The Crystal Structures of the Dichloride and Isomorphous Dibromide and Diiodide of the *N,N'*-Dimethyl-4,4'-bipyridylium Ion

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N,N'-Dimethyl-4,4'-bipyridylium (paraquat) dichloride crystallizes in the orthorhombic system, space group *Pnma* with four molecules in a cell of dimensions $a=9\cdot22$, $b=10\cdot76$, $c=15\cdot88$ Å, all $\pm0\cdot01$ Å. The chloride ions lie in mirror planes at $y=\frac{1}{4}$ and $\frac{3}{4}$ and the paraquat ions lie across centres of symmetry half-way between the mirror planes at $y=0$ and $\frac{1}{2}$ and are orientated such that one of the two crystallographically independent chloride ions is approximately perpendicularly above or below the nitrogen atom of each paraquat plane at a distance of 3·36 Å. The dibromide is monoclinic, space group $P2_1/c$ with two molecules in a cell of dimensions $a=5\cdot86\pm0\cdot01$, $b=8\cdot226\pm0\cdot006$, $c=13\cdot51\pm0\cdot01$ Å, $\beta=95\cdot8\pm0\cdot2$ Å. The diiodide is isomorphous with the dibromide and the cell dimensions are $a=6\cdot04\pm0\cdot01$, $b=8\cdot342\pm0\cdot006$, $c=14\cdot27\pm0\cdot01$ Å, $\beta=96\cdot2\pm0\cdot2°$. In these two isomorphous structures lines of paraquat ions along the *a* axis lie across centres of symmetry at $\frac{1}{2}$0 and $\frac{1}{2}$0½ and between these at $z=\frac{1}{4}$ and $\frac{3}{4}$ are pleated, pseudo-hexagonal layers of anions. Each anion lies almost perpendicularly above or below the nitrogen atom and an adjacent ring carbon atom of a paraquat ion with distances $Br\cdots N=3\cdot68$, $Br\cdots C=3\cdot53$, $I\cdots N=3\cdot84$, $I\cdots C=3\cdot67$ Å. These close approaches are consistent with spectroscopic evidence for charge-transfer interaction in these compounds.

Introduction

The crystal structures of *N,N'*-dimethyl-4,4'-bipyridylium dichloride (pqCl₂), dibromide (pqBr₂) and diiodide (pqI₂) have been determined as part of a series of structure determinations of compounds containing the 4,4'-bipyridylium ion
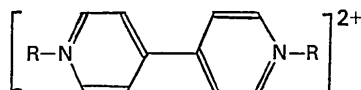
This ion has a practical application as the herbicide paraquat (Boon, 1964) and further interest arises from its use as an oxidation-reduction indicator under the name viologen (Michaelis & Hill, 1933*a,b*). Crystal structure determination should throw some light on the nature of the charge transfer in the present compounds, suggested by Nakahara & Wang (1963), Macfarlane & Williams (1969) and Russell & Anex (1968). The transfer of charge is presumed to occur from the halide ion to the paraquat ion and is suggested by the colours of the compounds: the diiodide is red, the dibromide a very pale yellowish green and the dichloride white. These colours are in accordance with the increase in ionization potential from I^- to Br^- to Cl^-.

Experimental

Crystals of the compounds were kindly supplied by the Mond Division of Imperial Chemical Industries Ltd. Oscillation and zero, first and second layer, equi-

inclination Weissenberg photographs were taken with the crystal rotating about the *a* axis for pqCl₂ and pqBr₂ and the *a* and *b* axes for pqI₂, using Cu *K*α radiation ($\lambda=1\cdot542$ Å). Unit-cell dimensions, as determined from these photographs, were later refined with the use of a linear diffractometer (Arndt & Phillips, 1961) using Mo *K*α radiation ($\lambda=0\cdot7107$ Å). Intensity data were collected for the 0*kl*, 1*kl*, ..., 9*kl* reciprocal lattice levels of pqCl₂ and for the 0*kl*, 1*kl*, ..., 6*kl* reciprocal lattice levels of both pqBr₂ and pqI₂ on the linear diffractometer, which employs the moving-crystal stationary-counter technique. Intensity measurements were made with a scintillation counter and a pulse height analyser. In the cases of pqBr₂ and pqI₂ cylindrically-shaped crystals of length *ca.* 0·5 mm and radius 0·2 mm were used, whereas an approximately spherical crystal of diameter 0·5 mm was used for pqCl₂. The numbers of independent reflexions measured were 1184, 1088 and 1046 for pqCl₂, pqBr₂ and pqI₂ respectively, and these were corrected for Lorentz and polarization factors but not for absorption or extinction. The quality of data for pqCl₂ was adversely affected by the unstable nature of the crystals. The intensities decreased with time and successive layers of data were put on the scale of the first-measured zero layer by factors derived from the decrease of a group of standard reflexions.

Crystal data

pqCl₂

N₂C₁₂H₁₄Cl₂, M.W. 256·9, orthorhombic, $a=9\cdot22\pm0\cdot01$, $b=10\cdot76\pm0\cdot01$, $c=15\cdot88\pm0\cdot01$ Å, $U=1575$ Å³, $D_m=1\cdot26$ g.cm⁻³, $Z=4$, $D_c=1\cdot08$ g.cm⁻³, $F(000)=536$, Mo *K*α ($\lambda=0\cdot7107$ Å), $\mu=4\cdot0$ cm⁻¹. Absent spectra, *hk*0 when *h* is odd, 0*kl* when *k*+*l* is

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odd. Space group $Pn2_1a$ (No. 33) or $Pnma$ (No. 62). A pyroelectric test did not indicate the absence of a centre of symmetry and the space group $Pnma$ was therefore assumed.

pqBr₂

$N_2C_{12}H_{14}Br_2$, M.W. 345·8, monoclinic, $a=5·86\pm 0·01$, $b=8·226\pm0·006$, $c=13·51\pm0·01$ Å, $\beta=95·8\pm 0·2°$, $U=647·9$ Å³, $D_m=1·77$ g.cm⁻³, $Z=2$, $D_c=1·78$ g.cm⁻³, $F(000)=340$, Mo $K\alpha$ ($\lambda=0·7107$ Å), $\mu=66·1$ cm⁻¹. Absent spectra, $h0l$ when l is odd, $0k0$ when k is odd. Space group $P2_1/c$ (No. 14).

pqI₂

$N_2C_{12}H_{14}I_2$, M.W. 439·8, monoclinic, $a=6·04\pm 0·01$, $b=8·342\pm0·006$, $c=14·27\pm0·01$ Å, $\beta=96·2\pm 0·2°$, $U=714·8$ Å³, $D_m=2·03$ g.cm⁻³, $Z=2$, $D_c=2·03$ g.cm⁻³, $F(000)=412$, Mo $K\alpha$ ($\lambda=0·7107$ Å), $\mu=44·3$ cm⁻¹. Absent spectra, $h0l$ when l is odd, $0k0$ when k is odd. Space group $P2_1/c$ (No. 14).

In view of the similarity of crystal data for pqBr₂ and pqI₂, the two structures were assumed to be isomorphous.

Determination and refinement of the structures

pqCl₂

Sharpened and unsharpened, three-dimensional Patterson syntheses were computed, from which it was hoped the eight chloride ions in the unit cell would be located. A consistent set of peaks in general positions could not be found and it was concluded from this and the accumulation of peaks on the Harker section at $y=0·5$ and the Harker lines at $y=0·5$, $z=0·5$ and $x=0·5$, $y=0$ that the chloride ions were in two independent fourfold positions on the mirror planes. This presented a problem of interpretation in that a large number of isovectorial structures were possible for any consistent set of peaks on the Patterson synthesis. Various techniques for the analysis of vectors, including those described by Garrido (1951) and Tokonami & Hosoya (1965), were employed and structure factor calculations were carried out on each reasonable trial structure for the chloride ions only. The lowest residual R obtained, where $R=\sum |F_o|-|F_c|\ /\sum|F_o|$, was 0·5 but this was considered a satisfactory result as the amplitudes of all of the most intense reflexions agreed well with their corresponding calculated values. A three-dimensional Fourier synthesis was computed using the observed amplitudes and calculated phases and from this the locations of all carbon and nitrogen atoms in the asymmetric unit were deduced. Structure factor calculations on hkl reflections with these positions of the chloride ions and carbon and nitrogen atoms gave a residual of 0·45.

Refinement was carried out using the block-diagonal least-squares method with a weighting scheme:

$$\sqrt{w}=1 \text{ if } |F_o|<F^* \text{ otherwise } \sqrt{w}=F^*/|F_o|\ .$$

The value of F^* was adjusted in the later stages of refinement to give approximately constant values of average $w\varDelta F^2$ values for all ranges of $|F_o|$.

Table 1. *Fractional coordinates and thermal parameters, with standard deviations in parentheses, for paraquat dichloride*

Values, except those denoted by an asterisk, are multiplied by 10⁴.

	x/a	y/b	z/c	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cl(1)	2767 (4)	¼*	1807 (2)	120 (10)	76 (7)	16 (3)	0 (0)	22 (3)	0 (0)
Cl(2)	8935 (6)	¼*	−261 (3)	171 (12)	100 (7)	59 (4)	0 (0)	9 (6)	0 (0)
C(1)	5669 (12)	44 (9)	247 (5)	148 (20)	76 (10)	19 (4)	−16 (18)	−7 (10)	−33 (8)
C(2)	5787 (13)	766 (9)	955 (15)	157 (21)	90 (11)	30 (5)	28 (21)	−38 (13)	−38 (9)
C(3)	6906 (12)	−582 (9)	−7 (6)	107 (19)	94 (11)	31 (4)	35 (18)	−11 (11)	−45 (9)
C(4)	7039 (13)	820 (10)	1395 (6)	122 (20)	105 (12)	34 (5)	15 (20)	8 (12)	−41 (10)
C(5)	8203 (16)	−523 (11)	457 (7)	187 (24)	94 (12)	37 (5)	34 (22)	−6 (14)	−33 (11)
C(6)	9567 (16)	385 (15)	1570 (7)	151 (25)	189 (20)	51 (19)	68 (31)	−55 (17)	−69 (16)
N	8243 (10)	219 (8)	1140 (5)	146 (17)	92 (3)	30 (4)	−39 (17)	−35 (10)	−32 (8)

Table 2. *Fractional coordinates and thermal parameters, with standard deviations in parentheses, for paraquat dibromide*

Fractional coordinates for the non-hydrogen atoms are multiplied by 10⁴ and for the hydrogen atoms by 10³. The anisotropic temperature factors are multiplied by 10⁴.

	x/a	y/b	z/c	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Br	6764 (6)	−827·0 (9)	1758·1 (5)	252 (5)	181 (3)	34 (1)	34 (3)	52 (1)	0 (1)
C(1)	5994 (10)	4493 (7)	146 (4)	176 (17)	103 (9)	29 (3)	−53 (17)	33 (9)	−7 (8)
C(2)	6746 (11)	4186 (9)	1139 (4)	232 (20)	181 (12)	22 (3)	76 (23)	18 (10)	−4 (10)
C(3)	7299 (11)	3810 (7)	−570 (4)	265 (21)	111 (10)	26 (3)	17 (19)	17 (11)	−19 (8)
C(4)	8606 (11)	3192 (9)	1389 (4)	227 (21)	189 (13)	26 (3)	−9 (23)	23 (11)	−1 (10)
C(5)	9147 (11)	2869 (8)	−286 (4)	228 (20)	140 (11)	29 (3)	0 (20)	8 (11)	−32 (9)
C(6)	11773 (12)	1510 (9)	977 (5)	219 (21)	154 (12)	50 (5)	42 (23)	9 (13)	−12 (12)
N	9795 (8)	2556 (7)	681 (4)	194 (16)	136 (9)	33 (3)	−44 (17)	22 (9)	−1 (9)

Table 2 (cont.)

	x/a	y/b	z/c	B
H(1)	611 (15)	456 (9)	168 (6)	1·7 (1·5)*
H(2)	679 (30)	413 (15)	−115 (12)	10·7 (4·8)
H(3)	905 (21)	300 (15)	203 (9)	5·8 (3·1)
H(4)	1033 (14)	247 (10)	−71 (6)	2·2 (1·6)
H(5)	1263 (16)	127 (10)	46 (7)	2·4 (1·9)
H(6)	1289 (18)	210 (12)	146 (8)	4·2 (2·2)
H(7)	1016 (29)	64 (16)	128 (13)	8·2 (4·0)

* Thermal parameters for hydrogen atoms are isotropic B (Å^2) in the expression exp $(-B\sin^2\theta/\lambda^2)$.

The scattering factors of Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955) were used for all atoms. Four cycles of isotropic least-squares refinement were carried out on 1184 reflexions, as a result of which the residual fell to 0·28. This was followed by three further cycles with the thermal parameters varying anisotropically, when the residual fell to 0·23. An agreement analysis between observed and calculated structure factors showed that a number of the smallest reflexions were giving bad agreement and as these were barely significant above the background they were excluded from the subsequent analysis. After two further cycles of least-squares refinement on the remaining 1131 reflexions the residual converged at a value of 0·15. In view of the fact that the calculated density is lower than the observed density and the observed tendency of the crystals to
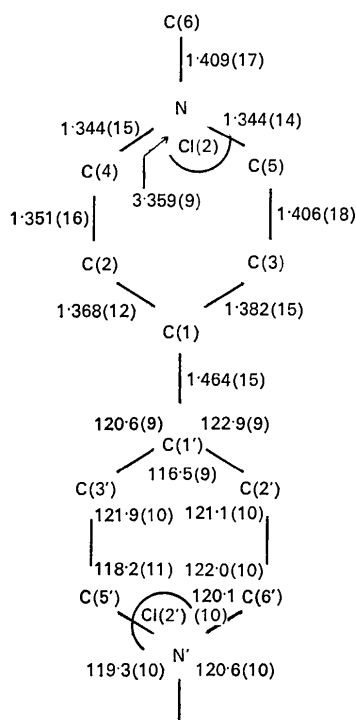

Fig. 1. Bond lengths (Å) and angles in N,N'-dimethyl-4,4'-bipyridylium dichloride with standard deviations in parentheses.

take up atmospheric moisture, it was assumed that some water molecules were present in the structure that had not been taken into account in the refinement. Approximately 2·3 water molecules would be required for each $pqCl_2$ to make the calculated density equal to the observed density. Three-dimensional Fourier and difference Fourier maps revealed a number of low intensity peaks which could correspond to disordered water molecules in the empty regions of the structure. Inclusion of partial atoms in these positions for the purposes of structure factor calculations brought scarcely any reduction in the residual, and attempts to refine them failed. The relatively high thermal parameters of one of the chloride ions suggested disorder for these ions also. However, refinement of occupation numbers were carried out and little shift from unit occupation was found at each chloride ion site. The residual did not drop significantly despite full-matrix least-squares refinement. The quality of agreement between $|F_o|$ and $|F_c|$ appeared to be evenly distributed and the relatively high final residual was therefore attributed to low quality data combined with the inability to locate the disordered water molecules. The final residual of 0·15 was obtained on 82 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 Table 1. The anisotropic thermal parameters in this Table and in Tables 2 and 3 are B_{ij} in the expression exp $[-(B_{11}h^2+B_{22}k^2+B_{33}l^2+B_{12}hk+B_{13}hl+B_{23}kl)]$. Fig. 1 shows the bond lengths and interbond angles, together with their standard deviations (and the position of the closest chloride ion, which will be referred to in the discussion).

$pqBr_2$, pqI_2

A three-dimensional Patterson synthesis was computed using the dibromide data from which the positions of the bromide ions were determined. Using these positions, a three-dimensional structure factor calculation for the bromide ions only gave a residual R of 0·33, indicating that the bromide ion positions were probably nearly correct. A three-dimensional Fourier synthesis was computed using the observed amplitudes and calculated phases and from this the locations of all carbon and nitrogen atoms in the assymetric unit were deduced.

Refinement of both structures was carried out using the same block-diagonal, least-squares method used for $pqCl_2$. For $pqBr_2$, five cycles of isotropic refinement reduced the residual R to 0·14 and five more cycles with anisotropic thermal parameters resulted in an R value

of 0·082. The same weighting scheme was used as in the refinement of pqCl$_2$. In the sub. ·quent refinement, 33 reflexions were excluded because they appeared to be affected by extinction or because they were near to the rotation axis and so inaccurately measured. Also 61 small reflexions were excluded because they were not significantly above the background measurement. An R value of 0·059 was thus obtained for 994 reflexions. A difference Fourier synthesis showed the positions of all the hydrogen atoms and they were included in the final two cycles of refinement with isotropic thermal parameters. Convergence was reached with a residual of 0·056 for 101 positional, thermal and scale parameters.

The atomic coordinates of the refined dibromide structure were used as the starting point for the refinement of the diiodide. The iodide ion was placed at the bromide ion position, the hydrogen atoms were not included and all atoms were givn isotropic vibrational parameters. During four cycles of refinement with 1046 reflexions the residual dropped from 0·32 to 0·26. The iodide ion was then allowed anisotropic vibrational parameters and three further cycles of refinement reduced the residual to 0·076. At this stage 35 reflexions were excluded from the analysis either because they were barely significant in magnitude or because they were close to the rotation axis of the crystal and were hence difficult to measure. After two further
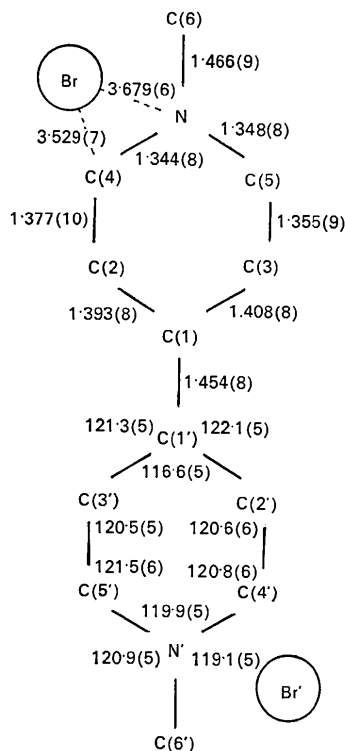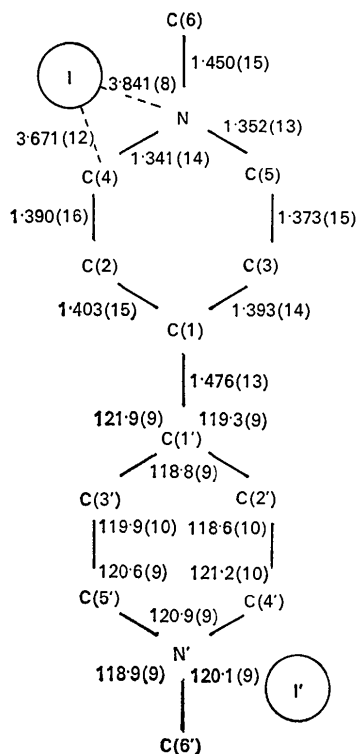

Fig. 3. Bond lengths (Å) and angles in N,N'-dimethyl-4,4'-bipyridylium diiodide with standard deviations in parentheses.

cycles of least-squares, refinement converged at a final residual of 0·070 for 1011 reflexions and 73 positional, thermal and scale parameters. In view of the extent to which the iodide ion appeared to be dominating the structure factors, an attempt to locate the hydrogen atoms was not considered worth while.

The final positional and thermal atomic parameters for pqBr$_2$ together with their standard deviations are given in Table 2, and the bond lengths and interbond angles with their standard deviations are shown in Fig. 2. Bonds to hydrogen atoms are not included because they are not considered accurate enough to warrant discussion. The corresponding data for pqI$_2$ are shown in Table 3 and Fig. 3. As for the dichloride structure, Figs. 2 and 3 also show the position of the closest halide ions, which will be referred to in the discussion. The observed structure factors are compared with the values calculated from the final set of atomic parameters for both structures in tables available elsewhere (Russell, 1967).*

Description of the structures

pqCl$_2$

Fig. 4 shows the structure as viewed down the b axis. It consists of alternate layers of chloride ions and

Fig. 2. Bond lengths (Å) and angles in N,N'-dimethyl-4,4'-bipyridylium dibromide with standard deviations in parentheses.

paraquat ions, at $b/4$ spacings, perpendicular to the b axis. The chloride ions lie in the mirror planes at $y=\frac{1}{4}$ and $\frac{3}{4}$ and the paraquat ions are centred half-way between the mirror planes at $y=0$ and $\frac{1}{2}$. The orientation of each paraquat ion is obtained by twisting about the N–N axis 38° from the position where the molecular plane is parallel to (010) and then tilting the N–N axis 4° out of (010). The wedge shape thus formed between two mirror-related paraquat ions encloses a Cl(2) ion half-way between them. Each Cl(1) ion lies approximately in the planes of the two nearest paraquat ions. Half-way between successive Cl(1) ions along the b axis are the open regions of the structure where the disordered water molecules are thought to lie.

pqBr$_2$ and pqI$_2$

The structure is seen in projection along the b axis in Fig. 5. The centrosymmetric paraquat ions lie across centres of symmetry in the cell at $\frac{1}{2}\frac{1}{2}0$ and $\frac{1}{2}0\frac{1}{2}$. Their N–N axes make an angle of 35° (pqBr$_2$) or 34° (pqI$_2$) with the (010) plane and an angle of 15° in each case with the (001) plane. The anions form pleated, pseudo-hexagonal layers at $z=\frac{1}{4}$ and $\frac{3}{4}$ and the lines of paraquat ions along the a axis fit between the layers in such a way that one anion lies almost below or above the N,C(4) region of each pyridyl ring. Two paraquat ions related to each other by the centre of symmetry at $0\frac{1}{2}0$ are in parallel planes 3·52 Å apart in the bromide and 3·65 Å apart in the iodide. However, there is only a

Table 3. *Fractional coordinates and thermal parameters, with standard deviations in parentheses, for paraquat diiodide*

All values are multiplied by 10^4.

Atom	x/a	y/b	z/c	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
I	6698 (1)	−766·0 (9)	1758·2 (5)	223 (6)	177 (3)	37 (1)	24 (3)	55 (1)	−1 (1)
C(1)	6017 (16)	4524 (10)	128 (7)	133 (28)	114 (14)	26 (5)	−77 (26)	39 (15)	−1 (12)
C(2)	6754 (19)	4276 (14)	1083 (8)	178 (34)	190 (20)	32 (6)	44 (37)	18 (18)	4 (16)
C(3)	7203 (19)	3829 (13)	−552 (7)	199 (33)	146 (17)	28 (5)	22 (31)	39 (18)	−22 (14)
C(4)	8611 (19)	3314 (14)	1313 (7)	225 (36)	152 (18)	28 (5)	13 (33)	45 (18)	11 (15)
C(5)	9047 (18)	2911 (12)	−282 (7)	216 (32)	119 (15)	33 (5)	19 (30)	29 (18)	−36 (14)
C(6)	11632 (20)	1644 (14)	899 (8)	185 (35)	153 (19)	52 (7)	55 (35)	−15 (22)	31 (18)
N	9728 (14)	2673 (10)	642 (6)	176 (25)	110 (13)	35 (4)	−11 (24)	55 (14)	1 (12)
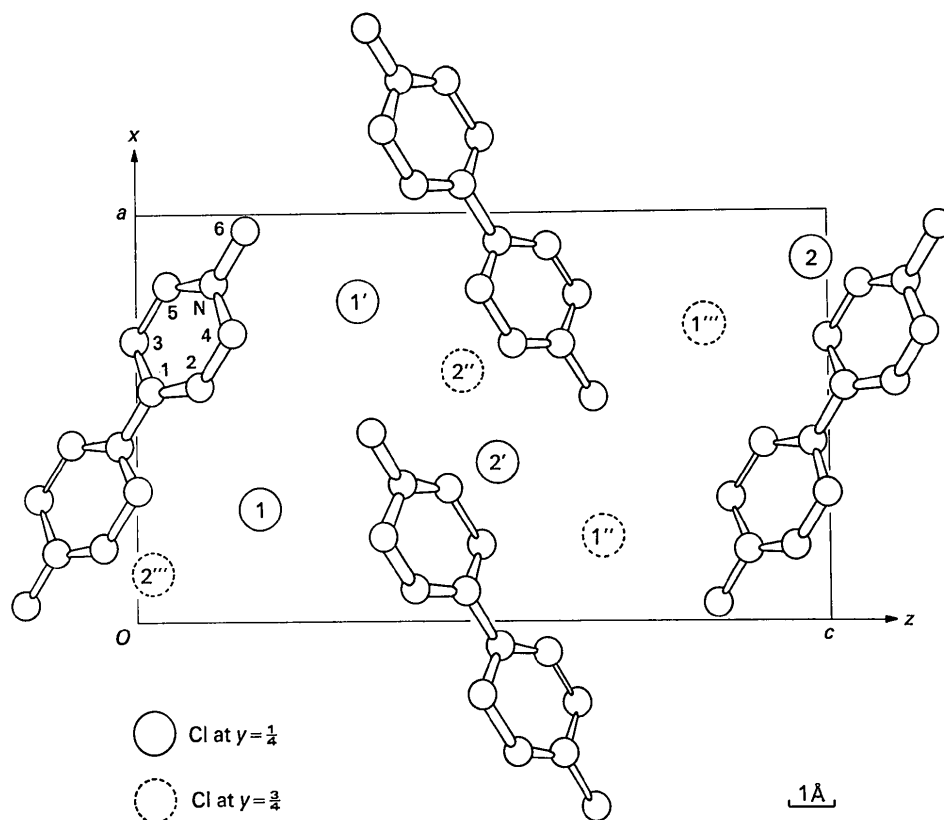
Fig. 4. The structure of pqCl$_2$ viewed along the b axis.

◯ Cl at $y=\frac{1}{4}$

⬭ Cl at $y=\frac{3}{4}$

1Å

little overlap of the ends of the two molecules and there are no close intermolecular contacts. The molecules are twisted about the N–N axes such that they are almost perpendicular to (001), making $87\frac{1}{2}°$ with it in the bromide and $89\frac{1}{2}°$ in the iodide. In each case this twist is such as to bring the C(2)–C(4) line of the molecule slightly nearer to the (010) plane at $y=0$ than the C(3)–C(5) side.

Discussion

The bond lengths and interbond angles of the paraquat ions in pqCl$_2$, pqBr$_2$ and pqI$_2$ shown in Figs. 1, 2 and 3, respectively, do not differ significantly from one another, nor do they differ from those in previously reported structures containing the bipyridylium ion (Russell & Wallwork, 1969, 1971; Prout & Murray-Rust, 1969). These Figures also show the positions of the closest halide ions to the paraquat ions, projected perpendicularly onto the cations. The following are the closest approaches involving the halide ions:

pqCl$_2$:	Cl(2)$\cdots$N	3·36 Å
pqBr$_2$:	Br$\cdots\cdots$N	3·68
	Br$\cdots\cdots$C(4)	3·53
pqI$_2$:	I$\cdots\cdots$N	3·84
	I$\cdots\cdots$C(4)	3·67

As pointed out by Prout & Murray-Rust (1969), it is difficult to know to what extent close approaches in this type of compound are to be ascribed to charge-transfer interaction and to what extent they represent ionic interactions. However, in view of the observation by Macfarlane & Williams (1969) of charge-transfer bands in solid pqBr$_2$ and pqI$_2$ it is probable that the close approaches listed are at least partially due to charge-transfer interaction. This will be of the $n-\pi$ type with the halogen ion acting as the donor and the paraquat ion as the acceptor. These findings are in agreement with work on other 4,4'-bipyridylium salts (Prout & Murray-Rust, 1969) where it is suggested that for transfer of electrons from a donor orbital of the halogen to the π acceptor orbital of the bipyridylium ion, the interaction is most likely to be directed towards the nitrogen atoms and not towards the ring centroid. This evidence might be extended to the case of *N*-methyl pyridinium iodide, in which Kosower & Burbach (1956) suggest the iodide ion will probably be located over either the nitrogen atom or the ring centroid. In this analogous system it seems reasonable to assume from the present evidence that the interaction will be directed towards the former position.

With *N,N'*-dimethyl-4,4'-bipyridylium tetrachlorocuprate (Russell & Wallwork, 1969) the situation is more complicated with a number of close approaches of both Cl$\cdots$N and Cl$\cdots$C. It appears, therefore, that in this case packing considerations are more important because of the bulky shape of the anion and the result is a compromise between this and a suitable orientation for charge transfer. The closest Cl$\cdots$N approach

is 3·505 Å which again is closer than the sum of the van der Waals radii, suggesting interaction. A similar compromise probably obtains in the case of *N,N'*-dibenzyl-4,4'-bipyridylium diiodide (Russell & Wallwork, 1971), which occurs as red crystals, suggesting charge transfer. The iodide ions in this case are located more to the side of the bipyridylium ion and it is difficult to envisage a specific I$\cdots$N interaction. However, an interesting and novel possibility here would be $\pi-\pi$ charge transfer between the benzyl group and the pyridinium ring of the adjacent molecule, as indicated by a number of intermolecular C$\cdots$C and C$\cdots$N close approaches.

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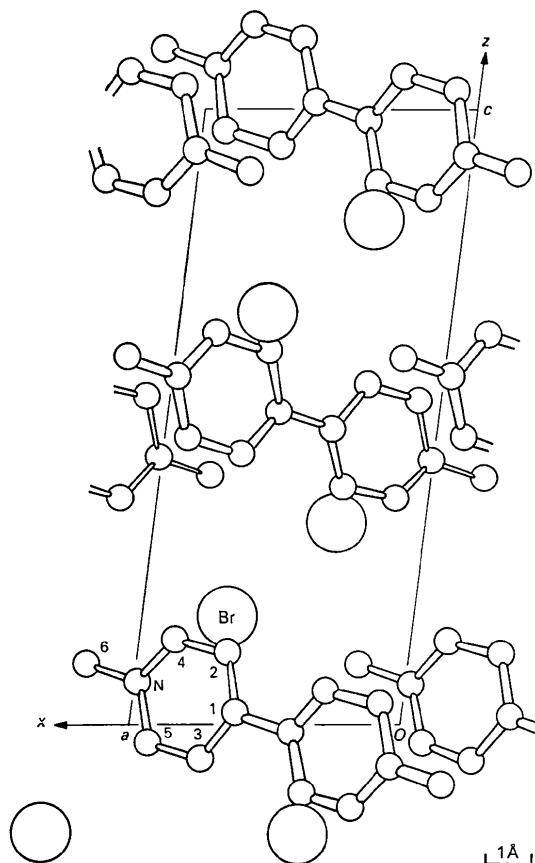ARNDT, U. W. & PHILLIPS, D. C. (1961). *Acta Cryst.* **14**, 807.

Fig.5. The structure of the isomorphous pqBr$_2$ and pqI$_2$ viewed along the *b* axis.

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The Crystal Structure of Potassium Dihydrogen *trans*-Aconitate

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Potassium dihydrogen *trans*-aconitate, $KH_2(C_6H_3O_6)$, crystallizes in the monoclinic space group $C2/c$, with lattice parameters $a = 11\cdot861 \pm 0\cdot002$, $b = 15\cdot919 \pm 0\cdot002$, $c = 8\cdot416 \pm 0\cdot001$ Å, and $\beta = 90\cdot90 \pm 0\cdot02°$ at 20°C. There are eight molecules per unit cell. The calculated and observed densities, D_x and D_m, are 1·78 and 1·77 g.cm^{-3} respectively. The structure was determined by Patterson methods from data collected with Mo $K\alpha$ radiation on a four-circle diffractometer. The final R value for the 2081 observed reflections after refinement by full-matrix least squares of all atoms including the hydrogen atoms is 0·043. The potassium ions are each surrounded by eight oxygen atoms at distances 2·70–3·32 Å. Each anion takes part in two hydrogen bonds, one of which is intramolecular (2·53 Å). A seven-membered ring is formed by the bidentate chelation of one potassium ion by the *trans*-aconitate ion.

Introduction

The crystal structure of potassium *trans*-aconitate was undertaken to supplement a study of the enzyme aconitase and the possible mechanism of its action as proposed by Glusker (1968). *trans*-Aconitate is a weak competitive inhibitor of the action of aconitase (Thomson, Nance, Bush & Szczepanik, 1966). It is an isomer of *cis*-aconitate, a substrate of aconitase, and is found to comprise at least 6% of a normal sample of *cis*-aconitate. The formula of *trans*-aconitic acid is shown below.

HOOC–CH₂　　　COOH
　　　＼　　／
　　　　C＝C
　　　／　　＼
HOOC　　　　H
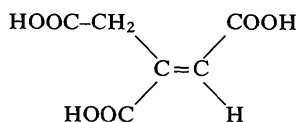
The two isomers of aconitic acid may be interconverted by changing the pH of the solution (Ambler & Roberts, 1948) or by the action of the enzyme aconitate isomerase (Rao & Altekar, 1971; Klinman & Rose, 1970). The structure of dipotassium *cis*-aconitate has been reported (Glusker, Orehowsky, Casciato & Carrell, 1972).

Experimental

Crystals of the monopotassium salt of *trans*-aconitic acid were grown by dissolving equimolar quantities of potassium hydroxide and *trans*-aconitic acid in water. A few drops of dilute hydroquinone were added to prevent the polymerization that occurred with the first batch of crystals that were left in contact with their mother liquor. The solution was allowed to stand, and large rectangular crystals formed. The crystal data are given in Table 1.

Table 1. *Crystal data for potassium dihydrogen trans-aconitate*, $KH_2(C_6H_3O_6)$

Formula weight: 212·205
System: monoclinic

$a = 11\cdot861 \pm 0\cdot002$ Å
$b = 15\cdot919 \pm 0\cdot002$
$c = 8\cdot416 \pm 0\cdot001$
$\beta = 90\cdot90 \pm 0\cdot02°$
λ (Mo $K\alpha_1$) = 0·70926 Å
$Z = 8$
$F(000) = 864$

Systematic absences: $h0l$, h odd, l odd; $0k0$, k odd; hkl, $h+k$ odd.

Space group: $C2/c$ (from systematic absences and intensity statistics).

$D_x = 1\cdot78$ g.cm^{-3}
$D_m = 1\cdot77$ g.cm^{-3} determined by flotation in bromoform and carbon tetrachloride.

$\mu = 6\cdot6$ cm^{-1}