

tions expérimentales. On peut donc conclure que les positions hydrogène sont essentiellement imposées par le champ cristallin.

En ce qui concerne le fait trouvé expérimentalement que H et D n'occupent pas les mêmes positions, il faut signaler que le champ cristallin possède autour des positions d'équilibre calculées des gradients peu accusés. De ce fait, un effet de masse (isotopique) peut jouer. Cet effet peut trouver son origine dans l'énergie vibrationnelle de point zéro qui n'est certainement pas négligeable pour fixer les positions moyennes des protons et des deutons. Un calcul sérieux de ce phénomène ne peut être entamé par nous pour le moment.

Conclusion

A notre connaissance, cette étude montre d'une manière nette l'effet isotopique de H et D dans une structure cristalline. Dans la littérature, on connaît trois composés pour lesquels les structures protonique et deutonique ont été déterminées simultanément. Pour $\text{NaHF}_2\text{-NaDF}_2$ (McGaw & Ibers, 1963) et pour l'acide oxalique dihydraté (Delaplane & Ibers, 1966), les auteurs ne signalent aucune différence sensible entre les positions H et D. Hamilton & Ibers (1963) ont étudié les acides HCrO_2 et DCrO_2 . La liaison O-D-O est sans aucun doute dissymétrique, par contre, pour la liaison O-H-O, le modèle symétrique est celui qui présente le meilleur accord avec l'expérience. Les mesures par absorption infrarouge confirment d'ailleurs ces résultats, (Snyder & Ibers, 1962). L'acide chromique constitue donc le seul exemple semblable à celui étudié ici.

Le calcul électrostatique que nous avons mené nous apparaît comme le premier exemple traité dans un cristal. Il est étonnant de voir combien il rend compte des faits expérimentaux, la dissymétrie des liaisons. L'énergie des liaisons hydrogène calculée est également raisonnable.

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The Crystal Structure of *N,N'*-Dimethyl-4,4'-bipyridinium Tetrachlorocuprate

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$(\text{CH}_3 \cdot \text{NC}_5\text{H}_4 \cdot \text{C}_5\text{H}_4\text{N} \cdot \text{CH}_3)^{2+}[\text{CuCl}_4]^{2-}$ forms orthorhombic crystals, space group *Pbcn*, and each unit cell of dimensions $a=12.63$, $b=16.18$, $c=7.52$ Å, all ± 0.01 Å, contains four bipyridinium ions and four tetrachlorocuprate ions arranged in layers perpendicular to the *b* axis. The tetrachlorocuprate ions have a flattened tetrahedral structure and the bipyridinium ions are planar. Each nitrogen atom has two neighbouring chlorine atoms, one on either side of the bipyridinium plane but not directly above and below it, so that the $\text{N} \cdots \text{Cl}$ distances are 3.51 and 3.55 Å and the $\text{Cl} \cdots \text{N} \cdots \text{Cl}$ angle is 144° .

Introduction

Some *N,N'*-dimethyl-4,4'-bipyridinium salts have powerful herbicidal properties (Boon, 1964), many are highly coloured, suggesting the possibility of charge transfer between the component ions, and many form

complexes with a wide variety of organic molecules. In view of these interesting properties, the crystal structures of a number of these salts have been determined and that of a complex between the dichloride and hydroquinone is under investigation. In this paper the crystal structure is reported of what was originally thought to be a complex between *N,N'*-dimethyl-4,4'-bipyridinium dichloride and copper(II) chloride but which soon turned out to be *N,N'*-dimethyl-4,4'-

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bipyridinium tetrachlorocuprate. It therefore provides additional information about the structure of the tetrachlorocuprate ion.

Experimental

Orange-yellow crystals of the tetrachlorocuprate were supplied by the Mond Division of Imperial Chemical Industries, Ltd. When the crystals were examined in plane-polarized light, a dichroic effect was observed, the colour ranging from orange to a very pale yellow. Maximum absorption of light occurred when the electric vector of the light was vibrating perpendicular to the needle (*c*) axis.

Oscillation and equi-inclination Weissenberg photographs were taken with a crystal rotating about its *c* axis with Cu *K*α radiation ($\lambda=1.542 \text{ \AA}$). Unit-cell dimensions determined from these photographs were later refined during more detailed examination with a linear diffractometer (Arndt & Phillips, 1961) with Mo *K*α radiation ($\lambda=0.7107 \text{ \AA}$). Intensity data for the *hk0*, *hk1*, ... *hk10* reciprocal lattice levels were collected by use of the moving-crystal, stationary-counter technique. Intensity measurements were made with a scintillation counter and a pulse height selector. The crystal was approximately spherical with a diameter of 0.4 mm. A total of 1676 independent reflexions were measured, which were then corrected for Lorentz and polarization factors but not for absorption or extinction.

Crystal data

$(\text{CH}_3)_2\text{NC}_5\text{H}_4\cdot\text{C}_5\text{H}_4\text{N}\cdot\text{CH}_3)^{2+}(\text{CuCl}_4)^{2-}$, $M=391.4$. Orthorhombic.

$a=12.63 \pm 0.01$, $b=16.18 \pm 0.01$, $c=7.52 \pm 0.01 \text{ \AA}$, $U=1536.7 \text{ \AA}^3$, $D_m=1.98 \text{ g.cm}^{-3}$, $D_c=2.00 \text{ g.cm}^{-3}$, $Z=4$, $F(000)=788$, Mo *K*α ($\lambda=0.7107 \text{ \AA}$), $\mu=21.5 \text{ cm}^{-1}$.

Absent spectra, *hk0* when $h+k$ is odd, *h0l* when l is odd, *0kl* when k is odd. Space group *Pbcn* (No. 60).

Determination and refinement of the structure

By interpretation of a three-dimensional Patterson synthesis, the copper atom was located on the two-

fold rotation axis, and it was deduced that the four chlorine atoms associated with the copper atom were either in a square planar or a tetrahedral arrangement around this atom. Structure factor calculations, for the *hkl* reflexions, for the copper and chlorine atoms confirmed the latter configuration. A three-dimensional Fourier synthesis was computed with use of the phases from the structure factors for the tetrahedral configuration and from this electron density function the positions of all the carbon and nitrogen atoms in the asymmetric unit were determined.

Refinement was carried out by the block-diagonal, least-squares method with the use of a program written by R.D. Diamand. The weighting scheme employed was $\sqrt{w}=1$ if $|F_o| < F^*$, otherwise $\sqrt{w}=F^*/|F_o|$ with F^* adjusted to give approximately equal $\Sigma w(|F_o| - |F_c|)^2$ for all ranges of $|F_o|$. The scattering factors of Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955) were used for all atoms. Reflexions too weak to be observed were not included in the analysis, leaving a total of 1672 reflexions for the initial stages of refinement. Five cycles of isotropic least-squares refinement reduced the residual $R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$, from 0.31 to 0.13. For subsequent refinement the temperature factors were allowed to vary anisotropically. Four further cycles reduced R to 0.081. An analysis of agreement between observed and calculated structure factors showed that sixteen reflexions were giving particularly bad agreement. As these were all either large and of very low $\sin \theta$, making extinction likely, or very close to the crystal rotation axis and hence difficult to measure, they were excluded from further refinement. After another three cycles R had dropped to 0.075. At this stage it was decided to exclude from the analysis the 122 reflexions which had an observed amplitude of less than unity on the absolute scale. These were so small as to be insignificantly above the background. The refinement with the remaining 1534 reflexions converged after two further cycles with $R=0.058$.

A three-dimensional difference Fourier synthesis computed with $(F_o - F_c)$ as coefficients revealed the locations of all the hydrogen atoms, though those of the methyl group were not clearly defined. Three cycles

Table 1. Fractional coordinates and thermal parameters (each $\times 10^5$), with standard deviations in parentheses, for atoms other than hydrogen

B_{ij} are coefficients in the temperature factor expression

$$\exp - [B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{23}kl + B_{13}hl + B_{12}hk].$$

	<i>x</i>	<i>y</i>	<i>z</i>	B_{11}	B_{22}	B_{33}	B_{23}	B_{13}	B_{12}
Cu	0	22141 (4)	25000	407 (9)	204 (5)	1748 (25)	0	-66 (12)	0
Cl(1)	10995 (9)	13396 (7)	39003 (20)	595 (10)	297 (6)	2188 (32)	246 (15)	-342 (20)	151 (8)
Cl(2)	11671 (8)	31149 (6)	13379 (20)	500 (10)	263 (6)	2065 (30)	198 (13)	155 (18)	-56 (7)
C(1)	44985 (30)	9577 (20)	20058 (50)	515 (25)	225 (13)	1338 (66)	-80 (42)	502 (62)	11 (29)
C(2)	40012 (40)	2254 (20)	15022 (60)	697 (31)	236 (15)	1857 (87)	-5 (52)	245 (82)	-133 (33)
C(3)	39949 (30)	16850 (20)	14891 (60)	566 (28)	218 (14)	1889 (85)	-142 (52)	178 (75)	27 (31)
C(4)	30684 (30)	2362 (20)	5548 (60)	633 (30)	274 (15)	1573 (78)	-5 (51)	381 (73)	-131 (33)
C(5)	30740 (40)	16667 (30)	5353 (60)	550 (28)	297 (16)	2056 (93)	1 (60)	291 (79)	69 (35)
C(6)	16248 (40)	9483 (30)	-9447 (70)	552 (30)	460 (22)	2297 (110)	-453 (74)	-176 (89)	2 (41)
N	26174 (30)	9525 (20)	856 (40)	474 (22)	352 (14)	1473 (59)	-139 (47)	-334 (57)	-19 (28)

of least-squares, including the hydrogen atoms with isotropic temperature factors, reduced the residual to its final value of 0.053 for 119 positional, thermal and scale parameters. The observed structure factors are compared with the values calculated from the final set of atomic parameters in a table available elsewhere (Russell, 1967).†

The final positional and thermal atomic parameters, together with their standard deviations, obtained by inversion of the least-squares normal-equations matrix, are summarized in Tables 1 and 2. Fig. 1 shows the bond lengths and interbond angles, together with their standard deviations.

Table 2. Fractional coordinates ($\times 10^3$) and isotropic thermal parameters, with standard deviations in parentheses, for hydrogen atoms

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å ²)
H(1)	427 (4)	-25 (4)	182 (7)	3.1 (1.2)
H(2)	427 (4)	222 (3)	186 (7)	2.4 (1.1)
H(3)	262 (4)	-24 (3)	22 (8)	3.8 (1.2)
H(4)	271 (4)	212 (3)	2 (7)	2.8 (1.1)
H(5)	383 (9)	384 (5)	472 (12)	10.4 (2.4)
H(6)	323 (7)	377 (5)	280 (12)	11.8 (2.3)
H(7)	358 (6)	460 (6)	350 (11)	7.8 (2.0)

Description of the structure and discussion

Fig. 2 shows the structure projected along the *c* axis.

† Copies of this Table may be purchased from the Science Librarian, The University, Nottingham, England.

It consists of layers of chlorocuprate ions, interleaved with double layers of bipyridinium ions, all the layers being perpendicular to the *b* axis. Each layer of chlorocuprate ions contains as many ions as a double layer of bipyridinium ions, so maintaining the 1:1 ratio of components.

The chlorocuprate ions are in an approximately hexagonal close packed arrangement within each layer as can be seen from Fig. 3. Each $[\text{CuCl}_4]^{2-}$ group has its copper atom on a twofold axis and its chlorine atoms in a distorted tetrahedral configuration, such that the $\text{Cl}(1)\text{-Cu-Cl}(1')$ plane makes a dihedral angle of 67.8° with the $\text{Cl}(2)\text{-Cu-Cl}(2')$ plane. The $\text{Cl}(1)\text{-Cu-Cl}(1')$ plane is almost parallel (dihedral angle 6°) to the planes of the bipyridinium ions which form the adjacent layer on one side of the $[\text{CuCl}_4]^{2-}$ ion and the $\text{Cl}(2)\text{-Cu-Cl}(2')$ plane is more accurately parallel (within 0.5°) to the planes of the bipyridinium ions in the adjacent layer on the other side. This is achieved by successive double layers of bipyridinium ions having their planes almost parallel to (101) and (10 $\bar{1}$). The perpendicular separation of the plane $\text{Cl}(2)\text{-Cu-Cl}(2')$ from the planes of the bipyridinium ions *c*/2 above and below it in the adjacent layer is 3.22 Å and the corresponding average separation for the plane $\text{Cl}(1)\text{-Cu-Cl}(1')$ and the planes of the bipyridinium ions *a*/2 above and below it in the other adjacent layer is 3.27 Å. However, the sideways displacement of the successive layers means that there are no interatomic distances as short as this, and the Cl atoms are not directly above and below the nitrogen atoms, as might

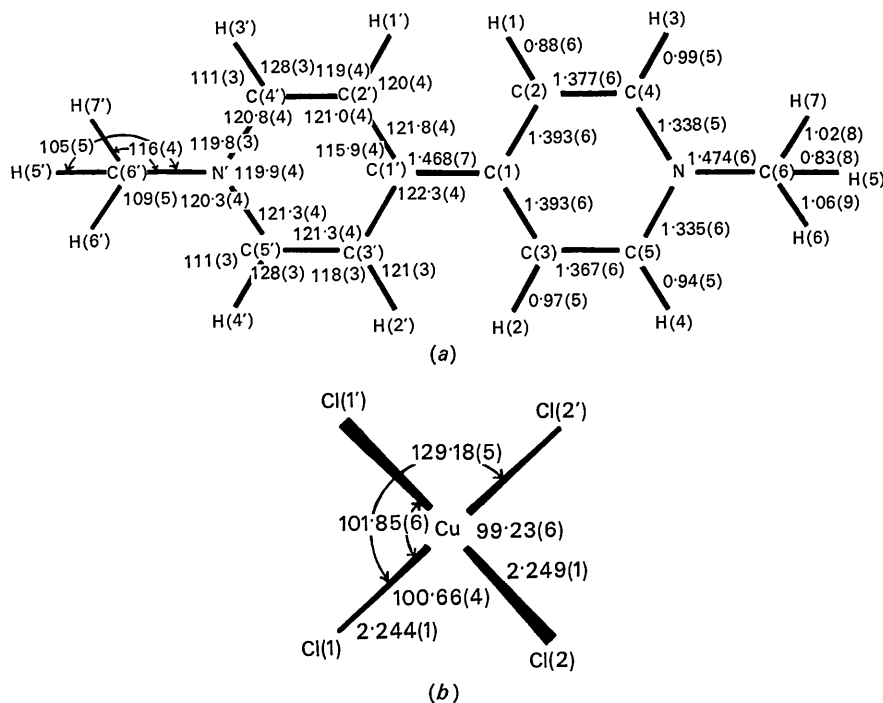


Fig. 1. Dimensions of (a) the *N,N'*-dimethyl-4,4'-bipyridinium ion and (b) the tetrachlorocuprate ion. Standard deviations are indicated in parentheses.

have been expected. Instead, on one side of each N atom there is a Cl(1) atom at a distance of 3.51 Å, and on the other side there is a Cl(2) atom at a distance of 3.55 Å, and the Cl(1)⋯N⋯Cl(2) angle is 144°. Without this sideways displacement a number of contacts between atoms would become too short. One of these contacts [Cl(1)⋯C(6) = 3.75 Å] accounts for the dihedral angle of 6° between the Cl(1)–Cu–Cl(1') and the bipyridinium ion planes. If the C(6) and Cl(1) atoms did not swing away from one another, the separation would be as short as 3.60 Å. Discussion as to whether the interionic contacts imply any charge transfer interaction will be deferred to a later paper.

Each bipyridinium ion is planar within the limits of accuracy (maximum deviation from the mean plane 0.011 Å or three standard deviations; root mean square deviation 0.009 Å). The C(1)–C(1') distance of 1.47 Å between the two rings is approximately that expected for a single bond between two *sp*²-hybridized carbon atoms, suggesting that there cannot be much conjugation between the rings. However, the C(2)–C(1)–C(3) angle of 115.9° in the ring and the coplanarity of the two rings both indicate a small amount of conjugation. All other bond lengths and angles in the bipyridinium ion are normal.

The bonds Cu–Cl(1) and Cu–Cl(2) differ by 0.005 Å (approximately 5 standard deviations). However, since there is no apparent reason for this difference, and since it is small, it may not be real. The 67.8° angle between the planes defined by Cl(1)–Cu–Cl(1') and Cl(2)–Cu–Cl(2') would be 90° for a regular tetrahedral arrangement and 0° for square planar. The configuration of the chlorocuprate ion may be envisaged by starting with a square arrangement with Cl(1) and Cl(2') at opposite corners and forcing these two atoms down from the plane, and the Cl(1') and Cl(2) atoms up from the plane, until the angles Cl(1)–Cu–Cl(2') and Cl(1')–Cu–Cl(2) both equal 129.18°. This is nearer to the 110° required for a tetrahedral configuration than to 180° for square planar, so the ion may best be described as having a flattened tetrahedral structure. The same ion has also been studied in this configuration in Cs₂CuCl₄ by Helmoltz & Kruh (1952), and in Cs₂CuCl₄ and [N(CH₃)₄]₂.CuCl₄ by Morosin & Lingafelter (1961). Of the six Cl–Cu–Cl angles in each of these structures, there are four of about 102° and two of about 127° and the mean Cu–Cl distance is about 2.22 Å. Considering that these values were derived from projections only, they are quite consistent with those found in the present, more accurate study.

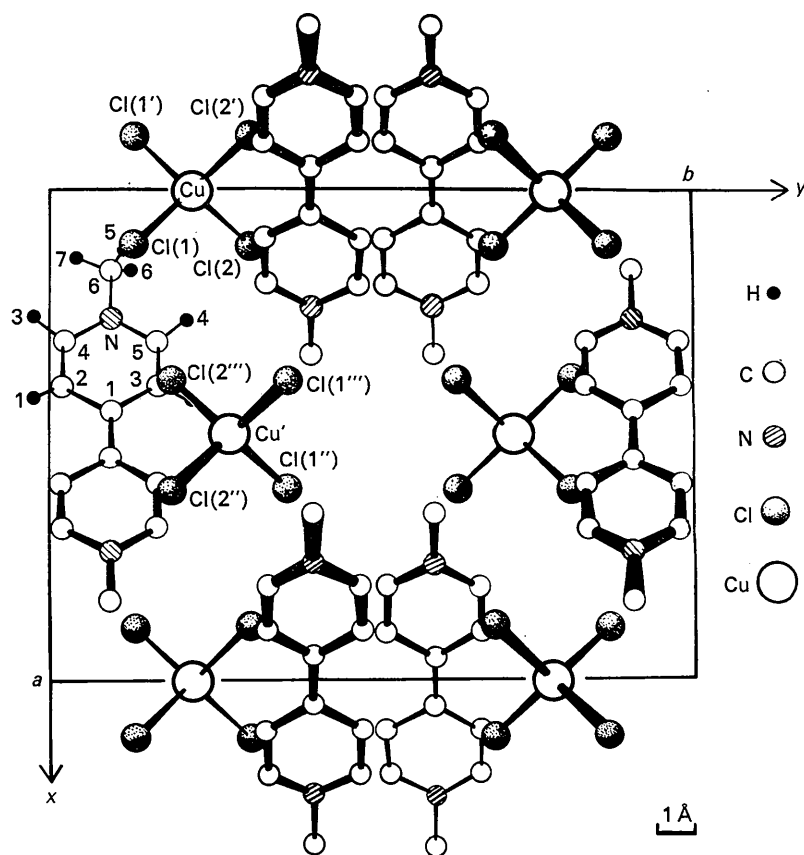


Fig. 2. The structure seen along the *c* axis, showing the numbering of atoms. Hydrogen atoms are omitted, for clarity, except on one ion.

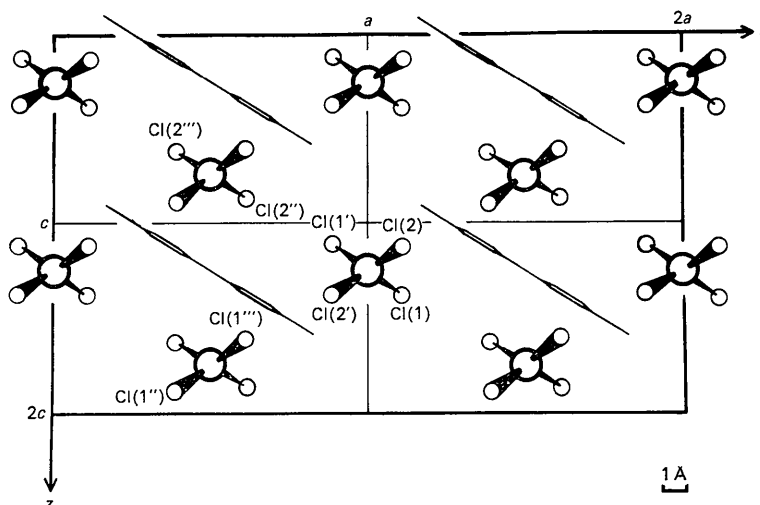


Fig. 3. One layer of tetrachlorocuprate ions parallel to (010) and a single adjacent layer of bipyridinium ions with smaller y coordinates.

A square planar $[\text{CuCl}_4]^{2-}$ ion was found in $(\text{NH}_4)_2\text{CuCl}_4$ by Willett (1964), having two pairs of Cu-Cl bonds of lengths 2.30 and 2.33 Å. This ion completes a distorted octahedral coordination sphere by forming two longer Cu-Cl bonds (2.79 Å) to adjacent ions. The extra bonding produced by this polymerization must be sufficient to overcome the steric repulsive forces of the square planar structure. The flattened tetrahedral structure in the other tetrachlorocuprate structures has been shown (Felsenfeld, 1956) to be a predictable compromise between orbital and steric forces for the isolated ion. In dimethylbipyridinium tetrachlorocuprate there are four $\text{Cl}\cdots\text{Cl}$ close approaches within the chlorocuprate ion: $\text{Cl}(1)\cdots\text{Cl}(2)$ and $\text{Cl}(1')\cdots\text{Cl}(2')$ both 3.459 Å, and $\text{Cl}(1)\cdots\text{Cl}(1')$ and $\text{Cl}(2)\cdots\text{Cl}(2')$ both 3.485 Å, compared with an expected van der Waals separation of 3.60 Å.

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