, $D_x = 1{\cdot}888$ g cm$^{-3}$, $\lambda$(Mo $K\alpha$) = 0·71069 Å, $\mu$(Mo) = 26·76 cm$^{-1}$, $F(000) = 784$, $T = 293$ K, $R = 0{\cdot}033$ for 1632 observed reflections. The structure consists of corrugated polymeric networks made up of tetracyanonickelate ions coordinated to Cd. The 2-amino-3-methylpyridine and ammonia molecules bound to Cd in *trans* positions are located on both sides of the network.

**Introduction.** This structure determination is part of a series of studies of Hofmann-type pyridine complexes, $M(C_5H_5N)_2Ni(CN)_4$, where $M$ is a transition metal. Our previous X-ray investigation of a single crystal of $Cd(C_5H_5N)_2Ni(CN)_4$ (Ülkü, 1975) and studies of powder samples of the analogous compounds with $M$ = Mn, Zn, Ni, Co, Fe and Cu (Morehouse, Aytaç & Ülkü, 1977) showed its complex nature. In the search for new Hofmann pyridine complexes, compounds with substituted pyridine derivatives were prepared. The first example of a Hofmann-type complex with a pyridine

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derivative (4-chloropyridine), instead of pyridine itself, has been reported recently (Büyükgüngör & Ülkü, 1987). A structure determination of the title compound containing 2-amino-3-methylpyridine was undertaken to permit a comparison of its structure with that of previously reported analogues.

**Experimental.** One mole per cent $Cd(CH_3COO)_2.2H_2O$ was dissolved in 50 ml ammonia and mixed with an aqueous solution of 0·01 mol $K_2Ni(CN)_4$. This solution was kept under a 2-amino-3-methylpyridine atmosphere. In about a week yellow prismatic crystals were obtained. Experimental data, methods used to solve the structure and other related parameters and procedures are given in Table 1. Difference Fourier calculations did not show clearly the electron density for H atoms. Therefore, H atoms were geometrically positioned 1·0 Å from C or N with coordinates and isotropic temperature coefficients ($U = 0{\cdot}05$ Å$^2$) kept fixed in the refinement process.

**Discussion.** Final coordinates and equivalent isotropic thermal parameters are given in Table 2.* Fig. 1 shows the structure as viewed down **c**. It consists of corrugated polymeric networks made up of square-planar tetracyanonickelate ions coordinated to Cd. The 2-amino-3-methylpyridine and the ammonia molecules are bonded to Cd in *trans* positions on both sides of the network. The ligands of one network fit into the cavities of the other, so that relatively good close packing is obtained. The coordination around Cd (Fig. 2) is a

Table 1. *Experimental details*

| | |
|---|---|
| Method of measuring $D_m$ | Flotation (bromoform, $CCl_4$) |
| Crystal shape and size (mm) | Prismatic, 0·5 × 0·5 × 1·0 |
| Diffractometer used and data-collection technique | $\omega$–$2\theta$ scan, CAD-4 four-circle diffractometer |
| Number and $\theta$ range of reflections used for measuring lattice parameters | 50 reflections with $15 < 2\theta < 45°$ |
| Absorption correction applied | Analytical absorption correction |
| Maximum value of $(\sin\theta)/\lambda$ reached in intensity measurements | 0·648 Å$^{-1}$ |
| Range of $h$, $k$ and $l$ | $0 \le h \le 17, 0 \le k \le 17, 0 \le l \le 8$ |
| Standard reflections and their intensity variation throughout experiment | $\bar{6}0\bar{5}$, $\bar{6}42$, $\bar{3}72$; variation (%) 2,1,1 respectively |
| Number of unique reflections | 1713 |
| Number of unobserved reflections | 81 |
| Criterion for recognizing unobserved reflections | $I < 2{\cdot}5\sigma(I)$ |
| Method used to solve structure | Direct methods |
| Use of $F$ or $F^2$ magnitudes in least-squares refinement | $F$ |
| Parameters refined | (Coordinates and anisotropic temperature factors of non-hydrogen atoms) 171 |
| Values of $R$, $wR$ | 0·033, 0·029, $S$ not calculated |
| Method used to calculate $w$ | $w = 1/\sigma^2(F)$ |
| Final residual electron densities (e Å$^{-3}$) for max. peak | +0·53 |
| Max. $(\Delta/\sigma)$ | +0·876 |
| Source of atomic scattering factors and $f'$, $f''$ values | *International Tables for X-ray Crystallography* (1974) |
| Computer programs used | Max-Planck Institut Mülheim Crystal Package, *DATAP* (Coppens, Leiserowitz & Rabinovich, 1965); *SHELXS*84 (Sheldrick, 1984); *ORTEP* (Johnson, 1976) |

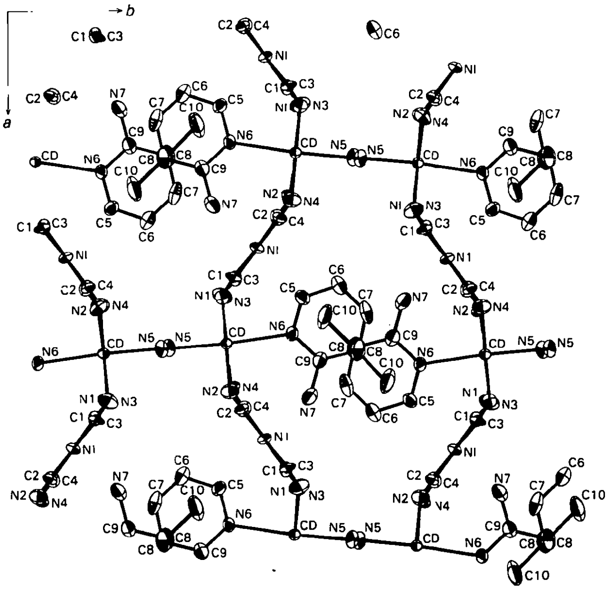

Fig. 1. Crystal structure as viewed down the $c$ axis.

Table 2. *Atomic coordinates* (×10$^4$) *and equivalent isotropic thermal parameters* (Å$^2$ × 10$^3$) *with e.s.d.'s in parentheses*

$$U_{eq} = \tfrac{1}{3}(U_{11} + U_{22} + U_{33}).$$

| | $x$ | $y$ | $z$ | $U_{eq}$ |
|---|---|---|---|---|
| Ni | 2634 | 2398 | 3886 (41) | 17·8 |
| Cd | 136 | 1603 | 8912 (41) | 16·0 |
| N1 | 1382 (14) | 1494 (10) | 6701 (45) | 38·2 |
| N2 | −1047 (12) | 1740 (10) | 6752 (43) | 27·4 |
| N3 | 1340 (12) | 1477 (9) | 11117 (43) | 24·6 |
| N4 | −1116 (13) | 1692 (11) | 11159 (45) | 34·3 |
| N5 | −12 (3) | −93 (4) | 8912 (50) | 31·3 |
| N6 | 392 (4) | 3322 (3) | 8994 (50) | 27·4 |
| N7 | −1255 (5) | 3777 (4) | 8829 (50) | 48·6 |
| C1 | 1845 (13) | 1824 (12) | 5629 (46) | 25·2 |
| C2 | 3400 (12) | 2935 (11) | 5620 (46) | 21·6 |
| C3 | 1868 (11) | 1799 (13) | 2169 (45) | 21·8 |
| C4 | 3446 (12) | 2999 (12) | 2158 (46) | 23·0 |
| C5 | 1347 (5) | 3589 (5) | 8816 (48) | 34·3 |
| C6 | 1667 (6) | 4548 (5) | 8630 (41) | 34·4 |
| C7 | 959 (7) | 5261 (5) | 8621 (44) | 46·0 |
| C8 | −40 (6) | 5043 (6) | 9075 (65) | 43·5 |
| C9 | −302 (4) | 4046 (4) | 8925 (51) | 31·5 |
| C10 | −839 (8) | 5817 (5) | 8773 (58) | 73·1 |

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44753 (39 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Bond lengths* (Å) *and bond angles* (°) *with e.s.d.'s in parentheses*

| | | | |
|---|---|---|---|
| Ni–C1 | 1·877 (16) | N2–C2 | 1·205 (25) |
| Ni–C2 | 1·835 (15) | N3–C3 | 1·162 (18) |
| Ni–C3 | 1·860 (14) | N4–C4 | 1·077 (25) |
| Ni–C4 | 1·903 (16) | N6–C5 | 1·350 (9) |
| Cd–N1 | 2·392 (16) | N6–C9 | 1·362 (7) |
| Cd–N2 | 2·308 (13) | N7–C9 | 1·343 (8) |
| Cd–N3 | 2·351 (14) | C5–C6 | 1·383 (9) |
| Cd–N4 | 2·417 (17) | C6–C7 | 1·363 (12) |
| Cd–N5 | 2·317 (6) | C7–C8 | 1·427 (15) |
| Cd–N6 | 2·365 (4) | C8–C9 | 1·407 (10) |
| N1–C1 | 1·125 (20) | C8–C10 | 1·527 (14) |
| C5–HC5 | 1·007 (19) | C6–HC6 | 1·046 (15) |
| N5–HN5*A* | 1·202 (36) | N5–HN5*B* | 1·009 (5) |
| N5–HN5*C* | 0·871 (19) | N7–HN7*B* | 0·838 (16) |
| N7–HN7*C* | 1·005 (6) | C10–H10*A* | 0·813 (29) |
| C10–H10*B* | 1·282 (39) | C10–H10*C* | 1·003 (18) |
| C7–HC7 | 1·036 (9) | | |

| | | | |
|---|---|---|---|
| C1–Ni–C2 | 88·5 (8) | C1–N1–Cd | 151·9 (14) |
| C1–Ni–C3 | 90·1 (2) | N7–C9–N6 | 117·9 (6) |
| C1–Ni–C4 | 178·7 (7) | C3–N3–Cd | 153·5 (12) |
| C2–Ni–C3 | 177·5 (8) | N4–Cd–N6 | 92·0 (6) |
| C2–Ni–C4 | 90·2 (2) | C5–N6–Cd | 113·8 (4) |
| C3–Ni–C4 | 91·2 (7) | C9–N6–Cd | 127·8 (4) |
| N1–Cd–N2 | 89·3 (7) | C9–N6–C5 | 117·5 (6) |
| N1–Cd–N3 | 90·8 (2) | N1–C1–Ni | 178·5 (15) |
| N1–Cd–N4 | 179·2 (5) | C6–C5–N6 | 124·3 (6) |
| N1–Cd–N5 | 89·9 (5) | N3–C3–Ni | 175·2 (14) |
| N1–Cd–N6 | 88·7 (6) | N5–Cd–N6 | 176·3 (4) |
| N2–Cd–N3 | 179·6 (3) | C7–C6–C5 | 116·9 (7) |
| N2–Cd–N4 | 91·0 (2) | C8–C7–C6 | 121·0 (8) |
| N2–Cd–N5 | 91·1 (5) | C10–C8–C9 | 118·3 (9) |
| N2–Cd–N6 | 92·3 (5) | C10–C8–C7 | 119·4 (13) |
| N3–Cd–N4 | 88·9 (7) | C9–C8–C7 | 114·9 (10) |
| N3–Cd–N5 | 89·3 (5) | C8–C9–N7 | 120·6 (6) |
| N3–Cd–N6 | 87·3 (5) | C8–C9–N6 | 121·3 (6) |
| N4–Cd–N5 | 89·3 (5) | HC5–C5–N6 | 112·7 (14) |
| HC5–C5–C6 | 115·3 (9) | HC6–C6–C5 | 111·1 (8) |
| HC6–C6–C7 | 127·7 (9) | HC7–C7–C6 | 118·0 (9) |
| HC7–C7–C8 | 120·6 (9) | HN7*B*–N7–C9 | 123·5 (14) |
| HN7*C*–N7–C9 | 106·2 (5) | HN5*A*–N5–Cd | 107·4 (9) |
| HN5*B*–N5–Cd | 111·1 (4) | HN5*C*–N5–Cd | 116·7 (10) |
| H10*A*–C10–C8 | 109·0 (23) | H10*B*–C10–C8 | 111·7 (18) |
| HN5*B*–N5–HN5*A* | 94·8 (22) | HN5*C*–N5–HN5*A* | 102·7 (17) |
| HN5*C*–N5–HN5*B* | 120·3 (21) | HN7*C*–N7–HN7*B* | 123·9 (15) |
| H10*B*–C10–H10*A* | 100·0 (16) | H10*C*–C10–C8 | 114·2 (8) |
| H10*C*–C10–H10*A* | 127·6 (19) | H10*C*–C10–H10*B* | 90·4 (29) |

slightly distorted nitrogen octahedron, involving four cyanide N atoms in the basal plane, and N(pyridine) and N(ammonia) in apical positions. The Cd–N–C–Ni sequence of atoms is bent, especially at N (Cd–N–C $\simeq$ 150°), and this is primarily responsible for the corrugated appearance of the networks observed along **c**. Similar corrugated layers are also reported in some other related compounds (Rayner & Powell, 1952; Ülkü, 1975; Büyükgüngör & Ülkü, 1987), though they all have different unit-cell symmetry. The bond lengths and angles (Table 3) agree with those observed in related compounds.

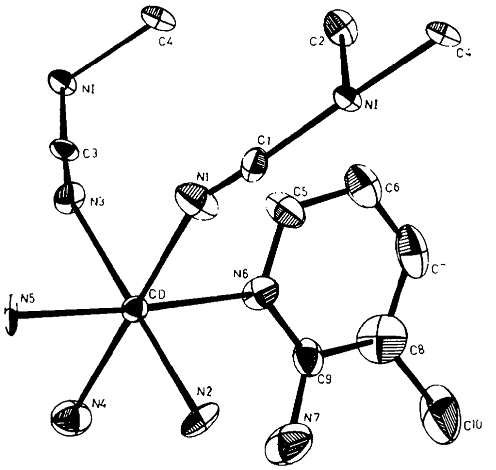

Fig. 2. An *ORTEP* (Johnson, 1976) drawing of the title molecule with the atom-numbering scheme. The thermal ellipsoids are drawn at the 50% probability level.

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