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N,N′-Dimethyl-4,4′-bipyridylium (Paraquat) Hexachlorodicuprate(II)

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Abstract. $C_{12}H_{14}N_2Cu_2Cl_6$, $M=526{\cdot}1$. Monoclinic, $P2_1/n$ (No. 14), $a=6{\cdot}30$ (1), $b=12{\cdot}94$ (1), $c=10{\cdot}63$ (1) Å, $\beta=97{\cdot}25$ (8)° from diffractometer. $Z=2$, $D_m=2{\cdot}03$ g cm^{-3} (flotation), $D_c=2{\cdot}05$ g cm^{-3}. The compound was prepared from $CuCl_2$ and paraquat dichloride in HCl solution and crystallized as dark-red needles. The structure, refined to $R=0{\cdot}063$, consists of planar paraquat dications and $Cu_2Cl_6^{2-}$ groups weakly joined into infinite chains by Cu···Cl interactions of 2·67 Å. The atoms are five-coordinate with an average distance of 2·29 Å for the four shorter Cu–Cl bonds and a geometry intermediate between trigonal bipyramidal and square.

Introduction. Systematic absences $h0l$: $h+l=2n+1$; $0k0$: $k=2n+1$ gave the space group as $P12_1/n1$ (No. 14); this setting is used throughout the rest of the paper. Data were collected for layers $0kl$ to $5kl$ and $h0l$ to $h12l$ with a Hilger–Watts linear diffractometer (Mo $K\alpha$ radiation). 1150 unique reflexions were recorded for which the intensity was greater than 3σ and the agreement between the two sets of data is shown in a merging R of 0·061 $[R=\sum|(F_1-F_2)|/\frac{1}{2}\sum(F_1-F_2)]$. Lorentz and polarization corrections were applied (but none for absorption) and layer scales were obtained through common reflexions. The structure was solved by Patterson and Fourier techniques and refined by full-matrix least-squares calculations with our adaptation of the *PORFLS* program in the CRYSTAL 69 system of Powell & Griffiths (1969). Five cycles of refinement of positional and isotropic thermal parameters gave $R=0{\cdot}105$ $[R=\sum|F_o|-|F_c|/\sum|F_o|]$ and when anisotropic temperature factors were introduced R fell to a final value of 0·063.* The weighting scheme was used $F\le 35$, $w=1$; $F>35$, $w=[1+(F-35)^2/1225]^{-1}$, and scattering factors were taken from *International Tables for X-ray Crystallography* (1968). No attempt was made to locate H atoms. Atomic parameters are given in Table 1, the structure (with the labelling of the atoms) in Fig. 1, bond lengths in Table 2 and bond angles in Table 3.

Table 2. *Intramolecular bond lengths* (Å)

Paraquat cation (e.s.d. = 0·01 Å)		Chlorocuprate anion (e.s.d. = 0·002 Å)	
N(1)–C(1)	1·475	Cu(1)–Cl(1)	2·305
N(1)–C(2)	1·365	Cu(1)–Cl(2)	2·668
N(1)–C(6)	1·345	Cu(1)–Cl(3)	2·238
C(2)–C(3)	1·373	Cu(1)–Cl(1′)	2·330
C(3)–C(4)	1·381	Cu(1)–Cl(2′)	2·281
C(4)–C(5)	1·407		
C(5)–C(6)	1·377		
C(4)–C(4′)	1·492		

Discussion. The structure consists of centrosymmetric cations and infinite $(CuCl_3^-)_n$ chains running along the short a axis. The geometry of the paraquat ions is very similar to that found in the tetrachlorocuprate(II) complex (Russell & Wallwork, 1969) and other chlorometallate salts (Prout & Murray-Rust, 1969) where the molecule is essentially planar. C(1) shows a small deviation [*ca* 0·07 (1) Å] from the mean plane but

Table 1. *Atomic positions and anisotropic temperature factors* (× 10⁴)

The expression used for the anisotropic temperature factor was:

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

	x/a	y/b	z/c	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu(1)	2555 (1)	443 (1)	563 (1)	84 (2)	25 (0)	66 (1)	2 (1)	25 (1)	−3 (0)
Cl(1)	−567 (2)	1077 (1)	−532 (2)	109 (4)	26 (1)	110 (2)	1 (1)	2 (2)	3 (1)
Cl(2)	4483 (2)	387 (1)	−1532 (1)	104 (3)	38 (1)	59 (1)	8 (1)	19 (1)	2 (1)
Cl(3)	3352 (3)	1987 (1)	1453 (1)	160 (4)	28 (1)	76 (1)	−3 (1)	16 (2)	−6 (1)
N(1)	265 (8)	1270 (4)	3763 (5)	114 (12)	31 (3)	66 (4)	−1 (4)	42 (6)	1 (3)
C(1)	−1662 (11)	1818 (5)	3169 (7)	163 (18)	38 (4)	88 (7)	12 (6)	12 (6)	8 (4)
C(2)	571 (11)	267 (5)	3441 (6)	185 (18)	27 (4)	67 (6)	−2 (5)	38 (7)	−5 (3)
C(3)	2420 (10)	−235 (5)	3926 (6)	140 (15)	29 (4)	68 (6)	−12 (5)	34 (7)	4 (3)
C(4)	3984 (9)	263 (4)	4747 (5)	110 (14)	27 (3)	58 (5)	−13 (4)	47 (6)	−5 (3)
C(5)	3618 (10)	1291 (5)	5053 (6)	146 (16)	30 (4)	77 (6)	−8 (5)	28 (7)	−10 (4)
C(6)	1745 (11)	1762 (5)	4538 (7)	148 (16)	29 (4)	94 (7)	0 (6)	46 (8)	−5 (4)

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30913 (11 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 3. *Intramolecular bond angles* (°)

Paraquat cation (e.s.d. = 0·4°)		Chlorocuprate anion (e.s.d. = 0·1°)	
C(1)–N(1)–C(2)	119·2	Cl(1)–Cu(1)–Cl(2)	92·2
C(1)–N(1)–C(6)	120·3	Cl(1)–Cu(1)–Cl(3)	91·6
C(2)–N(1)–C(6)	120·3	Cl(1)–Cu(1)–Cl(1′)	82·5
N(1)–C(2)–C(3)	119·6	Cl(1)–Cu(1)–Cl(2′)	172·5
C(2)–C(3)–C(4)	121·4	Cl(2)–Cu(1)–Cl(3)	106·0
C(3)–C(4)–C(5)	117·9	Cl(2)–Cu(1)–Cl(1′)	105·4
C(4)–C(5)–C(6)	119·0	Cl(2)–Cu(1)–Cl(2′)	86·0
C(5)–C(6)–N(1)	121·7	Cl(3)–Cu(1)–Cl(1′)	148·3
C(3)–C(4)–C(4′)	122·4	Cl(3)–Cu(1)–Cl(2′)	95·9
C(5)–C(4)–C(4′)	119·7	Cl(1′)–Cu(1)–Cl(2′)	90·8
		Cu(1)–Cl(1)–Cu(1′)	97·5
		Cu(1)–Cl(2)–Cu(1″)	94·0

there appears to be no obvious reason for this. Bond lengths are similar to those found in the above and other paraquat complexes (Russell & Wallwork, 1972).

The anion can be described as $(Cu_2Cl_6)^{2-}$ dimers linked by weak interactions into infinite chains. Similar anions are found in $(CH_3)_2NH_2^+CuCl_3^-$ (Willett, 1965) and $C_6H_5(CH_2)_2NH_2^+CH_3CuCl_3^-$ (Harlow, Wells, Watt & Simonsen, 1974) which are described by the respective authors as containing 'distorted octahedral ... with the sixth position unoccupied' (*i.e.* square pyramidal) and 'distorted trigonal bipyramidal' coordination about the Cu atom. In the first compound the longest Cu–Cl bond is 2·733 Å and in the second 2·528 Å; the corresponding value in the title compound [2·668 (2) Å] implies a geometry intermediate between these two. This is confirmed by the Cl(3)–Cu–Cl(1′) angle of 148·3°, which lies between the corresponding values of 156·0 and 133·0° respectively in the other two trichlorocuprates. Rather than attempting to label the coordination in too definite a manner, it may be best to regard the geometry as that of an intermediate lying on a reaction path between a trigonal bipyramidal (D_{3h}) $CuCl_5$ species and a planar (D_{4h}) $CuCl_4$ ion. [This type of description has already been applied to two other modes of distortion of a regular trigonal bipyramid (Bürgi, 1973; Muetterties & Guggenberger, 1974); the quantitative aspects of the present mode will be considered elsewhere.]

The structures of Willett (1965) and Harlow *et al.* (1974) both contain hydrogen bonds involving the N atoms of the cations and the non-bridging Cl atoms. This is not possible for the title compound, but there is a contact of 3·442 (10) Å between Cl(3) and the N atom (shown by a dotted line in Fig. 1), the vector of which lies roughly perpendicular to the plane of the aromatic ring. This type of interaction is common in chlorocompounds of paraquat and it was suggested (Prout & Murray-Rust, 1969) as being responsible for distortions observed in the anions. This, and the similarity to the hydrogen-bonded species, suggests that the geometry of the anion in the title compound may be slightly distorted by this interaction with the cation.

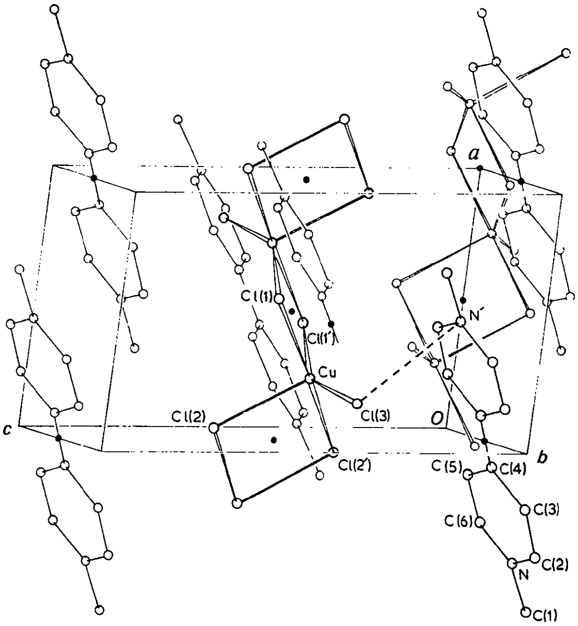

Fig. 1. The structure and unit-cell of paraquat hexachlorodicuprate. Half of the cation at $\frac{1}{2},1,\frac{1}{2}$ has been omitted for clarity and closed circles represent some of the centres of symmetry. The dotted line represents the cation–anion interaction described in the text.

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