

## Structure of Tetramethylammonium *trans*-Tetrachlorobis(dimethyl sulphide)iridate(III)

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**Abstract.**  $[\text{N}(\text{CH}_3)_4][\text{IrCl}_4\{\text{S}(\text{CH}_3)_2\}_2]$ ,  $\text{C}_4\text{H}_{12}\text{N}^+ \cdot \text{C}_4\text{H}_{12}\text{Cl}_4\text{IrS}_7^-$ ,  $M_r = 532.4$ , orthorhombic,  $a = 8.921$  (2),  $b = 14.109$  (2),  $c = 14.649$  (1) Å,  $Z = 4$ ,  $D_m = 1.93$  (2),  $D_c = 1.917$  Mg m<sup>-3</sup>,  $U = 1843.9$  Å<sup>3</sup>,  $F(000) = 1024$ ,  $\mu(\text{Mo } K\alpha) = 8.396$  mm<sup>-1</sup>. Space group  $Fmmm$  or  $F222$ ; the structure refined in both space groups equally well and the more symmetrical centrosymmetric space group  $Fmmm$  was chosen to report the results. The final  $R = 0.038$  for 473 observed reflections. The geometry at the Ir atom is *trans* octahedral with disordered methylthio groups [Ir–Cl = 2.359 (4), 2.349 (5), Ir–S = 2.335 (5), S–C = 1.92 (2) Å].

**Introduction.** The reaction of  $\text{Me}_4\text{NCl}$ ,  $\text{IrCl}_3 \cdot 3\text{H}_2\text{O}$  and  $\text{Me}_2\text{S}$  (1:1:2 mole ratio) in aqueous ethanol gives the compound  $[\text{Me}_4\text{N}][\text{IrCl}_4(\text{Me}_2\text{S})_2]$ , which can be separated into two isomers by acetone extraction. The major product (isomer *A* – orange colour) is acetone soluble and the minor product (isomer *B* – khaki colour) is acetone insoluble. Assignment of *cis* and *trans* structures for the anion was unclear from the vibrational spectra, but a tentative identification of *A* (*cis*) and *B* (*trans*) was proposed from the <sup>1</sup>H NMR spectra (Gulliver, Levason, Smith, Selwood & Murray, 1980). However, the EPR spectra of  $[\text{Ir}^{14}\text{Cl}_4(\text{Me}_2\text{S})_2]$  obtained by oxidation of these isomers casts doubt upon the original assignment (Gulliver, Higgins, Levason, Luckhurst & McCullough, 1981, unpublished work). In view of this observation, a crystal-structure analysis of isomer *A* was undertaken.

Air-stable orange crystals were obtained from acetone solution and found generally to be twinned or multiple crystals. One crystal was obtained which gave satisfactory photographs and this was used for the measurements.

Precise cell dimensions were obtained from 25 accurately centred reflections using an Enraf–Nonius CAD-4 diffractometer. The systematic absences are consistent with space groups  $F222$ ,  $Fmm2$  and  $Fmmm$ . Using Mo  $K\alpha$  radiation ( $\lambda = 0.7107$  Å), 473 unique reflections were recorded ( $\theta_{\min} = 1.5$ ,  $\theta_{\max} = 25.0^\circ$ ) at room temperature from a crystal  $0.60 \times 0.45 \times 0.15$  mm. There was no observed deterioration of the three

check reflections. An empirical absorption correction using a  $\phi$ -scan technique was applied.

The Patterson synthesis located all the atoms and established that the S atom was directed along the *x* direction and the Cl atoms along the *y* and *z* directions. Satisfactory models were developed in space groups  $F222$  and  $Fmmm$  with *trans* octahedral anions and disordered methylthio groups. The latter space group has four tetramethylammonium ions located on one half of the  $8(f)$  positions. For the model with all anisotropic atoms a residual of 0.054 was obtained in both space groups.

The large absorption coefficient makes the absorption correction important and the technique developed by Walker (1982) has been applied to the data. This proved particularly effective and with the weighting scheme  $W = 1/[\sigma^2(F) + 0.001F_0^2]$  least-squares refinement reduced the residual to a final value of 0.038 ( $R_w = 0.038$ ) with lower e.s.d.'s in the positional parameters. Again similar values were obtained in both space groups. All atoms were allowed to be anisotropic and no attempt was made to locate the H atoms. A final difference electron density synthesis showed all features in the range  $-1.50$  to  $+0.81$  e Å<sup>-3</sup>. The model in the centrosymmetric space group  $Fmmm$  with the smaller number of refined parameters (37) was chosen to present the results. The structure in the two space groups is virtually identical, differing only by small changes in the position of the methylthio C atom.

Scattering factors for neutral atoms and anomalous-dispersion corrections were taken from the *SHELX* package (Sheldrick, 1976) and *International Tables for X-ray Crystallography* (1974) (Ir atom). Calculations were performed with *SHELX*, *XANADU* (Roberts & Sheldrick, 1979), *PLUTO* (Motherwell & Clegg, 1978) and *ORTEP* (Johnson, 1965) on an ICL 2970 computer. Table 1 gives the final atomic coordinates and Figs. 1 and 2 show the details of the disordered anion including bond lengths and the unit-cell packing arrangement.†

† Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38004 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. Positional parameters ( $\times 10^4$ ) with e.s.d.'s in parentheses and equivalent isotropic thermal parameters ( $\text{\AA}^2 \times 10^3$ ) based on space group *Fm $\bar{3}m$*  (No. 69)

	x	y	z	$U_{eq}^*$
Ir	0	0	0	27.6
S	2617 (6)	0	0	70.1
Cl(1)	0	1672 (3)	0	54.8
Cl(2)	0	0	1604 (4)	78.6
N	2500	2500	2500	48.7
C(1)	1604 (36)	1842 (22)	3118 (21)	104.7
C(2)	3271 (33)	969 (24)	824 (25)	114.0

\*  $U_{eq}$  calculated as  $\frac{1}{3}$  (trace of orthogonalized  $U_{ij}$  matrix).

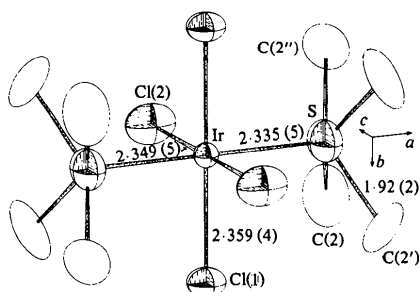


Fig. 1. The anion shown with the disordered C atoms (ellipsoids drawn at the 40% probability level).

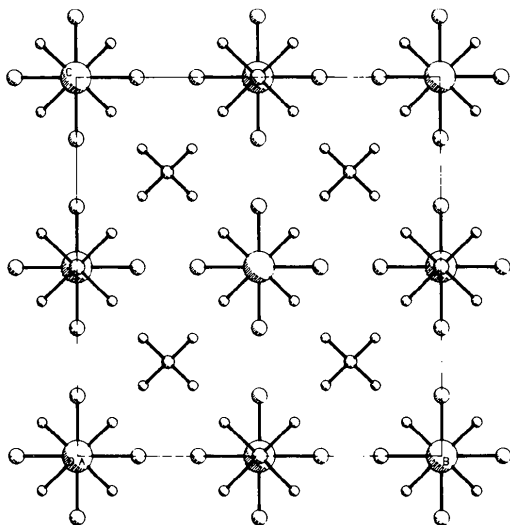


Fig. 2. View of the unit cell from the +x direction.

**Discussion.** This study has shown that the crystals grown from the orange isomer (*A*) contain *trans*-[IrCl<sub>4</sub>(Me<sub>2</sub>S)<sub>2</sub>]<sup>-</sup> anions. The Ir atom has local *mmm* site symmetry and the angle Ir-S-C(2) is 108 (1)°. The C(2)-S-C(2') and C(2)-S-C(2'') angles are

78.2 (1.7) and 91.1 (1.9)° where C(2') and C(2'') are related to C(2) by the mirror planes in the *xy* and *xz* planes respectively. It seems likely that the latter angle represents the correct choice of the C atoms within any one molecule. The possibility that photochemical isomerization, which is well established for some Ir<sup>III</sup> complexes (Brookes, Masters & Shaw, 1971), had occurred during crystal growth was eliminated by recording the <sup>1</sup>H NMR and IR spectra of crystals taken from the same batch that were subjected to X-ray examination. The results were identical to those reported (Gulliver *et al.*, 1980) and thus the assignment of *cis* and *trans* isomers in the original report is incorrect and should be reversed. The stereochemistry of the Ir<sup>IV</sup> complexes derived by chemical oxidation of both the Ir<sup>III</sup> compounds is now consistent with the EPR data (Gulliver *et al.*, 1981, unpublished).

X-ray structures of two isomers of formula Ir<sub>2</sub>Cl<sub>6</sub><sup>-</sup>(SEt<sub>2</sub>)<sub>4</sub> have recently been reported (Williams, Flack & Vincent, 1980). Similar values are observed for Ir-Cl distances in these compounds while the Ir-SEt<sub>2</sub>(*trans*) distance of 2.370 (7) Å is somewhat longer than the value in the present study [2.335 (5) Å].

The tetramethylammonium ion [N-C(1) 1.52 (2) Å] is slightly distorted (~8° maximum) from the ideal tetrahedral angles.

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