

A RE-DETERMINATION OF THE CRYSTAL STRUCTURE OF IODINE OXIDE TRIFLUORIDE

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SUMMARY

The crystal structure of iodine oxide trifluoride has been re-determined and the oxygen atom assigned to a different position from considerations of the detailed molecular geometry.

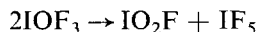
INTRODUCTION

During an investigation of the interaction of I_2 , IF_5 and SbF_5 in Pyrex apparatus, some colourless crystals suitable for X-ray examination were obtained. When crystallographic data collection was almost complete, the crystals were identified as IOF_3 , by a comparison of unit-cell dimensions with those previously reported by Viers and Baird¹. Since the molecular geometry previously reported seemed inconsistent with the assigned position for the oxygen atom, and since the authors claimed to have distinguished oxygen from fluorine by X-ray methods alone in the presence of the iodine atom, we have completed our re-determination of the structure and report the results here.

EXPERIMENTAL

Preparation of iodine oxide trifluoride

During an attempt to crystallise $[I_2]^+[Sb_2F_{11}]^-$ (ref. 2) from IF_5 solution directly in thin-walled Pyrex capillaries, colourless needle crystals were observed after the solution had been standing for some weeks. When these crystals were sealed in small sections of capillary under vacuum, they decomposed over a period of 1–2 days. However, in the presence of small amounts of IF_5 , the crystals were stable for several weeks. IOF_3 is reported³ to decompose on heating above 110 °C:



and to be regenerated by refluxing IO_2F in IF_5 . The behaviour reported above suggests an equilibrium at room temperature in the presence of glass:



Crystal data

Iodine oxide trifluoride (mol. wt. = 200) is orthorhombic, $a = 5.70(1)$, $b = 5.62(1)$, $c = 10.49(2)$ Å (Viers and Baird¹ report $a = 5.689$, $b = 5.638$, $c = 10.463$ Å), $U = 336$ Å³, $Z = 4$, calculated density = 3.95 g cm⁻³, $F(000) = 352$; space group $P2_12_12_1$ (D_2^4 , No. 19) from systematic absences: $h00$, $h \neq 2n$, $0k0$, $k \neq 2n$ and $00l$, $l \neq 2n$. X-Ray measurements were made using $\text{CuK}\alpha$ ($\lambda = 1.5418$ Å) and $\text{MoK}\alpha$ ($\lambda = 0.7107$ Å; $\mu = 101$ cm⁻¹) radiations and employing single crystal precession and Weissenberg photographs.

Structure determination

Integrated intensities were collected about the a axis (layers 0–4 k l) by use of $\text{MoK}\alpha$ radiation and a Nonius integrating camera. The relative intensities of 306 independent reflections were measured with a photometer of similar design to that described by Jeffery⁴, and were corrected for Lorentz and polarisation factors. Calculation of a three-dimensional Patterson map, and a subsequent electron-density map, gave the positions of the iodine atom and the four light atoms. Refinement of the positional and isotropic temperature parameters and layer scale factors was carried out by full-matrix least-squares methods, using scattering factors for neutral atoms⁵ for the structure factor calculations. The function $\sum w(|F_o| - |F_c|)^2$ was minimised in the refinement with unit weights throughout.

One of the light atoms was closer to iodine than the other three and was tentatively assigned as oxygen. Refinement proceeded to $R = 0.075$. After application of an absorption correction for a rectangular block crystal (dimensions $0.15 \times 0.10 \times 0.05$ mm), R was reduced to 0.060 and refinement was considered complete. The final parameter shifts were $< 0.1\sigma$ and an analysis of the variation of Δ^2 with increasing $\sin \theta/\lambda$ and with increasing $|F_o|$ was satisfactory.

Since Viers and Baird¹ had assigned light atom identities on the basis of separate refinements of models having the oxygen atom in the two alternative equatorial positions, we refined the model (referred to as VB) with the oxygen atom in the alternative position [F(3)]. This VB model refined to $R = 0.061$, essentially the same as previously. However, although the original model showed no significant difference between the temperature factors for the four light atoms, the VB model showed temperature factors significantly lower for the "oxygen" atom and significantly higher for "F(3)". This suggests an attempted compensation by the refinement process for the incorrect assignment of scattering factors. Although this evidence is insufficient to confirm the light atom identities, and although it seems unlikely that oxygen can be distinguished from fluorine by X-ray

methods alone in the presence of the iodine atom, it is in agreement with the stereochemical considerations described below.

Observed and calculated structure factors are listed in Table 1, final positional parameters and isotropic temperature factors in Table 2 and interatomic distances and angles together with the corresponding VB values in Table 3.

DISCUSSION

The interatomic distances and angles shown in Table 3 are in excellent agreement with those reported by Viers and Baird, the differences in all cases being not statistically significant. We do not consider that light atom identities can be assigned from the X-ray measurements directly, as discussed above, and we have therefore assigned the oxygen atom from the stereochemistry.

If initially only the nearest neighbours to the iodine atom are considered, the structure consists of IOF₃ molecules. Valence-shell electron-pair repulsion (VSEPR) theory⁶ predicts a trigonal-bipyramidal arrangement for the molecule, with the multiply-bonded oxygen atom and the non-bonding electron pair (which have greater repulsive effects than the fluorine atoms) in equatorial positions. The molecular shape shown in Figure 1 conforms to this prediction, with F(1) and F(2) in axial, and O and F(3) in equatorial positions.

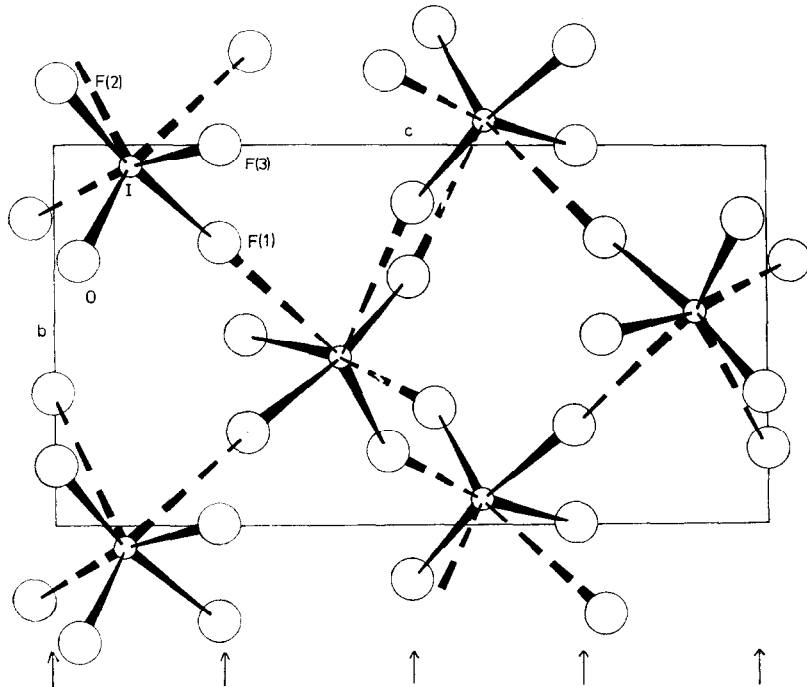


Fig. 1. Projection of the structure down [100]. The arrows indicate planes of approximately close-packed atoms.

TABLE I
OBSERVED AND CALCULATED STRUCTURE FACTORS

h	k	l	F _o	F _c	φ	h	k	l	F _o	F _c	φ	h	k	l	F _o	F _c	φ
0	0	4	57.3	53.0	180	2	38.3	35.9	205	3	1	13	41.2	41.3	270		
		6	108.9	113.5	180	3	66.5	68.0	276			1	55.3	91.5	182		
		8	52.0	56.9	0	4	32.3	26.2	125			2	42.5	42.7	324		
		10	77.3	84.2	0	6	20.7	21.3	85			3	49.6	46.3	37		
		12	22.3	0	0	7	54.9	55.7	46			4	52.8	49.1	84		
		2	196.9	167.5	90	8	37.6	24.7	249			5	107.7	104.1	257		
		3	35.8	34.7	270	9	31.1	27.6	109			6	44.5	28.2	144		
		4	75.5	71.7	90	0	22.4	20.3	90			7	34.9	25.1	348		
		5	55.6	51.6	270	1	40.9	41.4	206			8	28.2	29.6	187		
		6	70.1	66.3	270	2	39.5	40.3	110			9	50.3	51.5	186		
		8	100.4	99.9	270	3	29.1	19.6	322			11	24.8	22.7	171		
		12	49.0	54.1	90	4	26.7	27.9	323			3	2	0	98.4	100.1	270
		0	92.6	94.6	0	5	42.4	42.4	354			1	61.7	60.5	299		
		1	60.7	63.4	180	6	52.8	52.4	211			2	47.6	47.5	304		
		3	76.7	94.0	180	7	34.2	29.6	172			3	82.4	78.6	489		
		4	101.9	98.6	180	8	37.2	40.5	270			4	51.2	49.2	73		
		7	76.9	76.3	180	9	48.5	48.2	235			5	21.2	19.4	194		
		9	73.9	78.5	0	4	38.5	38.2	99			6	49.5	45.4	109		
		9	38.5	39.8	0	6	38.3	31.3	79			7	51.5	52.3	93		
		10	43.2	55.1	0	2	42.4	26.1	1			8	28.1	28.5	430		
		1	90.2	89.0	90	3	87.1	85.9	270			9	27.5	28.6	36		
		2	64.3	60.4	90	4	86.5	87.0	3			10	68.2	64.5	270		
		3	42.7	41.3	270	5	119.4	120.1	270			11	30.9	28.6	295		
		4	27.2	27.2	90	7	34.1	31.1	270			3	3	0	18.9	12.6	270
		5	117.5	115.1	270	8	42.2	45.6	90			2	94.0	92.6	347		
		8	40.6	36.1	270	10	44.4	53.8	180			3	31.2	23.8	70		
		9	57.5	54.5	90	11	22.1	20.4	90			4	50.8	50.7	14		
		11	43.6	47.6	90	2	89.6	91.6	244			6	40.3	39.8	179		
		0	22.6	20.1	180	4	55.2	51.6	286			7	27.2	26.0	276		
		1	72.9	71.0	180	5	38.6	36.7	72			8	61.9	58.5	183		
		2	27.0	24.8	180	6	60.3	52.8	64			9	30.4	25.2	13		
		3	105.1	104.7	180	7	62.6	61.7	2			12	37.9	36.6	357		
		7	71.9	74.0	0	8	58.9	59.9	108			3	4	0	74.0	76.5	270
		9	29.9	24.1	0	9	37.8	37.4	341			2	22.1	17.4	486		
		11	37.4	35.7	180	10	24.2	25.5	101			4	70.4	71.5	86		
		13	35.9	40.7	180	11	29.9	32.7	207			5	32.9	28.6	171		
		1	77.2	77.2	90	12	28.7	37.1	182			6	62.2	59.2	95		
		2	29.5	30.1	270	13	24.4	32.4	167			10	45.8	48.4	267		
		3	23.3	21.8	270	0	71.1	73.9	180			1	2	0	63.6	61.9	1
		5	67.6	65.6	270	1	87.1	84.6	62			4	38.2	36.2	355		
		9	43.3	49.4	90	2	74.9	71.5	257			4	38.4	35.1	133		
		11	29.1	24.5	90	3	58.1	56.0	359			8	42.4	42.8	176		
		0	45.0	42.6	180	4	68.0	66.1	217			8	48.6	44.3	270		
		1	26.9	26.2	180	6	87.1	84.6	362			3	6	0	48.6	44.3	270
		3	49.0	47.6	180	6	85.3	85.1	391			2	24.0	25.0	98		
		4	26.2	40.6	0	7	44.8	47.7	182			2	24.8	18.1	227		
		6	38.8	34.9	0	8	44.3	42.0	114			3	39.5	36.0	99		
		7	48.9	45.6	270	9	40.2	37.1	128			4	32.7	32.1	103		
		4	30.6	26.6	270	10	35.6	35.1	184			1	76.8	75.6	9		
		8	38.2	34.1	90	11	36.7	35.8	61			3	7	0	36.9	35.5	176
		1	41.0	41.1	180	12	32.2	30.2	254			4	0	3	17.2	41.1	90
		3	49.3	47.6	180	0	23.1	24.5	180			5	102.0	104.2	90		
		4	26.2	40.6	0	1	61.8	59.9	262			7	24.0	22.0	90		
		7	48.9	45.6	270	2	51.0	51.0	221			9	46.8	44.6	270		
		8	38.8	34.9	0	3	49.6	49.5	144			11	40.5	45.1	270		
		2	48.9	45.6	270	4	68.9	64.9	340			10	24.0	25.5	0		
		4	30.6	26.6	270	5	58.3	62.4	81			1	64.6	66.3	5		
		8	38.2	34.1	90	6	46.9	47.3	18			2	15.1	19.0	330		
		1	41.0	41.1	180	7	33.9	30.6	40			3	93.4	90.3	4		
		3	49.3	47.6	180	8	27.3	22.7	172			4	42.4	40.5	181		
		4	26.2	40.6	0	9	44.6	43.0	290			6	27.0	22.1	181		
		7	48.9	45.6	270	10	42.7	44.2	181			7	68.2	72.2	177		
		8	38.2	34.1	90	11	32.7	28.6	248			9	34.3	33.4	175		
		1	41.0	41.1	180	12	24.2	21.6	10			11	29.8	31.0	1		
		3	49.3	47.6	180	2	67.1	68.6	262			13	38.2	36.6	4		
		4	26.2	40.6	0	3	63.1	66.3	4			1	89.1	87.9	273		
		7	48.9	45.6	270	4	37.0	38.0	283			2	69.3	70.1	79		
		8	38.8	34.9	0	6	42.2	39.9	93			3	26.0	21.6	81		
		2	48.9	45.6	270	7	45.9	46.6	175			4	41.5	39.9	90		
		4	30.6	26.6	270	8	52.3	51.2	86			5	52.5	55.9	91		
		8	38.2	34.1	90	9	27.3	22.7	172			7	18.4	20.0	105		
		1	41.0	41.1	180	1	47.5	46.4	292			8	44.9	43.6	267		
		3	49.3	47.6	180	2	22.5	21.1	113			9	45.2	41.0	266		
		4	26.2	40.6	0	4	45.1	47.2	18			11	30.7	25.4	272		
		7	48.9	45.6	270	5	46.2	47.7	89			12	29.4	30.7	91		
		8	38.2	34.1	90	6	40.4	43.5	350			0	92.0	94.9	0		
		1	41.0	41.1	180	7	26.3	27.9	254			1	22.2	23.2	352		
		3	49.3	47.6	180	8	40.4	43.5	350			2	18.5	22.2	300		
		4	26.2	40.6	0	9	26.3	27.9	254			3	33.2	30.1	8		
		7	48.9	45.6	270	10	27.6	30.6	177			4	55.8	55.5	179		
		8	38.2	34.1	90	1	24.5	23.7	303			5	51.9	56.0	181		
		1	41.0	41.1	180	2	39.6	36.0	286			7	36.9	30.0	174		
		3	49.3	47.6	180	3	37.2	30.0	15			8	30.9	21.4	11		
		4	26.2	40.6	0	4	32.4	32.4	220			10	46.8	46.2	358		
		7	48.9	45.6	270	5	24.4	23.0	93			4	4	4	46.4	42.1	181
		8	38.2	34.1	90	6	40.4	43.5	350			6	39.3	42.0	276		
		1	41.0	41.1	180	7	27.7	30.4	103			8	53.2	53.7	271		
		3	49.3	47.6	180	8	28.1	30.8	9			9	38.5	34.8	89		
		4	26.2	40.6	0	9	23.9	29.0	0			12	38.5				

TABLE 2

FINAL ATOMIC POSITIONAL AND THERMAL PARAMETERS WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Atom	x/a	y/b	z/c	$B(\text{\AA}^2)$
I	0.1846(6)	0.0611(4)	0.1006(2)	1.45(4)
O	0.3209(99)	0.3019(49)	0.0330(26)	3.14(57)
F(1)	0.0516(72)	0.2566(44)	0.2306(24)	3.37(52)
F(2)	0.3665(52)	-0.1558(41)	0.0043(23)	2.84(51)
F(3)	0.3907(54)	0.0008(44)	0.2313(23)	3.37(62)

TABLE 3

INTERATOMIC DISTANCES (\AA) AND ANGLES (degrees) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES*

	Present work	VB results		Present work
I-O	1.71(4)	1.74(2)	I...O ^I	2.62(6)
I-F(1)	1.91(3)	1.90(2)	I...F(1 ^{II})	2.81(3)
I-F(2)	1.89(3)	1.83(2)	I...F(2 ^{III})	3.11(3)
I-F(3)	1.84(3)	1.82(2)	O...F(1)	2.59(5)
O...F(2)	2.60(4)		O...F(3)	2.71(4)
F(1)...F(3)	2.41(5)		F(2)...F(3)	2.54(3)
O...O ^I	2.99(2)		F(1)...O ^I	3.08(5)
F(2)...O ^I	3.71(6)		O ^I ...F(2 ^{III})	3.07(3)
F(1)...F(1 ^{II})	2.90(2)		F(1 ^{II})...F(2 ^{III})	2.96(4)
F(2)...F(2 ^{III})	3.04(2)		F(3)...F(1 ^{II})	2.90(5)
F(2)...F(1 ^{II})	3.70(4)		O...F(3 ^{IV})	3.17(5)
F(3)...F(2 ^V)	3.33(4)		F(2)...O ^{VI}	3.29(6)
F(1)...F(2 ^I)	3.50(4)			
O-I-F(1)	91.2(1.4)	90	O-I-O ^I	84.6(1.0)
O-I-F(2)	92.3(1.5)	95	O-I-F(1 ^{II})	163.7(1.1)
O-I-F(3)	99.5(1.8)	98	F(1)-I-O ^I	84.2(1.3)
F(1)-I-F(2)	165.9(1.3)	168	F(2)-I-O ^I	109.7(1.2)
F(1)-I-F(3)	80.0(1.3)	82	O ^I -I-F(1 ^{II})	97.9(1.1)
F(2)-I-F(3)	85.9(1.2)	86	F(3)-I-O ^I	163.7(1.1)
F(1)-I-F(1 ^{II})	73.1(1.3)		F(2)-I-F(2 ^{III})	70.1(1.2)
F(2)-I-F(1 ^{II})	101.9(1.0)		F(1 ^{II})-I-F(2 ^{III})	59.7(1.3)
F(3)-I-F(1 ^{II})	73.9(1.1)		O ^I -I-F(2 ^{III})	64.1(1.6)
I-O ^I -I ^I	128.3(1.1)		I-F(1 ^{II})-I ^{II}	173.0(1.8)
I-F(2 ^{III})-I ^{III}	170.0(1.7)			

* The Roman numerals as superscripts refer to atoms in the positions:

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

Our assignment of the oxygen atom position gives an I–O distance of 1.71 Å, significantly shorter than the equatorial I–F distance of 1.84 Å or the axial distance of 1.90 Å. This is compatible with a number of structures of compounds containing M–F and M–O terminal bonds, where the bonds to oxygen are significantly shorter than those to fluorine. This I–O distance is very similar to the I–O distance of 1.72 Å recently reported⁷ in CsIOF₄, and comparable with the mean (I–O)_{terminal} bond length of 1.79 Å in I₂O₅ and 1.777 Å in KIO₃, HIO₃, respectively^{8,9}.

The mean I–F distance of 1.88 Å in IOF₃ is close to those reported for IF₅. Electron-diffraction studies of the pentafluoride itself give an I–F distance¹⁰ of 1.86 Å, and in the molecular adduct XeF₂.IF₅ crystallographic results¹¹ show a mean I–F distance of 1.88 Å. The I–F distance of 1.97 Å in the IOF₄[−] anion is considerably larger⁷, but this may be due to the overall negative charge.

On VSEPR theory, a multiple M–O bond should have a greater repulsive effect on neighbouring ligands than a M–F bond. The F_{axial}–I–O bond angles would therefore be expected to be larger than the F_{axial}–I–F_{equatorial} angles in IOF₃. On our model this is so, with mean values for the angles of 91.7° and 83.0°, respectively. The latter angle is identical with the mean F_{axial}–I–F_{equatorial} angle in the IF₄⁺ cation¹² of [IF₄]⁺[Sb₂F₁₁][−] with which IOF₃ is isoelectronic.

We therefore conclude that the stereochemistry of the molecular arrangement in IOF₃ is consistent with our assignment of the oxygen atom position rather than that of Viers and Baird¹.

If the intermolecular contacts in the structure are considered (Table 3 and Fig. 1), the IOF₃ molecules are linked into a three-dimensional network through three weak bridging interactions. These are through O with an I...O distance of 2.62 Å, F(1) with an I...F(1) distance of 2.81 Å and F(2) with an I...F(2) distance of 3.11 Å. This last interaction must be very weak, although the I...F distance is less than the sum of Van der Waal's radii (3.5 Å). The two shorter interactions give a distorted octahedral coordination around the iodine atom, which, if the non-bonding electron pair is included, can be considered to be based on a 7-coordinate monocapped octahedral arrangement. This coordination arrangement is similar to that found for the selenium¹³, arsenic¹⁴ and tellurium¹⁵ atoms in [SeF₃]⁺[Nb₂F₁₁][−], SeOF₂, NbF₅, AsF₃, SbF₅ and [TeF₃]⁺[Sb₂F₁₁][−] respectively, although in these compounds there are three bonds and three long contacts compared with the four bonds and two long contacts in IOF₃. In all cases, the long interactions are grouped round the position assigned to the non-bonding electron pair on VSEPR theory. The longer interaction from F(2) in IOF₃ also avoids this position, but this contact may be due to the approach to close-packing of the light atoms in the structure, as can be seen from Figure 1.

The structure of IOF₃ is completely different from that of the isoelectronic TeF₄ in the solid state. The tellurium compound¹⁶ has a fluorine-bridged, zig-zag chain arrangement, with three terminal and two bridging fluorine atoms in a distorted square-pyramidal coordination around tellurium. The non-bonding

electron pair is considered to complete a distorted octahedral arrangement in this case. The $(\text{Te}-\text{F})_{\text{bridge}}$ distances are similar (2.08 and 2.26 Å) so that the structure can be described as predominantly derived from the covalently-linked infinite-chain arrangement with only a minor contribution from the formulation as separate molecules, the complete reverse of the situation in IOF_3 .

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