

Notes

Crystal Structure of IO₂F

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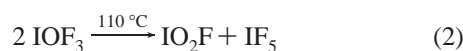
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Introduction

It is likely that in the series IF₅, IOF₃, IO₂F, and I₂O₅, the structures should get more polymeric character in the solid state, with increasing number of oxygen atoms. IF₅ is observed to be a monomer in the crystalline state, exhibiting intermolecular I–F contacts.¹ These contacts are divided into two groups, one defined as “primary polar contacts”, with a weighted average length of 3.01(6) Å, and another group called “secondary polar contacts”, with a weighted average distance of 3.25(2) Å.¹ In contrast to this, I₂O₅ was described by Selte and Kjekshus as a firm three-dimensional network of molecular I₂O₅ units linked by short intermolecular I–O contacts, with lengths between 2.23(3) and 2.72(3) Å.² The two iodine(V) oxofluorides IO₂F and IOF₃ should, therefore, be links between monomers and polymers. In this work, we use the term “monomer” to point out that the compound exhibits molecular units in the crystalline state linked only by intermolecular contacts, which are much longer than the sum of the covalent radii. On the other hand, we use the phrase “polymer” for compounds that are linked by very short intermolecular contacts, which are called secondary bonds.

In 1974, Edwards and Taylor were able to redetermine the crystal structure of IOF₃, and they observed IOF₃ molecules exhibiting intermolecular I–O (2.62(6) Å) and I–F (2.81(3) and 3.11(3) Å) contacts forming a three-dimensional network.³ For comparison, the sum of the covalent radii I–O and I–F are 1.94 and 1.92 Å, respectively.⁴ The lengths of the intermolecular I–F contacts are shorter within quoted esd's than those in IF₅, and the I–O contacts are significantly longer than those in I₂O₅.^{1–3} It was therefore desirable to determine the crystal structure of IO₂F, the missing link in this fundamental row.

Iodylfluoride was first prepared by Aynsley et al. in 1953 by the reaction of IF₅ with I₂O₅ (eqs 1 and 2).⁵



Schenk and Gerlatzek and later Carter and Aubke, reported the determination of the vibrational spectra of IO₂F, but they were not able to get detailed information about its molecular structure.^{6,7} The spectra exhibit splitting in the I–O valence

range, and the thermal stability of IO₂F is very high, thus a polymeric structure was assumed. Even IO₂F is very stable and has been known for a long time, no structural data have been reported yet.

In this work, we present the crystal structure of iodylfluoride, the first example of a detailed structure of a halogenylfluoride in the solid state.

Experimental Section

CAUTION! IF₅ is a highly reactive oxidizing agent. Skin contact with IF₅ and IO₂F should be avoided because their hydrolysis leads to HF, which causes burns and, in some cases, irreparable damage.

Preparation of IO₂F. I₂O₅ (0.67 g, 2 mmol) was loaded into a dry glass vessel with greaseless stopcocks (Young). Then, 2.22 g (10 mmol) of IF₅ was added, and the mixture was heated to 105 °C and held at this temperature for 50 min. After removing all volatiles in vacuo at 25 °C, the formation of a colorless solid and corroding of the glass vessel were observed. The amorphous residue was identified as IO₂F by Raman and IR spectra.^{6,7} The same reaction done in a Kel-F reactor yields IOF₃ quantitatively.

All synthetic work and sample handling were performed using standard Schlenck techniques and a standard glass vacuum line. Nonvolatile materials were handled under dry nitrogen. IO₂F was crystallized from a SO₂ solution at –30 °C, and the crystals were stored under dry nitrogen at –70 °C. The yield of crystals suitable for an X-ray single-crystal structure determination was less than 5%. Single crystals were placed in Lindemann capillaries in a cooled stream of dry nitrogen at about –70 °C, and an X-ray diffraction study at –100 °C was carried out using a Nonius Kappa CCD diffractometer. 372 frames via ω rotation and two times 30 s per frame were measured. The crystal-to-detector distance was 3.5 cm. Crystal decay was monitored by repeating the initial frames at the end of data collection. Based on an analysis of these duplicate reflections, there was no decay. For technical reasons, we were not able to perform an experimental absorption correction. Using the data reduction software SCALEPACK (Minor and Otwinowski), each measured frame is multiplied by a certain scale factor, which is generated by comparing the intensity of symmetrically related reflections. It seems unlikely that oxygen can be distinguished from fluorine by X-ray methods alone in the presence of the iodine atom, and therefore, we have assigned the fluorine atom from stereochemical considerations. The crystal structure was solved by direct methods. Searching for higher symmetry with the program PLATON indicated the acentric space group *P*2₁2₁2₁, and a final refinement with anisotropic thermal parameters gave values of *R*₁ = 0.0267 and *wR*₂ = 0.0573. For the data reduction, structure solution, and refinement, programs in the SHELXTL package and PARST were used.^{8–10} The crystal data are summarized in Table 1.

Results and Discussion

Crystal Structure of IO₂F. IO₂F crystallizes in the orthorhombic system in the space group *P*2₁2₁2₁ with *a* = 5.442(1),

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(10) Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Fachinformationzentrum Karlsruhe in Germany, as supplementary publication no. CSD-412209 (IO₂F). Copies of the data can be obtained free of charge on application to Fachinformationzentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (Fax: (+49)7247–808–666. E-mail: crysdata@fiz-karlsruhe.de).

Table 1. X-ray Diffraction Data for IO₂F.

chemical formula	IO ₂ F
space group	<i>P</i> 2 ₁ 2 ₁ 2 ₁
<i>a</i> , Å	5.442(1)
<i>b</i> , Å	5.667(1)
<i>c</i> , Å	7.690(1)
Volume, Å ³	1014.9(2)
$\rho_{\text{calcd.}}$, g cm ⁻³	4.982
<i>Z</i>	4
fw, g mol ⁻¹	177.90
μ , cm ⁻¹	132.34
<i>T</i> , °C	-100(2)
λ , Å	0.71069
R^a [$I > 2\sigma(I)$]	$R_1 = 0.0267$, $wR_2 = 0.0573$
R^a (all data)	$R_1 = 0.0285$, $wR_2 = 0.0578$

^a $R = \sum ||F_o| - |F_c|| / \sum |F_o|$. Refinement method: full-matrix least-squares calculations based on F^2 .

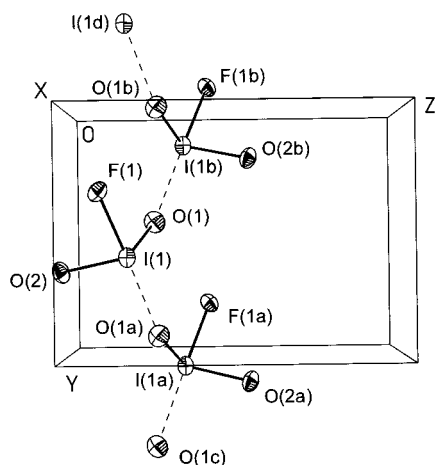


Figure 1. View of a part of the crystal structure of IO₂F in *x* orientation with the unit cell. The molecules are linked by secondary I–O bonds (---), with a length of 2.226(6) Å, into a polymeric bondage of alternating axial–equatorial linked ψ trigonal bipyramids. Thermal ellipsoids are drawn at the 50% probability level. Symmetry transformations are $a = -x, 1/2 + y, 1/2 - z$; $b = -x, -1/2 + y, 1/2 - z$; $c = x, 1 + y, z$; $d = x, -1 + y, z$.

Table 2. Bond Lengths (Å) and Selected Angles (deg) for IO₂F^a

I(1)–F(1)	1.903(5)	F(1)–I(1)–O(1)	94.6(2)
I(1)–O(1)	1.805(6)	F(1)–I(1)–O(2)	90.7(2)
I(1)–O(2)	1.773(6)	O(1)–I(1)–O(2)	99.2(3)
I(1)–O(1a)	2.226(6)	O(1)–I(1)–O(1a)	92.1(1)
I(1)–O(2d)	2.699(6)	O(2)–I(1)–O(1a)	90.5(2)
I(1)–O(2c)	2.854(6)	F(1)–I(1)–O(1a)	172.9(2)
I(1)–F(1c)	3.285(5)	I(1)–O(1)–I(1a)	144.5(3)
I(1)–F(1b)	3.280(5)		

^a Symmetry transformation used to generate equivalent atoms: $a = -x, 1/2 + y, 1/2 - z$; $b = 1 - x, 1/2 + y, 1/2 - z$; $c = 1/2 - x, 1 - y, 1/2 + z$; $d = 1/2 + x, 3/2 - y, -z$.

$b = 5.667(1)$, $c = 7.690(1)$ Å, and four formula units per unit cell. It is isostructural with IOF₃ and the isoelectronic molecules α -HIO₃ and XeO₃.^{3,11,12} The IO₂F molecules are linked by secondary I–O bonds to form a polymeric network (Figure 1). The resulting unsymmetrical I–O–I bridges have lengths of 1.805(6) and 2.226(6) Å and a bonding angle of 1.44(5)° (Table 2). The bond length of 2.226(6) Å is about 15% longer than the sum of the covalent radii I–O of 1.94 Å and about 36% below the sum of the van der Waals radii of 3.50 Å, reported by Bondi.⁴ According to Alcock, this bond can be described as

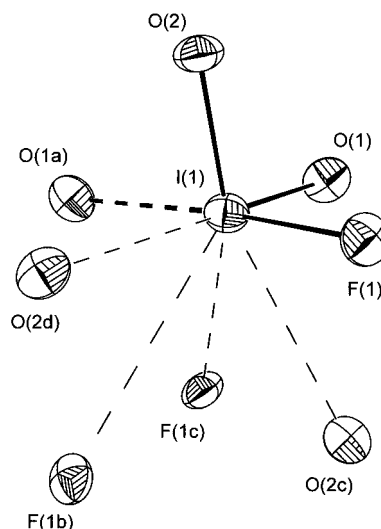


Figure 2. Projection of an IO₂F molecule with its intermolecular contacts. Distances [Å]: I(1)–F(1) 1.903(5), I(1)–O(1) 1.805(6), I(1)–O(2) 1.773(6), I(1)···O(1a) 2.226(6), I(1)···F(1b) 3.280(5), I(1)···F(1c) 3.285(5), I(1)···O(2c) 2.854(6), I(1)···O(2d) 2.699(6). Symmetry transformations are $a = -x, 1/2 + y, 1/2 - z$; $b = 1 - x, 1/2 + y, 1/2 - z$; $c = 1/2 - x, 1 - y, 1/2 + z$; $d = 1/2 + x, 3/2 - y, -z$. Thermal ellipsoids are drawn at the 50% probability level.

a secondary bonding.¹³ A similar linkage is found for I₂O₅, with I–O lengths of 1.92(2) and 1.95(3) Å and an angle I–O–I of 139.2(1.4)° for the I–O–I bridge.²

Bearing in mind the secondary bonds, the molecular structure of IO₂F can be described as alternating axial–equatorial linked ψ trigonal bipyramids and not pyramidal, as might be expected (Figure 1). In these bipyramids, the apical positions are occupied by fluorine and oxygen, and the double bonded oxygen takes an equatorial position. A similar arrangement is found for the isoelectronic TeO₂F⁻ anion.¹⁴ For the bridging Te–O bonds, lengths in the range from 1.884(3) to 1.919(3) Å and 2.072(3) to 2.091(3) Å are observed.¹⁴ In the crystalline state there are Te₃O₆F₃³⁻ trimers, and the tellurium atoms are linked by oxygen to form six membered rings, thus, a ψ trigonal bipyramidal coordination around tellurium results.¹⁴

The unusual binding situation in IO₂F is reflected in its vibrational spectra. In 1971, Carter and Aubke reported the Raman and IR spectra of IO₂F.⁷ During our investigations we were able to confirm these data and the following discussion is made on this basis. The Raman spectra are dominated by three very strong lines at 550, 705, and 807 cm⁻¹, even with strong IR intensities. The lines are assigned to ν I–F, ν I–O, and ν I=O, in comparison to the results of the crystal structure determination. Due to the difference in the I–O bond lengths, the symmetry is lower than C_{2v}, thus there are no symmetric or asymmetric IO₂ stretching modes. The secondary I–O bond has a length of 2.226(6) Å and is, therefore, expected to be found below 250 cm⁻¹, but in this range the spectra are rather complicated, and the lines cannot be reliably assigned to single vibrations. The complexity of the vibrational spectra allows only an approximate description of the bands for the bending modes, the secondary bond, and the intermolecular contacts.

In 1982, Oberhammer and Christe reported, that for trigonal bipyramidal molecules, double bonds can result in directional repulsion effects.¹⁵ They assumed the orientation of the π system of the double bond in ClOF₃ by determining the distortion of

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the angles observed in its gas-phase structure.¹⁵ For the bond angles of IO₂F, we observed some characteristic deviations in its crystal structure. The angles O(2)–I(1)–O(1a) and O(2)–I(1)–F(1) have values of 90.5(2) and 90.7(2)°, which are close to 90°, but the angles O(1)–I(1)–O(1a) and F(1)–I(1)–O(1) are about 92.1(3) and 94.6(2)° (Figure 2). This results in a compression of the angle O(1a)–I(1)–F(1) to 172.9(2)° in the direction of the domain of the lone pair around iodine. This demonstrates that occupations of the π bond orbitals differ in the equatorial and axial planes. For the I(1)–O(2) bond, the electron density occupies the equatorial plane, and the π electrons of the I(1)–O(1) bond are placed in the axial plane to minimize the repulsive interactions. Considering this, the value of 99.2(3)° for the angle O(1)–I(1)–O(2) becomes reasonable. Thus iodine has also a nonbonding, sterical active lone pair in an equatorial position; the two π systems of the double bonds I(1)–O(1) and I(1)–O(2) are twisted by about 90° to reduce their repulsive interactions.

Another explanation for the observed deviations in the crystal structure of IO₂F may be the additional intermolecular I–F and I–O contacts, with lengths below the corresponding van der Waals radii, which form a three-dimensional network in the solid state (Figure 1). There are two I–O contacts, I(1)–O(2c) 2.854(6) Å and I(1)–O(2d) 2.699(6) Å, which, in addition to the three primary bonds and the secondary bond I(1)–O(1a),

result a distorted octahedral coordination around iodine (Figure 2). These contacts are about 18 and 23% shorter than the sum of the van der Waals radii of 3.5 Å, thus they cannot be neglected.⁴ Additionally, iodine forms two intermolecular I–F contacts with lengths of I(1)–F(1b) 3.280(5) Å and I(1)–F(1c) 3.285(5) Å, respectively, which are about 5% below the sum of the van der Waals radii of 3.45 Å.⁴ Thus, a coordination polyhedron similar to that found for IF₅ and a coordination number of eight are observed (Figure 2).¹ Due to the tendency of the incoming lone pairs to avoid the domains of the other electrons in the valence shell of iodine, deviations of bond angles in the coordination polyhedron of iodine become reasonable. In our opinion, both effects, directional repulsion effects of double bonds in trigonal bipyramidal molecules and, on the other hand, intermolecular linkage, are responsible for the observed deviations and the resulting coordination polyhedron around iodine.

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Supporting Information Available: One X-ray crystallographic file in CIF format is available. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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