X-Ray Crystal Structure of Iodine Trifluoride Dioxide

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Summary Single crystal *X*-ray studies of iodine trifluoride dioxide have shown that the compound exists as a dimeric species in the crystalline state; the dimers are centrosymmetric with oxygen bridges and *trans* equatorial terminal oxygens.

Many fluorides and fluoride oxides of the transition metals have been synthesized and structurally characterized. For both classes of compounds, where polymerization occurs it is *via* fluorine bridging. In contrast, few fluoride oxides of the main-group metals have been made and there is a comparative dearth of structural information. In the isoelectronic series SbF_5, TeF_4O, IF_3O_2, and XeF_2O_3, SbF_5[1–3] forms strong fluorine-bridged polymers in the solid, liquid, and gas phase, whereas XeF_2O_3[4] has been shown to be monomeric. The compounds TeF_4O[5] and IF_3O_2[6] have been prepared only recently. From spectroscopic and molecular weight data, TeF_4O has been assigned as a centrosymmetric oxygen-bridged dimer.[3,5] There has, however, been considerable discussion in the literature regarding the structure of IF_3O_2. Engelbrecht *et al.* originally proposed[6] a monomeric formulation and, from ^{19}F n.m.r. data, inferred that two inseparable isomers (C_{2v} and C_s) were present. Beattie and Van Schalkwyk,[7] from molecular weight and spectroscopic data, suggested that the compound was an oxygen-bridged polymer. Engelbrecht *et al.*[8] subsequently endorsed this; further work by Beattie[3] *et al.* and by Vasile *et al.*,[9] including mass spectrometric and molecular beam electric deflection measurements, has indicated the presence of electrically centrosymmetric oxygen-bridged dimers as the main constituent of the vapour. In contrast to this, Gillespie and Krasznai[10] have proposed a trimeric structure on the basis of ^{19}F n.m.r. spectra taken in BrF_5, and Carter *et al.*[11] have suggested that the species is only weakly associated. In view of this, it appeared that an *X*-ray crystal structure determination would resolve the problem.

Crystal data: $F_6O_4I_2$, M 431·8, monoclinic, space group $P2_1/c$, $a = 7{\cdot}604(4)$, $b = 9{\cdot}745(4)$, $c = 10{\cdot}052(4)$ Å, $\beta = 108{\cdot}88(4)°$, $Z = 4$, $\mu(\text{Mo-}K_\alpha) = 91{\cdot}4\ \text{cm}^{-1}$, $F(000) = 768$.

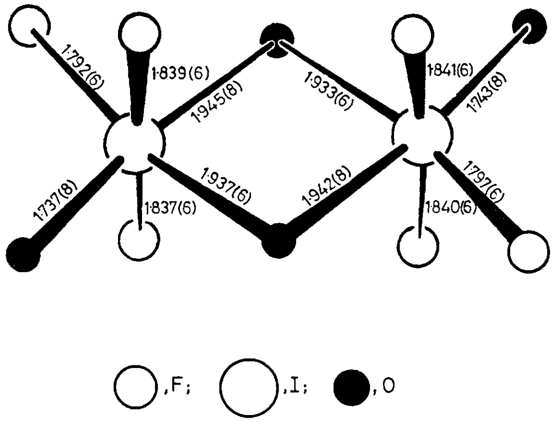

Figure. View of one molecule of $I_2F_6O_4$ showing the individual bond lengths.

The colourless crystal was grown in a quartz Lindemann capillary; intensity data from it were collected at −80 °C on a Syntex $P2_1$ diffractometer. The structure was solved by heavy atom methods and refined [111 parameters: 2968 independent absorption-corrected reflections, with $I_0 > 2{\cdot}5\sigma(I)$ and $2{\cdot}9° < 2\theta < 70°$] by full-matrix least-squares techniques to $R = 0{\cdot}056$ at the present time.

The results show unequivocally that iodine trifluoride dioxide exists as dimeric units (Figure) in the crystal. The oxygen and fluorine atoms have been distinguished on the basis of their bond lengths and the refinement of their thermal parameters. The molecule possesses a (non-crystallographic) centre of symmetry, with two octahedrally co-ordinated iodine atoms [I · · · · I, 3·016(2) Å] bridged by equatorial oxygen atoms. The four axial sites and two *trans* terminal equatorial sites are occupied by fluorine atoms. There is no significant asymmetry in the bridge bonds, but the axial I–F bonds (mean 1·839 Å) are longer than the equatorial (mean 1·795 Å).

The Raman spectrum of the crystalline sample used in this determination agrees well with that in ref. 3.

I thank Professor I. R. Beattie for suggesting the problem, P. J. Jones and R. Crocombe for preparing the samples, Dr. P. Woodward for helpful discussion, and the S.R.C. for support.

(*Received*, 28*th April* 1977; *Com.* 406.)

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