Crystal Structure of $(IOF_3{\cdot}IO_2F_3)_2$[†]

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The crystal structure of $(IOF_3{\cdot}IO_2F_3)_2$ has been determined from three-dimensional *X*-ray counter data at −45 °C. Crystals are monoclinic with $a = 9.832(4)$, $b = 8.307(5)$, $c = 10.187(7)$ Å, $\beta = 125.46(7)°$, $U = 677.7$ Å^3, $Z = 4$, and $D_c = 4.08$ g cm^{-3}. The structure has been refined in the space group $P2_1/n$ to a final conventional R' index of 0.061 for 1 289 independent reflections. It consists of two IOF_2 and two IO_2F_4 units linked by asymmetric oxygen bridges to give a cyclic molecule. These molecules are weakly bounded together in sheets by additional weak oxygen bridges.

In two recent papers [1,2] we discussed the preparation and the ^{19}F n.m.r. and Raman spectra of IO_2F_3 and of a number of acid–base adducts of IO_2F_3 including the adduct $IO_2F_3{\cdot}IOF_3$. On the basis of the spectroscopic data it was concluded that IO_2F_3 is a trimeric oxygen-bridged polymer although a recent *X*-ray determination of the structure [3] has shown it to be di- rather than tri-meric. The spectroscopic data also showed that the adducts are polymers containing IO_2F_4 units and, in the case of $IO_2F_3{\cdot}IOF_3$, IOF_2 units linked by oxygen bridges.

In order to verify the spectroscopic conclusions concerning the structure of IO_2F_3 and to obtain more detailed information on bond lengths and angles we attempted to obtain a crystalline sample suitable for a single-crystal *X*-ray diffraction study. Considerable difficulties were encountered but eventually a small crystal was grown by very slow sublimation of a sample of IO_2F_3 in a sealed capillary tube under a slight temperature gradient. When the structure determination had been completed however, it proved to be of a crystal of the adduct $IO_2F_3{\cdot}IOF_3$. It appears that some of the IO_2F_3 decomposed during the sublimation process to give IOF_3 and that this combined with undecomposed IO_2F_3 to give the adduct $IO_2F_3{\cdot}IOF_3$. The structure of this material is now reported here.

EXPERIMENTAL

Preparation of IO_2F_3 *and* $IO_2F_3{\cdot}IOF_3$.—The compound IO_2F_3 was prepared by the method of Engelbrecht and Peterfy [4,5] and was purified by pumping it through a U tube containing dry potassium sulphate to absorb any fluorosulphuric acid. A few milligrams of pure IO_2F_3 were transferred to a quartz capillary tube which was sealed under vacuum. The tube was then enclosed in a 0.375 in glass jacket covered with aluminium foil to minimize photodecomposition of the IO_2F_3, and allowed to sublime under a 5—10 °C thermal gradient. It was not possible to exclude light at all times, especially when the capillary was examined under a microscope, and some decomposition was evident. In particular there was some formation of a white amorphous solid and droplets of a colourless liquid, which were probably IO_2F and IF_5 respectively. One of the colourless crystals that had sublimed along the tube was used for the *X*-ray crystallographic study.

Crystal Data.—$IO_2F_3{\cdot}IOF_3$, $M = 416.0$, Monoclinic, $a = 9.382(4)$, $b = 8.307(5)$, $c = 10.187(7)$ Å, $\beta = 125.46(7)°$, $U = 677.7$ Å^3, $Z = 4$, $D_c = 4.08$ g cm^{-3}, $F(000) = 736$, $\lambda(\text{Mo-}K_{\bar{\alpha}}) = 0.710\,69$ Å, $\mu(\text{Mo-}K_{\bar{\alpha}}) = 95.0$ cm^{-1}. The unit-cell parameters were obtained from a least-squares refinement of 15 reflections in the region $20 < 2\theta < 30°$. The diffractometer data indicated that reflections were absent for $h0l$ when $h + l = 2n + 1$ and $0k0$ when $k = 2n + 1$, indicating the space group $P2_1/n$ which is an alternative setting of $P2_1/c$ (no. 14). The equivalent positions of the non-standard space group are: x,y,z; $\bar{x},\bar{y},\bar{z}$; $\frac{1}{2} - x,\frac{1}{2} + y,\frac{1}{2} - z$; and $\frac{1}{2} + x,\frac{1}{2} - y,\frac{1}{2} + z$.

X-*Ray Intensity Measurements*.—An approximately spherical crystal of diameter 0.020 cm was examined on a Syntex $P2_1$ automatic diffractometer equipped with a low-temperature device. The temperature of the capillary was maintained at -45 ± 5 °C during data collection. The crystal was mounted with *b* approximately coincident with the ϕ axis of the diffractometer. Intensity data were collected by the θ—2θ scan technique, with scan rates varying from 4.0 to 24.0° min^{-1} (in 2θ) so that weaker reflections were measured more slowly to reduce counting errors. Stationary-background counts, with a time equal to half the scan time for each reflection, were made at each end of the scan range. The scan width varied from 2° at low 2θ to 2.5° for higher angles. One standard reflection was checked between every 16 reflections to monitor the stability and alignment of the crystal. No significant drop in intensity was observed. 1 649 Reflections within a quadrant with $2\theta < 55°$ were measured. Subsequent averaging resulted in 1 289 independent reflections, 1 056 of which had intensities greater than three times their standard deviation based on counting statistics. Lorentz and polarisation corrections were applied to the intensity data. An absorption correction was computed with $\mu R = 0.95$, assuming the crystal to be spherical.

Solution and Refinement of the Structure.—The positions of two independent iodine atoms were located from inspection of the three-dimensional Patterson function. These atoms were assigned neutral iodine scattering curves which were corrected for anomalous dispersion using the values for the real and imaginary parts.[6] Least-squares refinement of positional and isotropic thermal parameters gave a conventional *R* index of 0.18. The positions of nine light atoms, assumed to be fluorine, were located from a three-dimensional electron-density map. Further refinement reduced *R* to 0.098. All the I(1)–light-atom distances were found to be 1.82(2) Å, while there were two I(2)–light-atom distances of 1.85(2) Å, two of 2.27 Å, and one of 1.76 Å. It was reasonable to assume that the 1.76 Å distance represented an I=O terminal double bond while the atoms at 2.27 Å from I(2) and 1.82 Å from I(1) were assumed to be bridging oxygen atoms. The remainder of the light atoms were

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[†] Bis(iodosyl trifluoride-iodyl trifluoride).

assumed to be fluorine atoms. The appropriate scattering curves were applied and anisotropic temperature factors were introduced for all atoms. Further least-squares refinement gave a final R' index, $= \Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2)^{\frac{1}{2}}$ where $w^{\frac{1}{2}} = (84.5 + 1.29F_o + 0.58F_o^2)^{-1}$, of 0.061 3 and R index of 0.063 2 for 1 289 and 1 056 independent reflections respectively. Examination of the observed and calculated structure factors indicated a uniform distribution of $(|F_o| - |F_c|)^2$ over the F_o^2 and $(\sin \theta)/\lambda$ ranges. The maximum shift (Δ/σ) was <0.1 in the final cycle of refinement and a final difference Fourier had no peak greater than 0.27 e Å^{-3}. The final positional parameters and interatomic bond lengths and angles are listed in Tables 1 and 2 respectively. Structure amplitudes and thermal parameters are listed in Supplementary Publication No. SUP 22661 (9 pp.).*

TABLE 1

Positional parameters ($\times 10^3$) for $IO_2F_3 \cdot IOF_3$

Atom	x/a	y/b	z/c
I(1)	−152.2(2)	101.9(2)	169.3(1)
I(2)	157.2(2)	225.9(1)	87.2(1)
F(1)	−94(1)	−71(1)	301(1)
F(2)	−350(1)	96(2)	150(1)
F(3)	−88(2)	220(2)	349(1)
F(4)	−222(1)	294(1)	64(2)
F(5)	253(1)	346(1)	9(1)
F(6)	123(2)	421(1)	153(1)
O(1)	−43(2)	214(2)	−96(1)
O(2)	54(1)	125(2)	217(1)
O(3)	249(2)	16(2)	12(2)

TABLE 2

Bond lengths (Å) and angles (°) in $(IOF_3 \cdot IO_2F_3)_2$

I(1)–F(1)	1.82(1)	I(2)–F(5)	1.84(2)
I(1)–F(2)	1.84(2)	I(2)–F(6)	1.86(1)
I(1)–F(3)	1.83(1)	I(2)–O(1)	1.76(1)
I(1)–F(4)	1.82(1)	I(2)–O(1″)	2.88(1)
I(1)–O(2)	1.80(1)	I(2)–O(2)	2.25(2)
I(1)–O(3)	1.80(1)	I(2)–O(3′)	2.29(2)
F(1)–I(1)–F(2)	85.4(7)	F(5)–I(2)–F(6)	85.9(7)
F(1)–I(1)–F(3)	84.7(6)	F(5)–I(2)–O(1)	96.0(7)
F(1)–I(1)–F(4)	168.0(8)	F(5)–I(2)–O(1″)	86.7(5)
F(1)–I(1)–O(2)	93.5(7)	F(5)–I(2)–O(2)	167.8(6)
F(1)–I(1)–O(3)	94.5(6)	F(5)–I(2)–O(3′)	82.2(6)
F(2)–I(1)–F(3)	81.4(7)	F(6)–I(2)–O(1)	96.1(5)
F(2)–I(1)–F(4)	87.0(7)	F(6)–I(2)–O(1″)	74.3(4)
F(2)–I(1)–O(2)	170.9(6)	F(6)–I(2)–O(2)	82.8(7)
F(2)–I(1)–O(3)	88.8(7)	F(6)–I(2)–O(3′)	166.9(7)
F(3)–I(1)–F(4)	85.0(6)	O(1)–I(2)–O(1″)	169.9(7)
F(3)–I(1)–O(2)	89.5(7)	O(1)–I(2)–O(2)	89.9(7)
F(3)–I(1)–O(3)	170.2(7)	O(1)–I(2)–O(3′)	90.8(6)
F(4)–I(1)–O(2)	92.6(7)	O(1″)–I(2)–O(2)	85.7(4)
F(4)–I(1)–O(3)	94.6(6)	O(1″)–I(2)–O(3′)	99.2(4)
O(2)–I(1)–O(3)	100.3(7)	O(2)–I(2)–O(3′)	108.4(6)
I(1)–O(2)–I(2)	134.8(6)		
I(1)–O(3)–I(2)	133.1(6)		

DISCUSSION

The structure (Figure 1) consists of individual molecules containing two IO_2F_4 and two IOF_2 groups linked by *cis* oxygen bridges. The molecules are linked by rather long iodine–oxygen interactions into infinite sheets.

If all the interactions longer than 1.90 Å are neglected then the structure can be regarded to a first approximation as consisting of $[IOF_2]^+$ cations and $[IO_2F_4]^-$ anions (I). The $[IOF_2]^+$ cation has the pyramidal shape expected for an AX_3E type molecule [7] and has IO and IF bond lengths of 1.76 and 1.85 Å (mean) respectively. The short IO bond length indicates considerable double-bond character and the FIO bond angle of 96.0° is larger than the FIF angle of 85.9°, presumably because of the stronger repulsive effect of the double bond.

In the anion $[IO_2F_4]^-$ the mean IF bond length is 1.83 Å and the IO bond length is 1.80 Å. The IO bonds are somewhat longer than in the $[IOF_2]^+$ ion. This may be attributed to the negative charge of the anion and the fact that these oxygen atoms are involved in relatively strong bridging. The angles are distorted from the 90° angles of a regular octahedron by the presence of two partially double-bonded oxygens. The greater repulsion exerted by the partial double bonds enlarges all the angles made by these bonds so that the OIO angle is 100° and the FIO angles average 92° whereas the remaining FIF angles average only 85°.

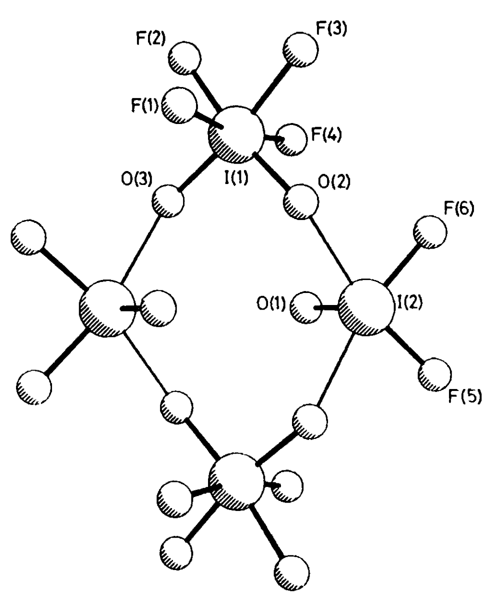
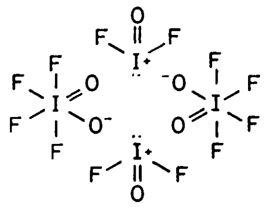
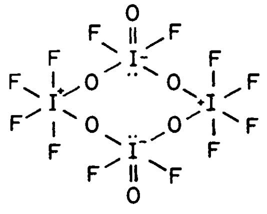


FIGURE 1 Structure of dimeric $IOF_3 \cdot IO_2F_3$

If the I–O distances of 2.25 and 2.27 Å are regarded as partial covalent bonds then the IOF_2 and IO_2F_4 groups are seen to be linked by asymmetric oxygen bridges to give the dimer $[IO_2F_3 \cdot IOF_3]_2$ which has an eight-membered ring of alternate oxygen and iodine atoms (II) with a 'chair' type of conformation. The bridging oxygen atoms are more closely associated with I(1) than with I(2) [I(1)–O 1.80, I(2)–O 2.27 Å (mean)]. The $I(2)O_3F_2$ unit has a square-pyramidal AX_5E type of geometry with the terminal oxygen atom occupying the



(I)



(II)

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

axial position. The four atoms F(5), F(6), O(2), and O(3) are in the same plane and this plane lies below the central iodine atom. This distortion of the square pyramid, which is in the opposite sense from that normally observed in simple AX_5E molecules, may be attributed to the large repulsive effect of the axial I=O double bond and to the weakness of the other two IO bonds.

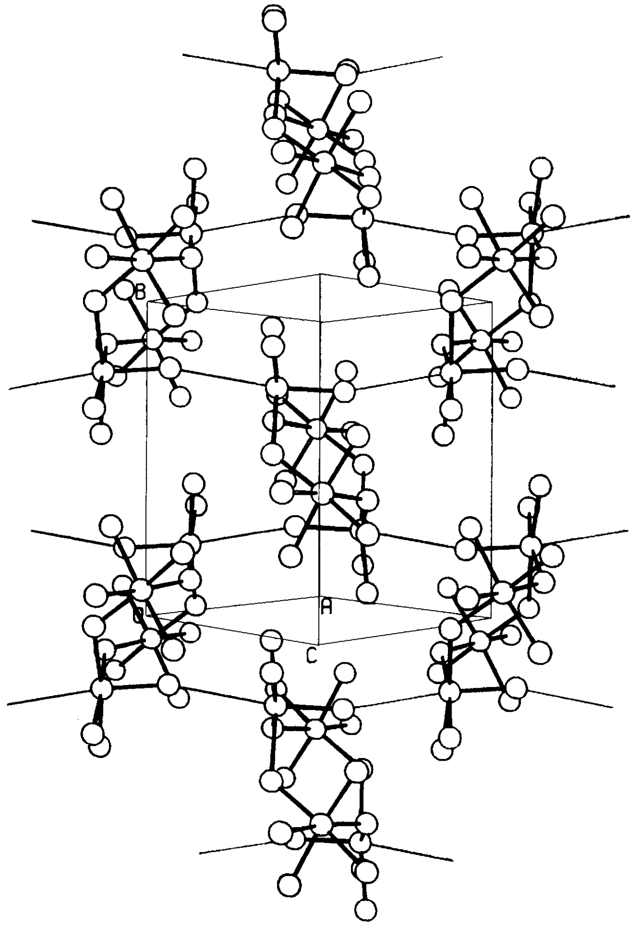

FIGURE 2 Projection of the structure down the [011] axis

The cyclic molecules are linked together into infinite layers by further weak oxygen bridges (2.88 Å) formed between the terminal O(1) atoms and the I(2) atom of an adjacent molecule (Figure 2). This weak bridge is approximately *trans* to the I(2)–O(1) bond (169.9°) giving a distorted octahedral geometry of four oxygen and two fluorine atoms around I(2). This can also be equally well regarded as overall AX_6E co-ordination around iodine with a monocapped octahedral geometry with three short bonds and the lone pair in the capping position between three long bonds. The average angle between the shorter IO(1), IF(5), and IF(6) bonds is 89° while that between the longer IO(3), IO(2), and IO(1) bonds surrounding the lone pair is 98°.

The fluorine and oxygen atoms form an approximately close-packed structure as is shown by the volume of 18.8 $Å^3$ per light atom which is only slightly greater than that of SbF_5 (17.8 $Å^3$).[8] The difference may be attributed mainly to the presence of the lone pair. The efficiency of the packing is reflected in the I(1)–O(2)–I(2) and I(1)–O(3)–I(2) angles of 134.8 and 133.1° respectively, which are very close to the angle of 132° expected for hexagonal close packing.

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