Crystal Structure of Trichlorosulphonium(IV) Tetrachloroiodate(III)

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The structure of the title compound has been determined by the heavy-atom method from 2 012 reflections, measured with a diffractometer, and refined by full-matrix least-squares methods to R 0.060. Crystals are monoclinic, space group $P2_1/c$, with a = 10.42(1), b = 15.20(1), c = 8.27(1) Å, and β = 108.6(2)°. The cation has a pyramidal geometry while that of the anion is square planar, but interionic interactions lead to a distortion of the square plane, and to additional contacts to the sulphur atom. This gives a greatly distorted octahedral arrangement around sulphur with three S–Cl bonds averaging 1.988 Å and three S $\cdots$ Cl contacts averaging 3.115 Å.

CONFLICTING reports on the orange crystalline material prepared by the interaction of iodine, sulphur, and chlorine, or by other methods,[1] have recently been resolved.[2] Elemental analysis and Raman-spectroscopic results were interpreted on the basis of the salt trichlorosulphonium(IV) tetrachloroiodate(III), existing in two forms, containing distorted square-planar $[ICl_4]^-$ anions. The present study was undertaken to confirm this result and to investigate the nature of the distortion.

EXPERIMENTAL

A sample of form (1) of the compound was kindly supplied by Dr. T. H. Page. Crystals of the moisture-sensitive material were grown in evacuated Pyrex-glass capillaries by applying a thermal gradient along the tube. Suitable single crystals were sealed in small lengths of the capillary tube. Unit-cell and space-group data were obtained photographically and intensity data with a diffractometer.

Crystal Data.—Cl_7IS, M = 407, Monoclinic, a = 10.42(1), b = 12.50(1), c = 8.27(1) Å, β = 108.6(2)°, U = 1 021 Å^3, Z = 4, D_c = 2.65 g cm^{-3}, $F(000)$ = 752, space group

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[1] M. P. Jaillard, *Ann. Chim. Phys.*, 1860, **59**, 454; R. Weber, *Ann. Phys. Chem.*, 1866, **128**, 459; O. Ruff, *Chem. Ber.*, 1904, **37**, 4519; Y. Tavares-Forneris and R. Forneris, *J. Mol. Structure*, 1975, **24**, 205.

[2] A. Finch, P. N. Gates, and T. H. Page, *Inorg. Chim. Acta Letters*, 1977, **25**, L49.

$P2_1/c$ (C_{2h}, no. 14) from systematic absences $0k0$ when $k \neq 2n$, $h0l$ when $l \neq 2n$, Mo-K_α radiation (λ 0.710 7 Å, μ 48 cm^{-1}). The density of the crystals was not measured but $Z = 4$ was assumed since the volume per chlorine atom was then 36 Å^3, comparable with that in similar compounds.

Structure Determination.—Intensity data were collected about the *b* axis (layers $h0$—$12l$) with a Stoe two-circle computer-controlled diffractometer as described previously.[3] Within the range $0.1 < (\sin\theta)/\lambda < 0.65$, 2 012 independent reflections having $I > 3\sigma(I)$ were observed. Data were corrected for Lorentz and polarisation factors but not for absorption.

TABLE 1

Final atomic positional parameters with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c
I	−0.275 85(4)	0.098 74(4)	0.155 22(6)
S	0.141 8(2)	0.086 2(1)	0.244 9(3)
Cl(1)	0.099 8(3)	0.109 3(2)	0.462 4(3)
Cl(2)	0.283 3(3)	0.196 7(2)	0.266 9(4)
Cl(3)	0.250 4(2)	−0.046 4(2)	0.298 3(3)
Cl(4)	−0.114 2(2)	−0.056 8(2)	0.139 1(3)
Cl(5)	−0.426 3(2)	0.246 1(2)	0.165 3(3)
Cl(6)	−0.422 9(2)	−0.031 0(2)	0.236 9(4)
Cl(7)	−0.115 1(2)	0.226 1(2)	0.076 2(3)

TABLE 2

Interatomic distances (Å) and angles (°) with estimated standard deviations in parentheses

(*a*) Distances

S–Cl(1)	2.002(3)	I–Cl(4)	2.603(2)
S–Cl(2)	1.986(3)	I–Cl(5)	2.437(2)
S–Cl(3)	1.977(3)	I–Cl(6)	2.469(3)
S · · · Cl(4)	3.097(3)	I–Cl(7)	2.543(3)
S . . . Cl(7)	3.129(3)	Cl(4) . . . Cl(6)	3.572(3)
S · · · Cl(4^{I})	3.119(3)	Cl(4) · · · Cl(7)	3.575(3)
Cl(1) · · · Cl(2)	3.071(3)	Cl(5) · · · Cl(6)	3.512(3)
Cl(1) · · · Cl(3)	3.074(3)	Cl(5) · · · Cl(7)	3.556(3)
Cl(2) · · · Cl(3)	3.078(3)		

(*b*) Angles

Cl(4)–I–Cl(6)	89.5(1)	Cl(5)–I–Cl(6)	91.4(1)
Cl(5)–I–Cl(7)	91.1(1)	Cl(4)–I–Cl(7)	88.0(1)
Cl(6)–Cl(4)–Cl(7)	98.0(1)	Cl(4)–Cl(7)–Cl(5)	90.0(1)
Cl(7)–Cl(5)–Cl(6)	90.3(1)	Cl(5)–Cl(6)–Cl(4)	90.7(1)
Cl(1)–S–Cl(2)	100.7(1)	Cl(1)–S–Cl(3)	101.2(1)
Cl(2)–S–Cl(3)	101.9(1)	Cl(4)–S–Cl(7)	70.1(1)
Cl(4)–S–Cl(4^{I})	81.5(1)	Cl(7)–S–Cl(4^{I})	79.8(1)
Cl(1)–S–Cl(4^{I})	154.9(1)	Cl(2)–S–Cl(4)	167.2(1)
Cl(3)–S–Cl(7)	156·4(1)		

(*c*) Contacts <3.7 Å

Cl(1) · · · Cl(4)	3.555(3)	Cl(1) · · · Cl(7)	3.577(3)
Cl(2) · · · Cl(5)	3.444(3)	Cl(3) · · · Cl(4)	3.606(3)
Cl(3) · · · Cl(6)	3.606(3)	Cl(1) · · · Cl(1^{II})	3.606(3)
Cl(4) · · · Cl(1^{II})	3.316(3)	Cl(6) · · · Cl(1^{II})	3.626(3)
Cl(2) · · · Cl(1^{III})	3.580(3)	Cl(7) · · · Cl(1^{III})	3.387(3)
Cl(4) · · · Cl(2^{I})	3.697(3)	Cl(4) · · · Cl(3^{I})	3.674(5)
Cl(5) · · · Cl(3^{IV})	3.135(3)	Cl(7) · · · Cl(3^{IV})	3.475(3)

Roman numerals as superscripts refer to atoms in the positions:

I $-x, -y, -z$ II $-x, -y, 1-z$
III $x, \frac{1}{2}-y, -\frac{1}{2}+z$ IV $-x, \frac{1}{2}+y, \frac{1}{2}-z$

The structure was solved by conventional Patterson–Fourier techniques. Scattering factors used were those for neutral atoms,[4] with corrections for the effects of anomalous dispersion.[5] Initial refinement by full-matrix least-squares methods was with layer scale factors refined separately, all the atoms vibrating isotropically and with unit weights. Refinement was continued with layer scale factors held constant and with the introduction of anisotropic thermal parameters, for all the atoms, of the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{23}klb^*c^* + 2U_{13}hla^*c^* + 2U_{12}hka^*b^*)]$. In the final stages of refinement the weighting scheme $w = [\sigma^2(|F_o|) + (0.014|F_o|^2)]^{-1}$ was found appropriate, giving a satisfactory analysis of the variation of $w\Delta^2$ with increasing $(\sin\theta)/\lambda$ and with increasing fractions of $|F_o|$. Final parameter shifts were $<0.1\sigma$, the final R was 0.060, and $R'\{=[\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}\}$ 0.063. The calculations were carried out on the ICL 1906A computer at Birmingham University Computer Centre using the program[6] SHELX-76. Observed and calculated structure factors and anisotropic thermal parameters are listed in Supplementary Publication No. 22346 (14 pp.),* final positional parameters, with their estimated standard deviations, in Table 1, and interatomic distances and angles in Table 2.

DISCUSSION

The atomic arrangement is illustrated in Figure 1. The nearest-neighbour chlorine atoms to sulphur and iodine define the trichlorosulphonium(IV) cation and the tetrachloroiodate(III) anion. Thus the recent formulation [2] of the compound is confirmed. The sulphur atom also has three longer contacts to chlorine atoms of $[ICl_4]^-$ anions, which are approximately equal, but are sufficiently long that the ionic formulation gives the best description of the structure.

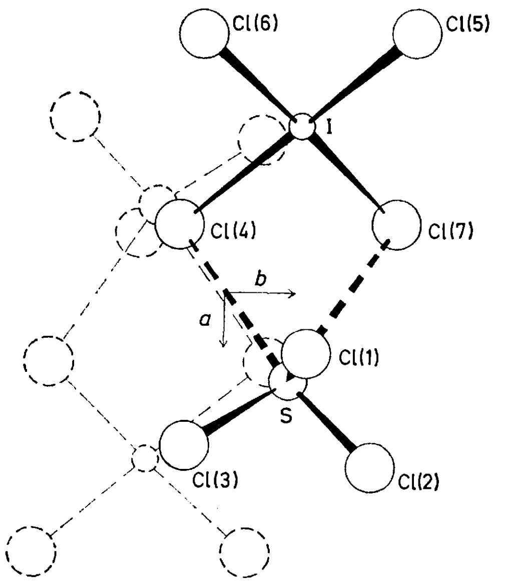

FIGURE 1 Projection of the structural unit, and of that related by the centre of symmetry (shown dashed), down [001]

The shape of the anion approximates to the square-planar configuration expected on valence-shell electron-pair repulsion (VSEPR) theory,[7] from an octahedral

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1977, Index issue.

[3] J. C. Dewan, A. J. Edwards, D. R. Slim, J. E. Guerchais, and R. Kergoat, *J.C.S. Dalton*, 1975, 2171.

[4] D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.

[5] D. T. Cromer, *Acta Cryst.*, 1965, **18**, 17.

[6] 'SHELX-76,' Program for Crystal Structure Determination, G. M. Sheldrick, Cambridge University, 1975.

[7] R. J. Gillespie, 'Molecular Geometry,' Van Nostrand–Reinhold, London, 1972.

arrangement of four bond pairs of electrons and two *trans* lone pairs. The anion is, however, distorted, as predicted from the previous spectroscopic measurements.[2] The different I–Cl distances can be correlated with the bridging interactions of the particular chlorine atoms involved. Thus the shortest distances [I–Cl(5) 2.437 and I–Cl(6) 2.469 Å] involve chlorine atoms with no contacts to sulphur. The intermediate distance (2.543 Å) involves Cl(7), which makes one contact to sulphur of 3.130 Å, and the longest distance (2.603 Å) involves Cl(4) which makes two contacts of 3.096 and 3.118 Å to two different sulphur atoms. The difference of 0.03 Å between the shortest bonds is possibly due to compensating effects, since Cl(5) with the shorter distance is opposite to Cl(4) with the longest I–Cl bond. The Cl–I–Cl angles in the anion are distorted from the expected 90° to retain virtually constant Cl–Cl distances and Cl–Cl–Cl angles, which are all closer to 90° than are those for Cl–I–Cl.

This distortion in the anion is very similar to that found in the structure[8] of $K[ICl_4]\cdot H_2O$, where an almost identical arrangement of one long, one intermediate, and two short bonds was found, and was correlated with interionic interactions of a similar nature.

The pyramidal arrangement in the $[SCl_3]^+$ cation has symmetry close to C_{3v}, as expected on VSEPR theory, with a co-ordination based on a tetrahedral configuration of three bond pairs and one lone pair. The S–Cl distances and Cl–S–Cl angles average 1.988 Å and 101.3° respectively. Thus the configuration is very similar to that of the isoelectronic species[9] PCl_3 in which the P–Cl distance is 2.043 Å and the Cl–P–Cl angle is 100.1°. In the cation the bond distance is 0.05 Å shorter and the bond angle 1.1° more obtuse than in the neutral molecule. A similar variation has been found for the corresponding fluoro-species[10] $[SF_3]^+$ and PF_3, where there is a decrease in bond distance of 0.07 Å, but the bond angles are not significantly different. The change in bond angle in the present case may be due to the chlorine–chlorine interaction being more significant than the fluorine–fluorine interaction.

The sulphur atom has three other contacts to chlorine atoms from $[ICl_4]^-$ anions. These contacts are approximately opposite the S–Cl bonds and give a distorted-octahedral arrangement around the sulphur atom. In VSEPR terms the contacts are grouped around the lone-pair position, and the total co-ordination can be described as seven-co-ordinate, with a distorted mono-capped-octahedral arrangement. Further theoretical elaborations could be made by considering the arrangement in terms of 'secondary bonds'[11] or the $\mathscr{C}$ configuration given by Brown.[12]

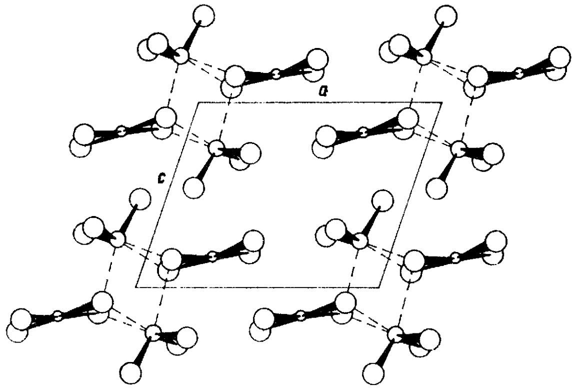

FIGURE 2 Projection down [010] of the section of the structure from $y = -\frac{1}{4}$ to $y = \frac{1}{4}$ showing the packing arrangement

A similar co-ordination is found for the $[SF_3]^+$ ion in $[SF_3][BF_4]$ but the interaction in the present case appears to be stronger, since the $[BF_4]^-$ ion showed no significant distortion from tetrahedral symmetry. The ratio S · · · F(bridge) : S–F(terminal) is 1.75 : 1 whereas the corresponding S–Cl ratio is 1.57 : 1, also supporting a stronger interaction.

These interactions between the sulphur atoms and the anions lead to an association into pairs of units, grouped around the centre of symmetry, as illustrated in Figure 1. The packing arrangement in the cell is shown in Figure 2.

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[8] R. J. Elema, J. L. de Boer, and A. Vos, *Acta Cryst.*, 1963, **16**, 243.

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[11] N. W. Alcock, *Adv. Inorg. Chem. Radiochem.*, 1972, **15**, 1.

[12] I. D. Brown, *J. Solid State Chem.*, 1974, **11**, 214.