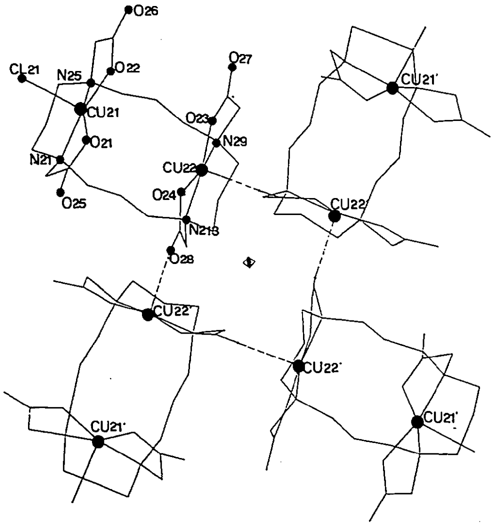

Fig. 2. View of the tetrameric moiety *B* showing the fourfold rotatory inversion axis.

**Discussion.** The structure consists of two similar anionic units $Cu_2L(H_2O)Cl^-$ (*A*) and $[Cu_2LCl]_4^-$ (*B*) and a $Cu(H_2O)_6^{2+}$ counterion together with extensive solvent. Ion *A* contains two five-coordinated $Cu^{2+}$ ions in a square pyramidal arrangement and is shown in Fig. 1. Cu(11) is bound to two N atoms of the macrocycle, two carboxylate groups and an apical chloride, Cl(11), and Cu(12) shows the same arrangement with a water molecule O(41) instead of the chloride at the apex. Unlike the anions of type *A*, which are isolated in the lattice, the anions *B* are linked by carboxylate bridges into tetramers. The subunits are related by the crystallographic fourfold rotatory inversion axis parallel to **c** (Fig. 2). The carboxylate group O(24)—C(224)—O(28) acts as a bridge between Cu(22) and the symmetry related Cu(22'). O(28''') is the apex of the pyramid like O(41) in the first moiety.

The intramolecular metal–metal distances are Cu(11)—Cu(12) 4·903 (4) and Cu(21)—Cu(22) 4·848 (4) Å. The solvent part of the structure consists of the seven coordinated water molecules mentioned above and 19 other sites of which 14 are only partially occupied. The arrangement for all of them is reasonable for hydrogen bonds.

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# Structures of the $P2_1/c$ Phases of $[(CH_3)_4P]_2CoI_4$ and $[(CH_3)_4P]_2CoBr_4$

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**Abstract.** Bis(tetramethylphosphonium) tetraiodocobaltate(II), $[C_4H_{12}P]_2[CoI_4]$, $M_r = 748{\cdot}8$, monoclinic, $P2_1/c$, $a = 9{\cdot}859\,(2)$, $b = 16{\cdot}762\,(2)$, $c = 13{\cdot}716\,(1)$ Å, $\beta = 90{\cdot}05\,(1)°$, $V = 2266{\cdot}6\,(6)$ Å$^3$, $Z = 4$, $D_x = 2{\cdot}19$ g cm$^{-3}$, $\lambda$(Mo $K\alpha$) = 0·7107 Å, $\mu = 62{\cdot}7$ cm$^{-1}$, $F(000) = 1364$, $T = 293$ K, final $R = 0{\cdot}073$ for 3481 unique reflections with $F > 3\sigma(F)$. Bis(tetramethylphosphonium) tetrabromocobaltate(II), $[C_4H_{12}P]_2[CoBr_4]$, $M_r = 560{\cdot}8$, monoclinic, $P2_1/c$, $a = 9{\cdot}489\,(2)$, $b = 15{\cdot}985\,(3)$, $c = 13{\cdot}106\,(2)$ Å, $\beta = 89{\cdot}52\,(2)°$, $V = 1987{\cdot}9\,(7)$ Å$^3$, $Z = 4$, $D_x = 1{\cdot}87$ g cm$^{-3}$, $\lambda$(Mo $K\alpha$) = 0·7107 Å, $\mu = 89{\cdot}7$ cm$^{-1}$, $F(000) = 1076$, $T = 293$ K, final $R = 0{\cdot}088$ for 2019 unique reflections with $F > 3\sigma(F)$. The two structures are of the slightly distorted $\beta$-$K_2SO_4$ type. $[(CH_3)_4P]_2CoI_4$ is virtually isostructural with the

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$P2_1/c$ phase of several $[(CH_3)_4N]_2MX_4$ compounds, characterized by a counter-clockwise rotation around [010] of all ions with respect to an assumed, high-temperature *Pmcn* structure. $[(CH_3)_4P]_2CoBr_4$ is uniquely characterized by a clockwise rotation of all ions, if the coordinate system with $\beta = 90{\cdot}48°$ is chosen for reference. The actual structural differences, however, are quite small, as is shown by considering the structure in reference to the same unit cell, but with the alternative coordinate system having $\beta = 89{\cdot}52°$.

**Introduction.** $[(CH_3)_4P]_2CoI_4$ and $[(CH_3)_4P]_2CoBr_4$, hereafter $(TMP)_2CoI_4$ and $(TMP)_2CoBr_4$, have $P2_1/c$ symmetry at room temperature and undergo phase transitions at 376·0 (6) K with $\Delta S_{tr} = 1{\cdot}1\ (2)\ R$ $[(TMP)_2CoI_4]$ and 366·8 (8) K with $\Delta S_{tr} = 1{\cdot}1\ (2)\ R$ $[(TMP)_2CoBr_4]$ (Pressprich, Bond & Willett, 1991). In both cases the DSC transition profiles were $\lambda$ shaped, indicating continuous or nearly continuous transitions. In analogy to well characterized $(TMA)_2MX_4$ compounds $\{TMA = [(CH_3)_4N]^+, X =$ halide ion$\}$, the transitions probably correspond to transformations to prototype $\beta$-$K_2SO_4$ *Pmcn* phases. No other transitions were observed down to 103 K $[(TMP)_2CoI_4]$ or 113 K $[(TMP)_2CoBr_4]$. The analogous ammonium salt $(TMA)_2CoBr_4$ has been studied (Gesi & Ozawa, 1983; Gesi, 1982) and shows only one (continuous) transition to the *Pmcn* phase at 287·0 K. Results for $(TMA)_2CoI_4$ have not been reported. The closely related ammonium–zinc analogues, $(TMA)_2ZnBr_4$ and $(TMA)_2ZnI_4$, have, however, been well characterized (Perret, Godefroy & Arend, 1987, and references therein; Hasebe, Asahi & Gesi, 1990, and references therein; Asahi, Hasebe & Gesi, 1988, and references therein). $(TMA)_2ZnBr_4$ shows only one (continuous) transition at 288 K with $\Delta S_{tr} = 0{\cdot}98\ R$, transforming from *Pmcn* to $P2_1/c$. $(TMA)_2ZnI_4$ shows an analogous transition at 254 K, but also has an additional transition from $P2_1/c$ to $Pbc2_1$ (doubled *b* axis) at 210 K.

**Experimental.** The syntheses of $(TMP)_2CoI_4$ and $(TMP)_2CoBr_4$ have been reported (Pressprich, Bond & Willett, 1991). X-ray data were collected on a Syntex $P2_1$ diffractometer upgraded to Siemens/Nicolet *P3F* specifications using graphite-monochromated Mo $K\alpha$ ($\lambda = 0{\cdot}7107$ Å) radiation. The space group for each compound was uniquely determined to be $P2_1/c$ from systematic extinctions. No significant changes in check reflection intensities, monitored every 96 reflections, were observed during data collection. The structures were solved by direct methods (*SHELXTL*; Sheldrick, 1986). The function minimized was $\sum w(|F_o| - |F_c|)^2$ with $w$ clarified in Table 1. The atomic scattering factors of *SHELXTL* were used. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were constrained to C—H distances of 0·96 Å and their isotropic thermal parameters were set at ~1·2 times the equivalent isotropic thermal parameters of associated carbon atoms. 137 parameters were refined for each structure. Other lattice and data-collection parameters are listed in Table 1.

Table 1. *X-ray data-collection parameters*

| | $[(CH_3)_4P]_2CoI_4$ | $[(CH_3)_4P]_2CoBr_4$ |
|---|---|---|
| Reflections for lattice-constants determination | 25 | 25 |
| $\theta$ range | $30 < 2\theta < 32°$ | $25 < 2\theta < 30°$ |
| Crystal size | 0·3 × 0·65 × 0·55 mm | 0·42 × 0·42 × 0·42 mm |
| Crystal shape | Irregularly shaped | Cube shaped |
| Absorption correction | Empirical/ellipsoidal | Numerical |
| Transmission range | 0·377–0·951 | 0·023–0·095 |
| Data collection | $\omega$ scans | $\omega$ scans |
| Scan range | 0·75° | 0·80° |
| Scan speeds | 3·9–29·3° $min^{-1}$ | 3·9–29·3° $min^{-1}$ |
| Check reflections | $\bar{1}\bar{1}0$; $2\bar{1}\bar{1}$ | 127; 170; 383 |
| Total reflections | 4893 | 3892 |
| Max. $(\sin\theta)/\lambda$ | 0·650 $Å^{-1}$ | 0·595 $Å^{-1}$ |
| Unique reflections | 4465, 3481 with $F < 3\sigma(F)$ | 3477, 2019 with $F < 3\sigma(F)$ |
| $R_{int}$ | 0·044 | 0·012 |
| $h,k,l$ range | $0 \leq h \leq 11$<br>$0 \leq k \leq 21$<br>$-17 \leq l \leq 17$ | $0 \leq h \leq 11$<br>$0 \leq k \leq 18$<br>$-15 \leq l \leq 15$ |
| $R$ | 0·073 (0·089 all data) | 0·088 (0·141 all data) |
| $wR$ | 0·119 (0·122 all data) | 0·085 (0·091 all data) |
| Weighting function | $w = 1/[\sigma^2(F) + g(F)^2]$, $g = 0{\cdot}0024$ | $w = 1/[\sigma^2(F) + g(F)^2]$, $g = 0{\cdot}0008$ |
| $S$ | 1·79 | 1·52 |
| $\Delta/\sigma\|_{max}$ | 0·015 | 0·026 |
| Largest peak on final difference map | 2·1 e $Å^{-3}$ near I(2) | 1·6 e $Å^{-3}$ near Br(1) |
| Most negative peak on final difference map | −0·9 e $Å^{-3}$ | −0·9 e $Å^{-3}$ |

**Discussion.** The final atomic parameters for $(TMP)_2CoI_4$ and $(TMP)_2CoBr_4$ at room temperature are listed in Table 2* and bond lengths and angles are shown in Table 3. The crystal structure of $(TMP)_2CoI_4$ is shown in Fig. 1.

The room-temperature phase of $(TMP)_2CoI_4$ is virtually isostructural with lower temperature, isomorphic phases of several $(TMA)_2MX_4$ compounds. For instance, the close similarity of $(TMP)_2CoI_4$ at 293 K and $(TMA)_2ZnI_4$ at 250 K may be seen by comparing Fig. 1 with the analogous Fig. 2 of Hasebe, Asahi & Gesi (1990). Other isomorphic and nearly isostructural phases of $(TMA)_2MX_4$ salts for which structures have been completed include $(TMA)_2ZnBr_4$ at 286, 284, 279, 275, 263, 233 and 173 K (Asahi, Hasebe & Gesi, 1988) and 193 K (Trouélan, Lefebvre & Derollez, 1985); and $(TMA)_2MnCl_4$ at 168 K (Mashiyama &

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* Lists of observed and calculated structure factors, anisotropic thermal parameters and hydrogen-atom coordinates, and stereographic packing diagrams of the unit cells of $[(CH_3)_4P]_2CoI_4$ and $[(CH_3)_4P]_2CoBr_4$ and a thermal ellipsoid plot of $[(CH_3)_4P]_2CoBr_4$ have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53718 (57 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Positional parameters* ($\times 10^4$) *and equivalent isotropic thermal parameters* ($\text{Å}^2 \times 10^3$)

The equivalent isotropic $U$ values are defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

| | $x$ | $y$ | $z$ | $U_{eq}$ |
|---|---|---|---|---|
| (*a*) $[(CH_3)_4P]CoI_4$ | | | | |
| Co | 2755 (2) | 3979 (1) | 2472 (1) | 53 (1) |
| I(1) | 2198 (1) | 3980 (1) | 616 (1) | 71 (1) |
| I(2) | 3130 (2) | 5413 (1) | 3153 (1) | 93 (1) |
| I(3) | 690 (1) | 3352 (1) | 3348 (1) | 98 (1) |
| I(4) | 4969 (1) | 3167 (1) | 2782 (1) | 84 (1) |
| P(1) | 2398 (4) | 967 (3) | 1412 (3) | 71 (1) |
| C(1) | 2829 (34) | 976 (17) | 2661 (13) | 158 (15) |
| C(2) | 2599 (32) | −80 (14) | 1004 (19) | 147 (13) |
| C(3) | 3493 (20) | 1521 (10) | 680 (14) | 93 (7) |
| C(4) | 812 (27) | 1359 (18) | 1339 (27) | 198 (18) |
| P(2) | 2463 (4) | 8414 (2) | 4967 (3) | 63 (1) |
| C(5) | 2551 (29) | 7367 (11) | 4704 (20) | 161 (14) |
| C(6) | 1898 (23) | 8938 (15) | 3917 (11) | 131 (11) |
| C(7) | 4130 (18) | 8751 (11) | 5317 (14) | 93 (7) |
| C(8) | 1286 (15) | 8565 (9) | 5954 (11) | 73 (5) |
| (*b*) $[(CH_3)_4P]_2CoBr_4$ | | | | |
| Co | 2768 (2) | 3992 (1) | 2439 (2) | 45 (1) |
| Br(1) | 2207 (2) | 4009 (1) | 656 (1) | 66 (1) |
| Br(2) | 3152 (3) | 5366 (1) | 3126 (2) | 86 (1) |
| Br(3) | 800 (2) | 3369 (2) | 3308 (2) | 88 (1) |
| Br(4) | 4904 (2) | 3193 (1) | 2690 (1) | 73 (1) |
| P(1) | 2429 (5) | 959 (3) | 1385 (3) | 53 (2) |
| C(1) | 2869 (22) | 1035 (12) | 2690 (12) | 89 (9) |
| C(2) | 2498 (27) | −88 (12) | 993 (16) | 117 (12) |
| C(3) | 3620 (21) | 1525 (12) | 631 (14) | 88 (9) |
| C(4) | 778 (23) | 1362 (16) | 1213 (17) | 129 (13) |
| P(2) | 2434 (4) | 8391 (3) | 5030 (3) | 48 (2) |
| C(5) | 2622 (23) | 7300 (11) | 4777 (18) | 116 (11) |
| C(6) | 1856 (21) | 8890 (14) | 3917 (14) | 99 (10) |
| C(7) | 4081 (19) | 8784 (12) | 5369 (14) | 86 (9) |
| C(8) | 1236 (23) | 8583 (13) | 6017 (15) | 110 (11) |

Table 3. *Bond lengths* (Å) *and angles* (°) *at* 293 K *with e.s.d.'s in parentheses*

| $[(CH_3)_4P]_2CoI_4$ | | $[(CH_3)_4P]_2CoBr_4$ | |
|---|---|---|---|
| Co—I(1) | 2·603 (2) | Co—Br(1) | 2·402 (3) |
| Co—I(2) | 2·604 (2) | Co—Br(2) | 2·403 (3) |
| Co—I(3) | 2·589 (2) | Co—Br(3) | 2·396 (3) |
| Co—I(4) | 2·607 (2) | Co—Br(4) | 2·420 (3) |
| P(1)—C(1) | 1·76 (2) | P(1)—C(1) | 1·77 (2) |
| P(1)—C(2) | 1·85 (2) | P(1)—C(2) | 1·75 (2) |
| P(1)—C(3) | 1·74 (2) | P(1)—C(3) | 1·75 (2) |
| P(1)—C(4) | 1·70 (3) | P(1)—C(4) | 1·71 (2) |
| P(2)—C(5) | 1·79 (2) | P(2)—C(5) | 1·78 (2) |
| P(2)—C(6) | 1·78 (2) | P(2)—C(6) | 1·76 (2) |
| P(2)—C(7) | 1·80 (2) | P(2)—C(7) | 1·75 (2) |
| P(2)—C(8) | 1·80 (2) | P(2)—C(8) | 1·74 (2) |
| | | | |
| I(1)—Co—I(2) | 112·4 (1) | Br(1)—Co—Br(2) | 112·9 (1) |
| I(1)—Co—I(3) | 106·8 (1) | Br(1)—Co—Br(3) | 106·8 (1) |
| I(1)—Co—I(4) | 109·6 (1) | Br(1)—Co—Br(4) | 109·3 (1) |
| I(2)—Co—I(3) | 108·7 (1) | Br(2)—Co—Br(1) | 108·8 (1) |
| I(2)—Co—I(4) | 107·7 (1) | Br(2)—Co—Br(4) | 107·6 (1) |
| I(3)—Co—I(4) | 111·7 (1) | Br(3)—Co—Br(4) | 111·5 (1) |
| C(1)—P(1)—C(2) | 106 (2) | C(1)—P(1)—C(2) | 110 (1) |
| C(1)—P(1)—C(3) | 114 (1) | C(1)—P(1)—C(3) | 111 (1) |
| C(1)—P(1)—C(4) | 106 (2) | C(1)—P(1)—C(4) | 109 (1) |
| C(2)—P(1)—C(3) | 105 (1) | C(2)—P(1)—C(3) | 108 (1) |
| C(2)—P(1)—C(4) | 117 (1) | C(2)—P(1)—C(4) | 111 (1) |
| C(3)—P(1)—C(4) | 109 (1) | C(3)—P(1)—C(4) | 109 (1) |
| C(5)—P(2)—C(6) | 110 (1) | C(5)—P(2)—C(6) | 109 (1) |
| C(5)—P(2)—C(7) | 108 (1) | C(5)—P(2)—C(7) | 108 (1) |
| C(5)—P(2)—C(8) | 109 (1) | C(5)—P(2)—C(8) | 112 (1) |
| C(6)—P(2)—C(7) | 110 (1) | C(6)—P(2)—C(7) | 110 (1) |
| C(6)—P(2)—C(8) | 110 (1) | C(6)—P(2)—C(8) | 109 (1) |
| C(7)—P(2)—C(8) | 110 (1) | C(7)—P(2)—C(8) | 109 (1) |

Koshiji, 1989). The structure of the room-temperature phase of $(TMP)_2CoBr_4$ is discussed below.

The three $(TMA)_2MX_4$ compounds, and presumably $(TMP)_2CoI_4$ and $(TMP)_2CoBr_4$, all transform to high-temperature phases having $Pmcn$ symmetry, with which the distorted $P2_1/c$ phases may be compared. The ferroelastic distortion from orthorhombic to monoclinic symmetry involves the deviation of the $\beta$ angle from 90° and the loss of mirror planes perpendicular to $x$. These planes would lie at $x = \frac{1}{4}$ and $x = \frac{3}{4}$ in Fig. 1. In right-handed coordinate systems chosen with $\beta > 90°$ the $P2_1/c$ phases of $(TMP)_2CoI_4$ and the three $(TMA)_2MX_4$ compounds are characterized by a counter-clockwise rotation around [010] of all ions with respect to the orthorhombic phase, as can be seen in the figure. In the analogous coordinate system with $\beta > 90°$ $(TMP)_2CoBr_4$ shows the opposite rotation of all ions. However, switching to a coordinate system with $\beta < 90°$ *via* the trivial transformation of basis vectors $\mathbf{a}' = -\mathbf{a}$, $\mathbf{b}' = -\mathbf{b}$ and $\mathbf{c}' = \mathbf{c}$ reverses the sense of rotation and clearly shows the structural similarities of $(TMP)_2CoBr_4$, $(TMP)_2CoI_4$ and $(TMA)_2MX_4$. The coordinates of Table 2 are given with respect to this basis. A thermal ellipsoid plot of $(TMP)_2CoBr_4$, which has been deposited, emphasizes the structural similarities, as it is quite similar to Fig. 1.

We plan no further studies of these salts and will be happy to share our small amounts of the crystalline samples with other research groups.

The X-ray diffraction facility was established in part through funds from NSF Grant CHE-8408407 and from the Boeing Company.

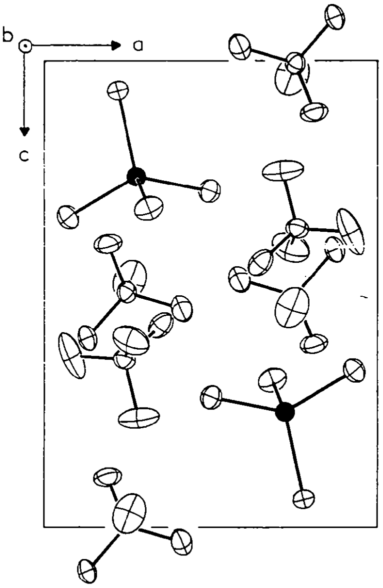

Fig. 1. Thermal ellipsoid plot of $(TMP)_2CoI_4$ at 30% probability. The following ions, generated from the positions given in Table 2, are included in the plot: $CoI_4^{2-}$ $x, y, z$; $1-x, 1-y, 1-z$; $(TMA)^+(1)$ $1-x, 0{\cdot}5+y, 0{\cdot}5-z$; $x, 0{\cdot}5-y, 0{\cdot}5+z$; $(TMA)^+(2)$ $x, y, z$; $1-x, 1-y, 1-z$; $x, 1{\cdot}5-y, 0{\cdot}5+z$; $1-x, -0{\cdot}5+y, 0{\cdot}5-z$. $CoI_4^{2-}$ ions drawn with filled-in Co atoms.

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# Structural Investigation of $Ni^{II}$ Complexes.
# VIII. Structure of Tris(2,4-dimethylpyridine)bis(isothiocyanato)nickel(II)

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**Abstract.** $[Ni(NCS)_2(C_7H_9N)_3]$, $M_r = 496{\cdot}34$, tetragonal, $P4_12_12$, $a = 13{\cdot}44$ (1), $c = 14{\cdot}191$ (5) Å, $Z = 4$, $V = 2563$ (3) Å$^3$, $D_m = 1{\cdot}285$ (6), $D_x = 1{\cdot}29$ g cm$^{-3}$, $\lambda$(Mo $K\alpha$) = 0·7107 Å, $\mu = 9{\cdot}3$ cm$^{-1}$, $F(000) = 1040$, room temperature, $R = 0{\cdot}049$, $wR = 0{\cdot}056$ for 1030 reflections with $I \geq 1{\cdot}96\sigma(I)$. Five N atoms surround the Ni atom, defining a coordination polyhedron intermediate between trigonal bipyramidal and tetragonal pyramidal. The complex lies on a crystallographic diad axis which passes through the Ni atom and one of the dimethylpyridine ligands which is disordered.

**Introduction.** Structural studies of $Ni(NCS)_2$(alkylpyridine)$_x$ complexes have shown that there is a direct relationship between the size and position of the pyridine alkyl substituents and the structure of the complex. 4- and 3-alkyl-substituted pyridines form pairs of the pseudo-octahedral complexes of different symmetry [Andreetti, Bocelli & Sgarabotto, 1972; Kerr & Williams, 1977 (4-methylpyridine complexes); Ďurčanská, Jamnický, Koman, Wnęk & Głowiak, 1986 (3-ethylpyridine complexes)] depending on the preparation mode whereas 2-alkyl-substituted pyridines cause a radical change in the coordination number of the $Ni^{II}$ atom, decreasing it from 6 (the usual value) to 4 or 5. The structure determination of $[Ni(NCS)_2$(2,5-dimethylpyridine)$_2]$ (Ďurčanská, Głowiak & Kožíšek, 1982) provides an example of square planar nickel(II) with 2-methylpyridine ligands; the corresponding pentacoordinate nickel(II) species $[Ni(NCS)_2$(2,5-dimethylpyridine)$_3]$ was too unstable for X-ray analysis. Instead we report the structure determination of the title complex. Spectral and magnetic measurements confirmed the pentacoordination of $Ni^{II}$ (Jóna, Jamnický & Šramko, 1978), X-ray analysis now gives a more precise picture of the coordination geometry and of its relationship with the steric properties of the 2-substituted pyridine ligands.

**Experimental.** Green bipyramids, 0·35 × 0·35 × 0·30 mm; density measured by flotation ($CCl_4$/acetone). Cell parameters refined on Syntex $P2_1$ diffractometer by least squares from 15 reflections with $4 \leq \theta \leq 17°$. Absorption and extinction ignored. Intensity measurements from $\theta$–$2\theta$ scans carried out for $0 \leq 2\theta \leq 55°$. *hkl* range $h$ −17 to 17, $k$ 0 to 17, $l$ 0 to 18. Two standard reflections every 50 measurements, decreased in intensity by 15% during the course of the experiment, 1030 independent reflections with $I \geq 1{\cdot}96\sigma(I)$ (725 unobserved reflections), $R_{\rm int} = 0{\cdot}032$ assuming $4/mmm$ Laue symmetry. Ni atom position from Patterson function; other non-H atoms from Fourier syntheses. The nine H atoms [of the N(2) pyridine ligand] were initially located from a difference map and then refined isotropically; the seven independent H atoms of the disordered N(1) ring were positioned geometrically, full-matrix refinement [except H atoms of N(1) ring] based on $F$, 173 parameters refined, $R = 0{\cdot}049$, $wR = 0{\cdot}056$, $w = 1/[\sigma^2(F) + 0{\cdot}0134\,(F)^2]$, $(\Delta/\sigma)_{\max}$ in final least-squares cycle 0·6 [for C(27)]; $\Delta\rho$ values between 0·27 and $-0{\cdot}32$ e Å$^{-3}$. No attempt was made to determine chirality by refinement in the alternative space group $P4_32_12$. *XTL* program system (Syntex, 1973) and

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