

The Crystal Structures of Copper Dipyrindine Dichloride and the Violet Form of Cobalt Dipyrindine Dichloride

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The structures of copper dipyrindine dichloride and α -cobalt dipyrindine dichloride have been determined by X-ray analysis.

CuPy_2Cl_2 is monoclinic, $a = 17.00$, $b = 8.59$, $c = 3.87$ Å, $\beta = 91^\circ 52'$, space group $P2_1/n$, two centrosymmetric molecules in the cell. The structure consists of square coplanar units (Cu-Cl, 2.28 Å; Cu-N, 2.02 Å) aggregated into chains running parallel to c by weaker Cu-Cl bonds (3.05 Å) which complete distorted octahedra about each copper.

α - CoPy_2Cl_2 is monoclinic and is referred to a pseudo-orthorhombic cell centred on the oblique face C , $a = 34.42$, $b = 17.38$, $c = 3.66$ Å, $\gamma = 90^\circ$, containing eight molecules. The corresponding primitive cell has space group $P2/b$. The cobalt atoms lie on twofold rotation axes and the crystal contains two formally independent sets of molecules. The structure consists of polymeric chains, running parallel to c , in which the coordination about the cobalt is octahedral (Co-Cl, 2.49 Å; Co-N, 2.14 Å). The two structures are closely related and appear virtually identical when viewed down the respective c axes.

Introduction

Cobalt dipyrindine dichloride exists in two crystalline forms, one (α -) violet, the other (β -) blue in colour. Although there has been considerable controversy regarding their structures, it now appears almost certain that the blue form contains discrete molecules with a tetrahedral disposition of bonds about the central atom (Bokai, Malinowski & Ablov, 1956) while the violet form is believed to contain polymeric chains in which the cobalt coordination is octahedral (Mellor & Coryell, 1938; Nyholm, 1953; Christie, Barclay, Gill & Nyholm, to be published). The present investigation was initiated in order to test the correctness of the octahedral polymeric structure, which is completely confirmed by the results.

The structure of copper dipyrindine dichloride has also been examined. It is isostructural with mercury dipyrindine dichloride (Grdenić & Krstanović, 1955) and very closely related to that of α -cobalt dipyrindine dichloride. It is convenient to discuss the copper structure first, before passing on to the cobalt compound.

Copper dipyrindine dichloride

The crystals are poorly developed greenish-blue needles, showing marked dichroism. In polarized light they appear deep blue when the electric vector is normal to the needle axis and a much paler blue-green when this vector is parallel to the needle. From oscillation and Weissenberg photographs with $\text{Cu } K\alpha$ radiation ($\lambda = 1.542$ Å) the unit cell is found to be monoclinic,

$$a = 17.00, b = 8.59, c = 3.87 \text{ Å}, \beta = 91^\circ 52',$$

space group $P2_1/n-C_{2h}^5$. The cell contains two molecules of CuPy_2Cl_2 (density, calculated, 1.72 g.cm.^{-3} ; found, 1.73 g.cm.^{-3}) and the copper atoms must therefore occur on centres of symmetry. A characteristic doubling of the reflexions occurs on the X-ray photographs from many but not all of the crystals. It is caused by twinning across (100) so that reflexions (hkl) and ($\bar{h}k\bar{l}$) from the two members of the twin occur at nearly the same scattering angle. Measurement of the separation leads to an accurate determination of the extent to which the interaxial angle differs from 90° . The above cell is only half as large as that reported previously by Cox, Sharrett, Wardlaw & Webster (1936), who gave a as 34 Å instead of 17 Å.

The structure determination is based on analysis of the ($hk0$) and ($h0l$) reflexions, which can be carried out in a quite straightforward fashion. Because of the occurrence of the copper atoms at symmetry centres, the Patterson functions are extremely simple and can be solved without difficulty, yielding approximate positions not only for the chlorine atoms but for the lighter atoms as well. The signs of all but the weak reflexions can be derived without the need for detailed structure-factor calculations. When $h+k+l$ is even, the sign must be positive unless the chlorine contribution is strongly negative (in which case the reflexion is generally weak). When $h+k+l$ is odd, the chlorine contribution, if large, fixes the sign of all but the weak reflexions. The contributions of the carbon and nitrogen atoms have to be taken into account only to fix the signs of the remaining weak reflexions, for which the numerical values of the structure factor were actually computed. These considerations lead to Fourier syntheses of the electron density projected

along [001] and [010] respectively. In the c -axis projection (Fig. 1(a)) every atom is resolved, and although this is not the case in the b projection (Fig. 2)

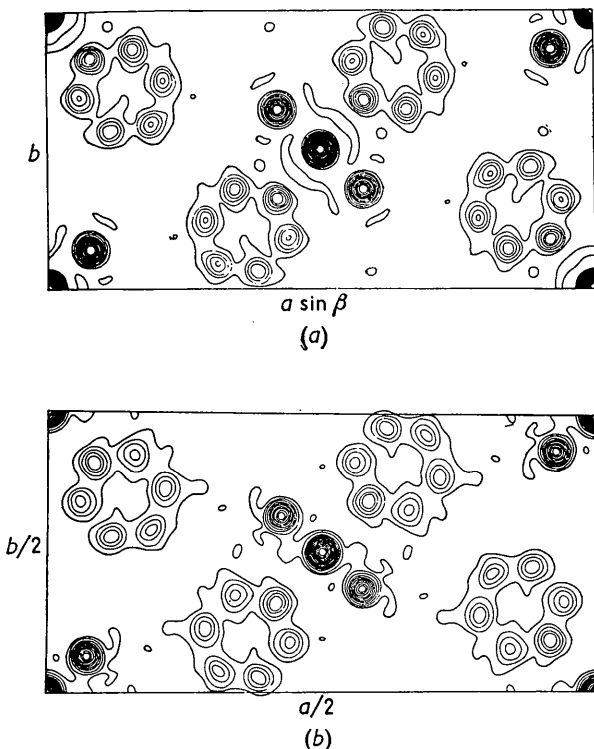


Fig. 1. Electron-density projections $\rho(x, y)$ (a) for copper dipyrindine dichloride, (b) for α -cobalt dipyrindine dichloride. Contours at approximately 1 e. \AA^{-2} intervals for pyridine rings and background, and at double this interval for the heavier atoms.

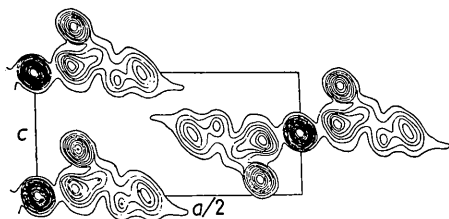


Fig. 2. Electron-density projection $\rho(x, z)$ for copper dipyrindine dichloride. Contours drawn at approximately 3, 6, 9, ... e. \AA^{-2} for copper and chlorine atoms, and at 3, 4.5, 6, 7.5, ... e. \AA^{-2} elsewhere.

Table 1. Fractional coordinates of atoms in asymmetric unit of copper dipyrindine dichloride

| | x/a | y/b | z/c |
|----------------|--------------------|---------------------|--------|
| Cu | 0 | 0 | 0 |
| Cl | 0.078 ₁ | -0.140 ₃ | 0.375 |
| N | 0.079 ₇ | 0.174 ₁ | 0.012 |
| C ₁ | 0.157 ₀ | 0.139 ₁ | -0.069 |
| C ₂ | 0.212 ₀ | 0.253 ₁ | -0.056 |
| C ₃ | 0.190 ₆ | 0.410 ₉ | 0.038 |
| C ₄ | 0.115 ₃ | 0.437 ₅ | 0.125 |
| C ₅ | 0.060 ₂ | 0.315 ₆ | 0.112 |

the tilt of the pyridine rings and the y coordinate of the chlorine atom can both be estimated quite reliably.

Inspection of the Fourier syntheses leads to the coordinates shown in Table 1, where the last significant figure is added mainly in order to eliminate rounding-off errors in the calculation of bond distances and angles (Fig. 3). It should be clear that the principal

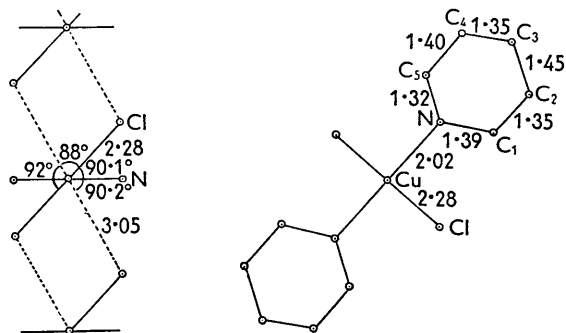


Fig. 3. Interatomic distances (\AA) and angles in copper dipyrindine dichloride, calculated from Table 1.

object of the analysis has been the establishment of the coordination about the central atom and not the attainment of high precision in the structural parameters. No special pains have been taken with the intensity estimates; they were carried out visually and are uncorrected for absorption errors which may be serious, especially for the ($h0l$) reflexions. Nor has the analysis been pushed to the limit of significance attainable with the available data. Indeed, since numerical values of the structure factors have been calculated only for reflexions of doubtful sign, it is not possible to assign a definite value for the precision of the final coordinates. A reasonable guess, based on analysis of the spurious detail present in the Fourier syntheses by a modification of Cochran's (1951) method, is that the chlorine coordinates are not in error by more than 0.02 \AA , so that the Cu-Cl distances should be accurate to ± 0.04 \AA . The carbon and nitrogen positions are much less reliable.

α -Cobalt dipyrindine dichloride

The crystals are again poorly developed needles, violet in colour. They are strongly dichroic, appearing pink when the electric vector is parallel to the needle axis and almost colourless at 90° to the needle. From oscillation and Weissenberg photographs (Cu $K\alpha$ radiation, $\lambda = 1.542$ \AA), the unit cell is monoclinic,

$$a = 34.42, b = 17.38, c = 3.66 \text{ \AA}, \gamma = 90^\circ,$$

where the axes are chosen to emphasize the relationship between this cell and that of the copper compound. The a and b axes are approximately doubled and the c axis, parallel to the needle, is approximately the same length. The symmetry axis is, however, not

the same in the two compounds. Here it is c ; in the copper compound it is b . The density calculated for 8 molecules of CoPy_2Cl_2 in the unit cell is 1.75 g.cm.^{-3} (found, $1.74\text{--}1.77 \text{ g.cm.}^{-3}$). Reflexions occur under the following conditions: (hkl) only if $h+k$ even, $(hk0)$ only if h and k even, $(h00)$ only if $h = 4n$, $(0k0)$ only if $k = 4n$. The first condition shows that the above cell is centred on the C face. Since the interaxial angle γ is not restricted by the lattice symmetry we could have chosen alternative a and c axes defining a primitive cell containing 4 molecules (Fig. 4), but it is

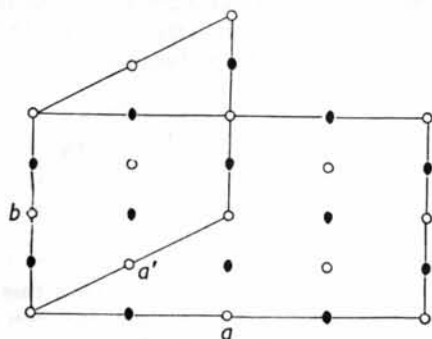


Fig. 4. α -Cobalt dipyridine dichloride. Relationship between C -centred cell (bounded by a, b) and primitive cell, space group P_2/b (bounded by a', b). The centres of symmetry occur at $z = 0$ and $z = \frac{1}{2}$.

more convenient to use the orthogonal non-primitive cell. From the second condition it follows that there exist glide planes normal to c with translation elements $\frac{1}{2}a$ and $\frac{1}{2}b$.

A previous investigation by Cox, Shorter, Wardlaw & Way (1937) led to a monoclinic cell described by

$$a = 17.2, b = 34.1, c = 3.65 \text{ \AA}, \beta \approx 90^\circ, \\ C \text{ centred.}$$

There is no serious disagreement between the axial lengths and those found in the present study but the assignment of b (our a) as the symmetry axis is incorrect.

The crystal has a very unusual type of pseudo-symmetry which made the elucidation of its true symmetry difficult. The interaxial angle γ is indistinguishable from 90° and the $(hk0)$ reflexions appear to possess perfect orthogonal symmetry not only in respect of spacings but also in intensities. The structure projected on (001) must therefore possess orthogonal symmetry and the extinctions require the projected cell described by $a' = \frac{1}{2}a$, $b' = \frac{1}{2}b$ and containing two molecules (Fig. 4), to have the plane group pgg . The cobalt atoms must then occur at centres of symmetry in this projection. Most crystals show an apparent equivalence between the intensities of general reflexions (hkl) and $(\bar{h}k\bar{l})$ (Fig. 5(a)) resulting in an apparently orthorhombic Laue symmetry. The (001) projection, although orthogonal, cannot be reconciled with any C -centred orthorhombic space group, however, so it was concluded that the apparently ortho-

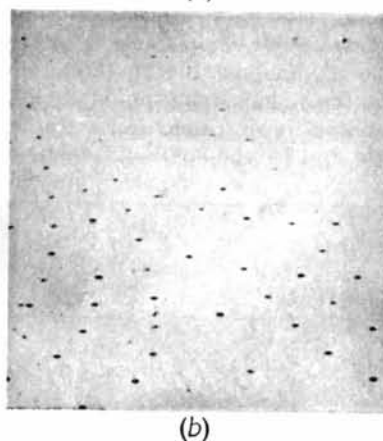
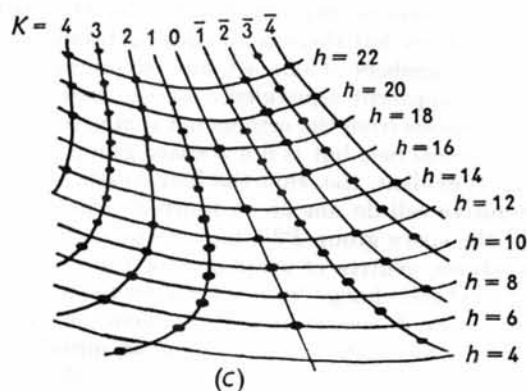
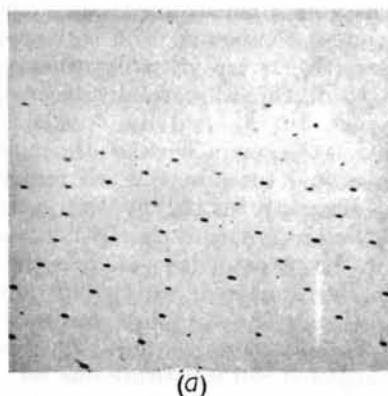


Fig. 5. α -Cobalt dipyridine dichloride. Corresponding portions of (hkl) equi-inclination Weissenberg photographs of (a) typical twinned crystal and (b) untwinned crystal. The (h, k) indexing is shown in (c).

rhombic symmetry must be an artifact arising as a result of twinning. This proved to be the case although more than a dozen crystals were examined before one was found to show the expected monoclinic symmetry in its X-ray pattern (Fig. 5(b)). The true symmetry is C_{2h}^1 ($P2/b$ referred to the primitive cell of Fig. 4). We have thus an example of a monoclinic crystal which appears to show perfect orthogonal symmetry in its projection down the unique axis.

A striking similarity is to be seen between the $(hk0)$

intensity patterns from α -cobalt dipyridine dichloride and from the copper compound. The corresponding Fourier syntheses (Fig. 1) are virtually isomorphous. It is important to distinguish carefully between the two cases, however. In Fig. 1(a) the b axis, in the plane of the paper, is the symmetry axis; the molecules at the cell corners and those at the cell centres are identical, being mutually related by the symmetry operations of the space group $P2_1/n$. In Fig. 1(b) the c axis, normal to the plane of the paper, is the symmetry axis and the projected cell covers only one quarter of the real cell. The structure consists of two sets of formally independent molecules; those at the corners of the projected cell constitute one set, those at the centres constitute another. Members of a given set are transformed into one another by the space-group operations but there is no such operation which transforms members of one set into members of the other. The apparent equivalence of the two sets in projection arises from the orthogonal symmetry of the $(hk0)$ reciprocal net, but is not a space-group requirement. It is evident, too, that the four cobalt atoms in the primitive cell do not lie on fourfold general positions of the space group $P2/b$ but on two sets of twofold positions, centres of symmetry or rotation axes.

The structural change from the copper to the cobalt structure cannot consist merely of some small displacement of alternate molecules from an initial array of identically oriented molecules, to double the a and b axes. The general reflexions with h and k both odd are not weak but are quite comparable in intensity to the others. Although analysis of the $(h0l)$ reflexions is complicated by the serious overlapping of the atoms in the corresponding projections down the b axis, 17.38 Å in length, and by the contributions from two

independent molecules to the asymmetric unit of the projected cell, the structure can nevertheless be derived (apart from one ambiguity) from the Patterson projection (Fig. 6(a)) together with the results of the (x, y) Fourier synthesis. In the first place it is evident that the z component of the cobalt-chlorine vector is $\frac{1}{2}c$ or very nearly so, which establishes that the structure consists of polymeric chains running parallel to c with octahedral coordination about the cobalt atoms. More detailed analysis of the Patterson function shows that the cobalt atoms cannot occupy two of the four pairs of symmetry centres of $P2/b$ but lie instead on the set of twofold rotation axes (Fig. 4). Denoting their x, z coordinates in the orthogonal centred cell as

$$0, z_1 \quad 0, \bar{z}_1 \quad \frac{1}{4}a, z_2 \quad \frac{1}{4}a, \bar{z}_2,$$

the best fit is obtained with $z_1 = 0.15$, $z_2 = 0.44$, values confirmed by structure-factor calculations based on a simplified model in which the cobalt atoms and pyridine rings of each molecule are assumed to lie exactly in a plane parallel with (001) with the chlorine atoms $\frac{1}{2}c$ above and below this plane. The general features of the structure are seen in the Fourier projection on (101) (Fig. 6(b)) in spite of the poor resolution. The Co-N bonds and the N-C₃ axes of the pyridine rings lie in a plane normal to c and any tilt of the rings must be quite small.

The ambiguity which cannot be resolved from the projections alone is whether the cobalt atoms have coordinates $(0, 0, 0)+$ and $(\frac{1}{2}, \frac{1}{2}, 0)+$ (a) or (b):

$$\begin{aligned} (a) & 0, \frac{1}{4}, z_1; 0, \frac{3}{4}, \bar{z}_1; \frac{1}{4}, 0, z_2; \frac{1}{4}, \frac{1}{2}, \bar{z}_2; \\ (b) & 0, \frac{1}{4}, z_1; 0, \frac{3}{4}, \bar{z}_1; \frac{1}{4}, 0, \bar{z}_2; \frac{1}{4}, \frac{1}{2}, z_2. \end{aligned}$$

Comparison of calculated structure factors with rough intensity observations for (hkl) reflexions leaves no doubt that alternative (b) is correct.

The structure may now be described as follows: The 8 Co atoms are situated on twofold rotation axes at $(0, 0, 0)+$ and $(\frac{1}{2}, \frac{1}{2}, 0)+$ coordinates (b). The coordinates of the atoms referred to each cobalt atom as origin are given in Table 2, where zero tilt of the pyridine rings about the Co-N-C₃ axis has been assumed. The two independent molecules, although not formally equivalent, appear to be identical. Their environments, identical in the (001) projection, are not identical in space. If the z separation between alternate molecules at $x = 0$ (and $x = \frac{1}{2}$) is taken to be $2z_1 = 0.30$, then the corresponding separation between molecules at $x = \frac{1}{4}$ (and $x = \frac{3}{4}$) is $1 - 2z_2 = 0.12$. Some interatomic distances and angles are given in Fig. 7.

Although the x, y parameters are of about the same accuracy as those derived in the analysis of the copper compound, the z parameters are rather less certain. In particular, a small tilt of the pyridine rings about the Co-N-C₃ axis is quite compatible with the X-ray results and, indeed, appears quite likely from packing considerations.

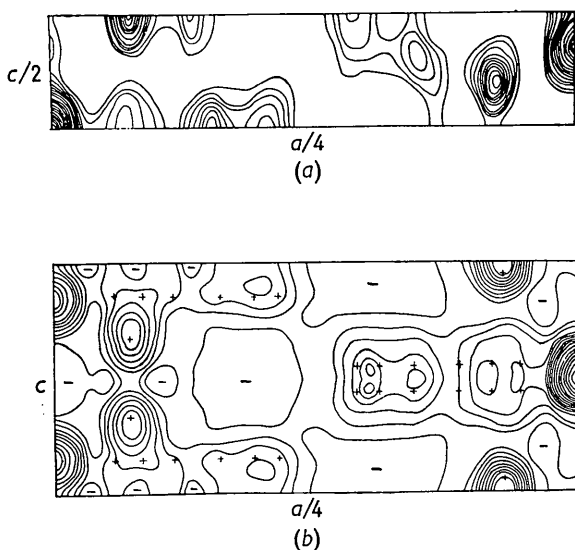


Fig. 6. α -Cobalt dipyridine dichloride. (a) Patterson projection $P(x, z)$, contours at equal but arbitrary intervals. (b) Electron-density projection $\rho(x, z)$, contours at approximately 3, 6, 9, ... e.Å⁻². Troughs are indicated by dashes.

Table 2. Coordinates of atoms in α -cobalt dipyridine dichloride referred to the cobalt atom as origin

$X = 2x/a$, $Y = 2y/b$, $Z = z/c$ are listed for comparison with coordinates of Table 1.

| | X | Y | Z |
|----------------|--------------------|---------------------|------|
| Co | 0 | 0 | 0 |
| Cl | 0.073 ₃ | -0.130 ₀ | 0.50 |
| N | 0.082 ₈ | 0.184 ₄ | 0 |
| C ₁ | 0.157 ₃ | 0.154 ₇ | 0 |
| C ₂ | 0.212 ₈ | 0.272 ₅ | 0 |
| C ₃ | 0.190 ₈ | 0.425 ₉ | 0 |
| C ₄ | 0.113 ₀ | 0.449 ₇ | 0 |
| C ₅ | 0.057 ₇ | 0.325 ₆ | 0 |

The 8 molecules occur at

$$\begin{aligned} (0, \frac{1}{2}, z_1) + x, y, z; & -x, -y, z; \\ & \frac{1}{2}+x, \frac{1}{2}+y, z; \quad \frac{1}{2}-x, \frac{1}{2}-y, z; \\ (0, \frac{1}{2}, -z_1) + x, y, -z; & -x, -y, -z; \\ & \frac{1}{2}+x, \frac{1}{2}+y, -z; \quad \frac{1}{2}-x, \frac{1}{2}-y, -z; \\ (\frac{1}{2}, 0, z_2) + -x, y, z'; & x, -y, z'; \\ & \frac{1}{2}-x, \frac{1}{2}+y, z'; \quad \frac{1}{2}+x, \frac{1}{2}-y, z'; \\ (\frac{1}{2}, 0, -z_2) + -x, y, -z'; & x, -y, -z'; \\ & \frac{1}{2}-x, \frac{1}{2}+y, -z'; \quad \frac{1}{2}+x, \frac{1}{2}-y, -z'; \end{aligned}$$

with $z_1 = 0.15$, $z_2 = -0.44$.

The $\pm z_1$ molecules are formally independent of the $\pm z_2$ molecules but their x, y coordinates are related by the orthogonality of the (001) projection.

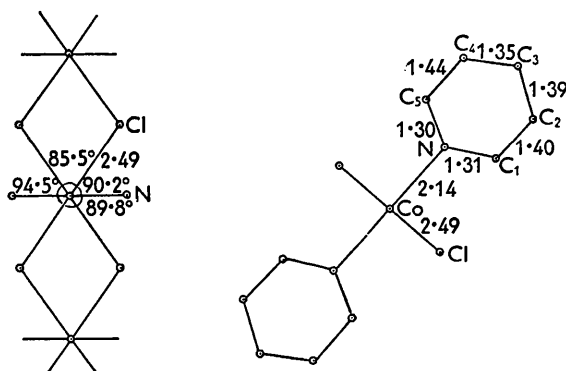
Fig. 7. Interatomic distances (\AA) and angles in α -cobalt dipyridine dichloride, calculated from Table 2.

Table 3. Intermolecular distances

- (A): CoPy_2Cl_2 with pyridine rings assumed to lie in planes normal to c_1
 (B): Same with pyridine rings tilted by about 10° about Co-N-C_3 line
 (C): CuPy_2Cl_2

See Fig. 8 for key

| Type | (A) | (B) | (C) |
|------------|-------------------|-------------------|-------------------|
| a | 3.36 \AA | 3.25 \AA | 3.32 \AA |
| b | 3.40 | 3.29 | 3.27 |
| c_1, c_2 | 3.78, 3.96 | 3.84, 3.89 | 3.81 |
| d_1, d_2 | 3.85, 3.79 | 3.90, 3.82 | 3.73 |
| e_1, e_2 | 3.45, 3.61 | 3.52, 3.52 | 3.76 |
| f_1, f_2 | 3.60, 3.75 | 3.66, 3.66 | 3.88 |
| g_1, g_2 | 3.70, 3.56 | 3.59, 3.64 | 3.75 |
| h_1, h_2 | 3.79, 3.65 | 3.69, 3.73 | 3.85 |

The assumption that the rings lie exactly parallel to the (001) plane leads to the intermolecular distances of Table 3. The packing is satisfactory but distances which appear equivalent in projection prove to be slightly different in space because of the non-equivalence of the two sets of molecules. These differences are minimized if a small tilt (of about 10°) of the pyridine rings about the Co-N-C_3 axis is assumed to occur, as in Fig. 8. Such a tilt is compatible with the

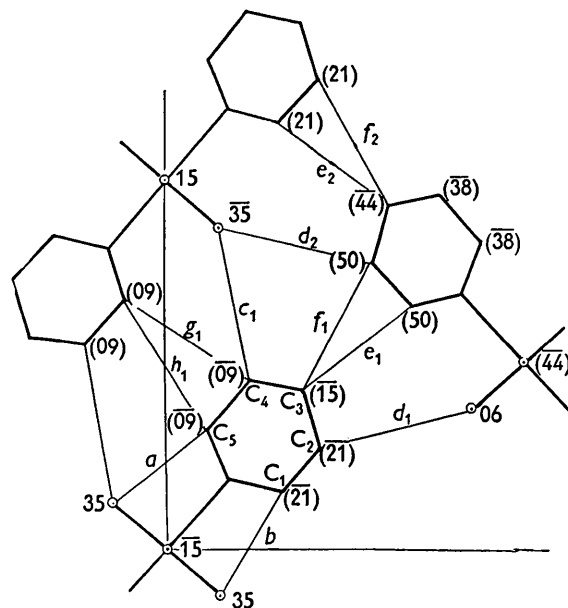


Fig. 8. Key to intermolecular distances listed in Table 3. Heights above or below $z = 0$ are given as multiples of $c/100$. In the untilted structure the carbon atoms have the same z coordinates as the cobalt atom of the same molecule. In the tilted structure their z coordinates are shown in brackets.

c -axis periodicity of 3.66 \AA if the thickness of the pyridine rings is taken as not more than 3.60 \AA . The resulting intermolecular approaches are at least as satisfactory as in the untilted model if not slightly better. In either case, the packing of the aromatic rings appears to be much tighter in α -cobalt dipyridine dichloride than in the simpler copper structure, and this is consistent with the smaller molecular volume found for the former, 274 \AA^3 , as against 283 \AA^3 for the latter.

Discussion

The principal points of stereochemical interest which emerge from this X-ray analysis of α -cobalt dipyridine dichloride and copper dipyridine dichloride are:

(1) Both structures consist of polymeric chains in which each metal atom is surrounded by four chlorine atoms and two nitrogen atoms.

(2) In CoPy_2Cl_2 the chlorines are equidistant from pairs of metal atoms, Co-Cl , 2.49 \AA (compare with the somewhat similar chain-like structure of

$\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$, Co-Cl, 2.53, 2.54 Å (Vainstein, 1949)). In CuPy_2Cl_2 each metal atom has two closer chlorine neighbours (2.28 Å) and two more distant (3.05 Å), a type of asymmetry often encountered in cupric complexes (see Wells, 1950). The metal-to-nitrogen distances are Co-N, 2.14 Å and Cu-N, 2.02 Å.

(3) In both structures the angles between the bonds at the metal atom are close to right-angles.

The difference between the violet and blue forms of cobalt dipyridine dichloride is not one of *cis-trans* isomerism, as had once been thought. The violet α -form is shown here to have a polymeric structure with octahedral coordination about the central atom, and, although X-ray evidence is not yet available for the blue dipyridine dichloride itself, a structure composed of discrete tetrahedral molecules is indicated from the X-ray analysis of blue cobalt di-*p*-toluidine dichloride (Bokai, Malinowski & Ablov, 1956) and by other physico-chemical evidence (Nyholm, 1953).

The occurrence of cobaltous diammines in two isomeric forms is quite general (Sidgwick, 1950) and the above distinction is likely to hold throughout, the violet or pink forms containing polymeric chains, the blue forms discrete tetrahedral molecules.

Manganous dipyridine dichloride is isostructural with α - CoPy_2Cl_2 (Cox *et al.*, 1937) and so must contain polymeric chains with octahedral coordination about the manganese atom, not discrete square coplanar molecules as previously reported.

The type of coordination found in CuPy_2Cl_2 , with four bonds in a square coplanar arrangement and two weaker bonds normal to the plane to complete a distorted octahedron, occurs in many cupric complexes. Here it is derived by a simple distortion of the more symmetrical coordination occurring in the cobalt compound in just the same way as the distorted octahedral environment of the copper atoms in $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (Harker, 1936; MacGillavry & Bijvoet, 1936) is derived from the more regular environment in $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$ (Vainstein, 1949). Orgel (1952, 1956) has pointed out that this type of distortion is related to the Jahn-Teller effect. The undistorted structure is unstable for Cu^{++} with 9 *d* electrons and there is a gain in stability if four coplanar bonds contract and the other two expand. A more detailed discussion of the stereochemistry of cupric compounds has recently been published (Orgel & Dunitz, 1957). It is of interest that the symmetry of the *bond angles* around the copper atom is retained, the distortion occurring entirely along the octahedral set of bond directions; even the angle between the nitrogen and the more distant chlorine atom is almost exactly 90°.

The structure of CuPy_2Cl_2 is isomorphous with that of HgPy_2Cl_2 (Grdenić & Krstanović, 1955), where the mercury atoms are surrounded by two chlorine atoms at 2.34 Å, two nitrogens at 2.60 Å and two more distant chlorines at 3.25 Å in a distorted octahedral arrangement. Grdenić regards this structure as being built from discrete molecules of HgCl_2 with pyridine

of crystallization, held together by the longer $\text{Hg} \cdots \text{Cl}$ contacts. Such a description is clearly inapplicable to CuPy_2Cl_2 , where the pyridine rings are bound very strongly to the metal.

At least four (Mn, Co, Cu, Hg) dipyridine dichlorides are thus known to exist with the polymeric chain-like structure, which would appear therefore to represent quite generally a very stable structure for this type of complex, although tetrahedral coordination also occurs, certainly for Co, and possibly for the other metals too. The stability of the chain-like structure can readily be understood for it is obvious that the packing of the chlorine atoms and pyridine rings within a single chain can hardly be improved on. In every case the chains are parallel to the *c* axis (Mn, 3.73; Co, 3.66; Cu, 3.87; Hg, 3.90 Å), which is the needle axis of the crystals.

The kind of structure represented by the CoPy_2Cl_2 , in which two or more independent molecules contribute to the asymmetric unit of the crystal, is unusual but in no way unique. The same situation is found in the structures of stilbene, azobenzene and tolane (Robertson & Woodward, 1937, 1938; de Lange, Robertson & Woodward, 1939), which are based on monoclinic but pseudo-orthorhombic cells of symmetry C_{2h}^5 containing two sets of non-equivalent molecules. The two types of molecules, although formally independent, are almost but not quite identical. The approximation to pseudo-orthorhombic character is much less pronounced in these compounds, compared with CoPy_2Cl_2 , and the similarity of corresponding reflexions holds good only for the low orders, even in tolane where the interaxial angle of the pseudo-orthorhombic cell is exactly 90°. In the cobalt complex, on the other hand, the oblique projection appears to have exact *pgg* symmetry, at least out to the limit of Cu $K\alpha$ radiation. The intermolecular packing in the stilbene, azobenzene and tolane structures is very similar to that in the cobalt complex, with the *p* carbon atom of each ring pointing approximately midway between the *o* and *m* carbons of an oppositely oriented molecule. Another example of a crystal showing apparently perfect orthogonal symmetry in its oblique projection is manganite, $\text{MnO}(\text{OH})$ (Buerger, 1936).

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Morphology and Structure of Anhydrous Nickel Sulphate

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The crystal structure of NiSO_4 has been determined. The crystals are orthorhombic with $a_0 = 5.155$, $b_0 = 7.842$, $c_0 = 6.338$ Å, $Z = 4$, space group $Cmcm$. The unknown parameters were determined by trial and error. The S atoms lie at the centre of an almost regular tetrahedron of O atoms. The Ni atoms lie at the centre of a distorted octahedron of O atoms.

1. Introduction

Among the compounds of the general formula MRO_4 there are some whose structure, notwithstanding their simple composition, is still unknown. Such compounds are, for example, the anhydrous sulphates of the bivalent metals copper, nickel, iron and cobalt.

The reason for our incomplete knowledge of the crystallographic properties of these compounds is that they either form unstable, very hygroscopic crystals which are difficult to handle for X-ray analysis, or do not form single crystals of satisfactory dimensions, but only a fine crystalline powder.

2. Experimental

In order to determine the structure of these compounds we have tried to prepare crystals suitable for X-ray analysis. Up to now we have succeeded, by slow evaporation of a nickel sulphate hydrate solution in sulphuric acid, in obtaining well formed crystals of anhydrous nickel sulphate, NiSO_4 , suitable for crystallographic measurements and X-ray analysis; the results are given in this paper.

So far as we know from the accessible literature no crystallographic and X-ray data are reported for anhydrous nickel sulphate. According to the litera-

ture, good light-yellow crystals can be obtained either by evaporation of a solution of nickel sulphate hydrate in dense sulphuric acid (Etard, 1878), or by co-fusion of nickel sulphate hydrate or nickel oxide with ammonium sulphate (Lepierre & Lachaud, 1892). Two crystal forms are mentioned, one octahedral and one prismatic, depending on the conditions of formation. For these two forms no further crystallographic or optical data are known.

The crystals we have prepared are of various dimensions up to 3 mm. in length. They are thick plates of rhombic habit, with a set of narrow planes parallel to the edges of the rhomb.

Under the polarizing microscope the extinction directions are found to coincide with the diagonals of the rhomb; γ is parallel to the shorter and α to the longer diagonal. Goniometric measurements show that the crystals belong to the orthorhombic bipyramidal class and are bounded by the forms $\{001\}$, $\{110\}$, $\{111\}$ and $\{112\}$, with $\{001\}$ dominant. Besides these platy crystals we have also observed some which have a prismatic shape along $[1\bar{1}0]$. Perhaps the supposed dimorphism of the nickel sulphate crystals mentioned in the literature is due to this difference in habit. The following mean values of the angles between the planes were measured goniometrically