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The Crystal Structure of Pyridinium Dichloroiodide

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Abstract. Pyridinium dichloroiodide, $C_5NH_6ICl_2$, is trigonal, space group $R\bar{3}m$, with $a=6{\cdot}165$ (4) Å, $\alpha=82{\cdot}45$ (6)°, $D_m=2{\cdot}06$ g cm^{-3} (by flotation), $Z=1$, $D_c=2{\cdot}04$ g cm^{-3}. The atomic positions have been determined by least-squares refinement of counter intensities, the final R being 0·023 for 227 reflexions. The dichloroiodide ion is symmetric with an I–Cl bond length of 2·546 Å.

Introduction. The yellow trigonal prisms were mounted with grease in thin-walled glass capillaries. Referred to rhombohedral axes, the forms commonly developed are $\{111\}$ and $\{1\bar{1}0\}$. The unit-cell dimensions were determined from a least-squares fit to the four angles optimized for 15 reflexions on a computer-controlled NONIUS CAD4 diffractometer. The intensities for 303 reflexions with $\sin\theta/\lambda \le 0{\cdot}7$ Å^{-1} were collected at 22–25°C with a $\theta/2\theta$ scan technique and Zr-filtered Mo radiation. A crystal approximately $0{\cdot}04\times0{\cdot}04\times0{\cdot}04$ cm was used. 227 unique reflexions were considered significant. The intensities were corrected for Lorentz and polarization effects. An absorption correction [μ(Mo $K\alpha$)$=41{\cdot}5$ cm^{-1}] was applied by the method of Busing & Levy (1957).

The unit-cell contents, observed symmetry relationships and lack of systematic absences indicate a similarity in structure to that of $CsICl_2$ (van Bolhuis & Tucker, 1973). Therefore of the possible space groups, $R32$, $R3m$ and $R\bar{3}m$, the latter was chosen by analogy with $CsICl_2$. This choice of space group requires the ICl_2^- ion to lie along the $\bar{3}$ axis with the iodine atom on the inversion centre at $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$, whereas the $C_5NH_6^+$ ion must be centred at the origin and perpendicular to the $\bar{3}$ axis. This implies that the cation shows sixfold rotational disorder. For an ordered $C_5NH_6^+$ ion the symmetry would be reduced to $P1$. On the basis of intensity measurements for reflexions related by $\bar{3}$ symmetry we have been unable to distinguish between an ordered $C_5NH_6^+$ ion in $P1$ or a disordered ion in $R\bar{3}m$. However, assuming the surroundings of the cation to have $\bar{3}$ symmetry, there is no physical reason to think that it would be ordered, and therefore, space group $R\bar{3}m$ was used in the refinement.

The C–H (or N–H) groups were found to lie on the twofold axes. The least-squares refinement was performed with the X-RAY 70 system of programs (1970), the function minimized being $\sum w(F_o-F_c)^2$. Scattering factors for the atoms were taken from *International Tables for X-ray Crystallography* (1962). The pyridinium ion was treated as six symmetry related C–H groups with a C–H bond length of 1·084 Å. The hydrogen atom temperature factor was fixed at $B=5{\cdot}0$ Å^2. The position of the carbon atom on the diad axis was refined. Four cycles of refinement on iodine and chlorine atom parameters alone reduced R to 0·172, confirming that the structure was essentially correct. Six cycles refining anisotropic thermal parameters for iodine and chlorine, four cycles refining carbon atom positional and anisotropic thermal parameters and a further five cycles refining all parameters reduced R to 0·023. The maximum parameter shift in the final cycle was 0·01σ. In the final cycles $\langle(F_o-F_c)^2\rangle$ appeared to be approximately independent of $|F_o|$ and $\sin\theta/\lambda$ and, in consequence, unit weights were used. The refinement of an extinction parameter (Zachariasen, 1968) shows a reduction in intensity of

Table 1. *Thermal parameters and final atomic positions with estimated standard deviations*

Temperature factors in the form $\exp[-2\pi^2(U_{11}h^2a^{*2}+U_{22}k^2b^{*2}+U_{33}l^2c^{*2}+2U_{12}hka^*b^*+2U_{23}klb^*c^*+2U_{13}hla^*c^*)]$.

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
I	0·0814 (3)	0·0814 (3)	0·0814 (3)	−0·0182 (2)	−0·0182 (2)	−0·0182 (2)
Cl	0·1234 (10)	0·1234 (10)	0·1234 (10)	−0·0427 (7)	−0·0427 (7)	−0·0427 (7)
C	0·0822 (18)	0·0822 (18)	0·0854 (28)	−0·0040 (18)	−0·0162 (13)	−0·0162 (13)
H	0·0633					

Table 1 (*cont.*)

	Site symmetry	x/a	y/b	z/c
I	$\bar{3}m$	0·5*	0·5*	0·5*
Cl	$3m$	0·2892 (2)	0·2892 (2)	0·2892 (2)
C	2	0·1661 (4)	−0·1661 (4)	0·0*
H	2	0·2995	−0·2995	0·0*

* Parameters fixed by symmetry.

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approximately 5% for the strongest low order reflexion, $0\bar{1}1$.

The final atomic parameters with estimated standard deviations are given in Table 1.*

Discussion. We were interested in investigating the structure of the ICl_3F^- ion (van Bolhuis & Tucker, 1973) and after attempts to prepare the caesium salt had failed we attempted to prepare the pyridinium salt by the method of Booth, Swartzel & Morris (1933). Instead of the expected compound, $C_5NH_6ICl_3F$, we obtained a product which, according to analysis (Table 2) could be $C_5NH_6ICl_2$. The assumed composition was confirmed by the crystal structure determination, which was carried out to compare the ICl_2^- ion in this compound with that in other compounds of known structure.

Table 2. *Analysis*

Calculated for $C_5NH_6ICl_2$:	C, 21·6; H, 2·2; N, 5·0; I, 45·6; Cl, 25·5%.
Found	C, 22·1; H, 2·4; N, 4·9; I, 40·3; Cl, 25·9%.

The I–Cl bond length of 2·530 (2) Å is shorter than that found in $CsICl_2$ [2·548 (2); van Bolhuis & Tucker, 1973]. However, an inspection of the thermal parameters for iodine and chlorine shows that the ICl_2^- ion may be considered to be librating. Referred to inertial axes $U_{11}(Cl)=0{\cdot}0495$, $U_{22}=U_{33}(Cl)=0{\cdot}1488$, $U_{11}(I)=0{\cdot}0586$ and $U_{22}=U_{33}(I)=0{\cdot}0893$ Å^2. The I–Cl bond length after correction for libration (Cruickshank, 1956) is 2·546 Å, in agreement with other determinations (Visser & Vos, 1964; van Bolhuis & Tucker, 1973). The libration of the cation is greater that than observed in $CsICl_2$, where the small correction to the I–Cl bond length (0·004 Å) was not applied. It may be that the large value of $U_{22}(Cl)$ in $C_5NH_6ICl_2$ is partly due to a disordering of the chlorine atom. Possibly this atom is displaced from the $\bar{3}$ axis towards whichever of the neighbouring positions on the diad axes is occupied by the nitrogen atom.

The pyridinium 'C–C' bond length is 1·350 (8) and 1·355 Å respectively before and after correction for libration. It is longer than the accepted aromatic C–N bond length (1·340 Å), shorter than the accepted aromatic C–C bond length (1·394 Å), and shorter than the weighted mean of these values (1·376 Å) expected for an averaged pyridinium ion.

$C_5NH_6ICl_2$ is similar in structure to $CsICl_2$ (Wyckoff, 1964), the pyridinium ion with its plane perpendicular to [111] replacing the caesium ion. It seems likely this is because the 'thickness' of an aromatic ring of 3·4 Å (Pauling, 1960) is roughly the same as the diameter of a caesium ion (3·38 Å; Pauling, 1960). However, whereas the non-bonded contacts in $CsICl_2$ suggest the packing is determined by the anion (van Bolhuis & Tucker, 1973), the non-bonded contacts in $C_5NH_6ICl_2$ suggest cation–anion interactions control the packing. The Cl···H distance of 2·905 Å is rather shorter than the sum of the van der Waals radii (Pauling, 1960) for the atoms, whereas the non-bonded I···Cl contacts, 3·957 Å in the caesium salt, are larger than 4 Å in the pyridinium salt. The remaining non-bonded contacts are unexceptional.

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* A list of observed and calculated structure factors has been deposited with the National Lending Library, England, as Supplementary Publication No. SUP 30196 (4 pp.). Copies may be obtained through the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.