

## Iodine(III) Bis-fluorosulphate Iodide. The X-Ray Crystal Structure of $\text{I}(\text{OSO}_2\text{F})_2\text{I}$

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The X-ray crystal structure of the product of the reaction of  $\text{I}_2$  and  $\text{S}_2\text{O}_6\text{F}_2$  shows that it is iodine(III) bis-fluorosulphate iodide,  $\text{I}(\text{SO}_3\text{F})_2\text{I}$ , and not iodine(I) fluorosulphate.

The existence of  $\text{I}^+$  in concentrated sulphuric acid or oleum has been claimed,<sup>1-3</sup> but it was subsequently shown<sup>4,5</sup> that the species obtained were cations of iodine in lower oxidation states, such as  $\text{I}_2^+$ ,  $\text{I}_3^+$ , and  $\text{I}_5^+$ . Iodine(I) halides are known,<sup>6</sup> but these are covalent compounds and no ionic species containing the  $\text{I}^+$  cation has so far been reported. The complexes  $[\text{I}(\text{pyridine})_2]^+[\text{I}_7]^-$ ,  $\{\text{I}[\text{SC}(\text{NH}_2)_2]_2\}^+\text{I}^-$ , and  $\{\text{I}[(\text{ethylenediamine})_2\text{Co}(\text{SCH}_2\text{CH}_2\text{NH}_2)_2]_2\}^{5+}(\text{NO}_3)_5^-$ .  $4\text{H}_2\text{O}$ , however, may be considered to be stabilized derivatives of the  $\text{I}^+$  cation.<sup>7-9</sup>

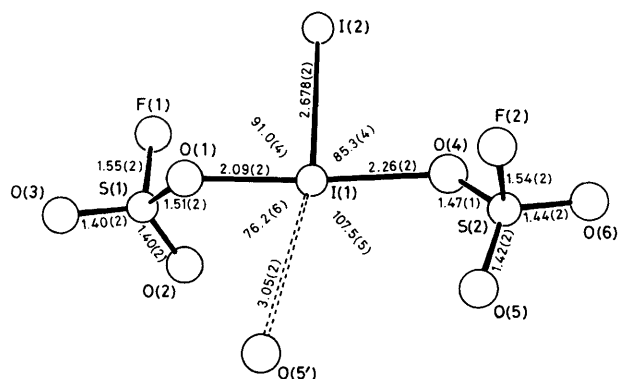
A compound claimed to be iodine(I) fluorosulphate was prepared by Aubke and Cady<sup>10</sup> by the reaction of equimolar amounts of iodine and peroxodisulphuryl difluoride (equation 1). No structural information on this compound has been reported. We now describe the X-ray determination of its structure. The product is not iodine(I) fluorosulphate,

$\text{IOSO}_2\text{F}$ , but iodine(III) bis-fluorosulphate iodide,  $\text{I}(\text{OSO}_2\text{F})_2\text{I}$ , with an I-I bond slightly longer than in iodine vapour.<sup>11</sup> It contains two iodine atoms formally in the  $\text{I}(+3)$  and  $\text{I}(-1)$  oxidation states rather than a monovalent  $\text{I}^+$  cation.



When equimolar amounts of  $\text{I}_2$  and  $\text{S}_2\text{O}_6\text{F}_2$  were allowed to react at room temperature an exothermic reaction took place giving a black viscous liquid from which black crystals formed overnight. The melting point of the crystalline material ( $49^\circ\text{C}$ ) was in good agreement with that reported by Aubke and Cady.<sup>10</sup> Single crystals were mounted in quartz capillaries in a dry-box.

*Crystal data:*  $\text{I}(\text{OSO}_2\text{F})_2\text{I}$ ,  $M = 451.92$ ,  $T = -50^\circ\text{C}$ , orthorhombic, space group  $P2_12_12_1$  ( $D_2^4$ ; No. 19),  $a = 5.457(2)$ ,  $b = 11.937(4)$ ,  $c = 13.547(4)$  Å,  $U = 882.5(8)$  Å<sup>3</sup>,



**Figure 1.** The  $\text{I}(\text{OSO}_2\text{F})_2\text{I}$  molecule, showing bond distances (Å) and angles (°).

**Table 1.** Some I—I bond lengths and stretching frequencies (from Raman spectra).

Compound	$d(\text{I—I})/\text{Å}$	$\nu/\text{cm}^{-1}$	Ref.
$[\text{I}_2]^+[\text{Sb}_2\text{F}_{11}]^-$	2.557	238	19
$\text{I}_2$	2.66	213	11, 19
$\text{I}(\text{OSO}_2\text{F})_2\text{I}$	2.678	197	<sup>a</sup>
$[\text{I}_3\text{Cl}_2]^+[\text{SbCl}_6]^-$	2.906	184	20

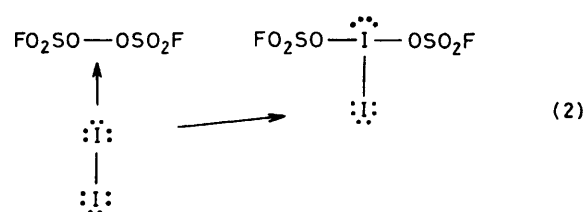
<sup>a</sup> This work.

$Z = 4$ ,  $D_c = 3.40 \text{ g cm}^{-3}$ . X-Ray data ( $2\theta < 55^\circ$ ,  $0 \leq h \leq 7$ ,  $0 \leq k \leq 15$ ,  $-17 \leq l \leq 17$ ) were collected with a Syntex P2<sub>1</sub> diffractometer using Mo- $K_\alpha$  radiation. Data reduction was performed using the XRAY-76 system<sup>12</sup> and the structure was solved using the conventional heavy atom, Fourier difference methods and refined using the SHELX system.<sup>13</sup> Currently  $R = 0.0797$ , based on 1985 unique reflections.<sup>†</sup>

The bond lengths and angles for the  $\text{I}(\text{OSO}_2\text{F})_2\text{I}$  molecule are given in Figure 1. Two fluorosulphate groups are linked to I(1) while I(2) is bonded only to I(1). The Raman spectrum of the black solid showed a strong band at  $197 \text{ cm}^{-1}$  which can be attributed to the I—I stretch. This is compared with the I—I stretch and bond length in related compounds in Table 1.

The geometry about I(1) can be described as a distorted trigonal bipyramid,  $\text{AX}_5\text{E}_2$ , with the two bonds to  $\text{OSO}_2\text{F}$  in axial positions and the I—I bond and the two lone pairs of electrons in the equatorial plane, as expected from the VSEPR model.<sup>14</sup> Similar geometries are observed for several organoiodine(III) compounds,<sup>15</sup> chlorine(III) in  $\text{ClF}_3$ ,<sup>6</sup> and for a large number of divalent tellurium complexes.<sup>16</sup> An additional feature of the geometry about I(1) in  $\text{I}(\text{OSO}_2\text{F})_2\text{I}$  is the close contact (secondary bond<sup>17</sup>) to an oxygen atom (5') from the fluorosulphate group of an adjacent molecule. This secondary bond is formed approximately opposite the I—I bond to give a distorted square-planar arrangement of bonds about I(1). Regular or distorted square-planar arrangements are commonly observed for iodine(III), for example in  $\text{I}_2\text{Cl}_6$ ,  $\text{KICl}_4 \cdot \text{H}_2\text{O}$ ,  $(\text{ICl}_2)(\text{AlCl}_4)$ ,  $(\text{ICl}_2)(\text{SbCl}_6)$ ,<sup>6</sup> and  $(\text{ICl}_2)(\text{SbF}_6)$ .<sup>18</sup> The nature of secondary bonding in iodine(III) compounds has previously been described.<sup>15</sup>

The axial I—O bonds in the present compound (mean  $2.17 \text{ Å}$ ) have very similar lengths to the I—O bonds in the



iodine(III) compounds  $(\text{MeCO}_2)_2\text{IPh}$  and  $(\text{CHCl}_2\text{CO}_2)_2\text{IPh}$  (mean  $2.156$  and  $2.150 \text{ Å}$  respectively).<sup>15</sup> There is considerable asymmetry in the I—O primary bond in  $\text{I}(\text{OSO}_2\text{F})_2\text{I}$  and a similar, but less pronounced, asymmetry is observed in  $(\text{CHCl}_2\text{CO}_2)_2\text{IPh}$ . The  $\text{OSO}_2\text{F}$  group involved in the longer, primary I—O bonds in  $\text{I}(\text{OSO}_2\text{F})_2\text{I}$  also forms two strong intermolecular secondary bonds [ $\text{I}(1) \cdots \text{O}(5') = 3.05(2) \text{ Å}$ ;  $\text{I}(2) \cdots \text{O}(6') = 2.63(2) \text{ Å}$ ], while the other  $\text{OSO}_2\text{F}$  group forms no short secondary bonds. The asymmetry in  $(\text{CHCl}_2\text{CO}_2)_2\text{IPh}$  can also be explained in terms of the differences in the secondary bonds formed by the two oxo-ligands.

The formation of  $\text{I}(\text{OSO}_2\text{F})_2\text{I}$  can be considered as an addition of electrons from the HOMO ( $\pi^*$ ) of one of the iodine atoms of  $\text{I}_2$  to the LUMO ( $\sigma^*$ ) of the peroxy bond of  $\text{S}_2\text{O}_6\text{F}_2$ . This results in oxidation of the iodine atom and the breaking of the oxygen—oxygen bond (reaction 2). Alternatively the reaction could occur by dissociation of  $\text{S}_2\text{O}_6\text{F}_2$  to  $\text{SO}_3\text{F}$  radicals followed by attack on an iodine atom of an iodine molecule.

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<sup>†</sup> The atomic co-ordinates for this work are available on request from Prof. Dr. G. Bergerhoff, Institut für Anorganisch Chemie, Universität, Gerhard-Domagk-Strasse 1, D-5300 Bonn 1, W. Germany. Any request should be accompanied by the full literature citation for this communication.