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## Crystal and Molecular Structure and Raman and $^{127}\text{I}$ Mössbauer Spectra of Iodine(III) Bis(fluorosulfate) Iodide, $\text{I}(\text{OSO}_2\text{F})_2\text{I}$

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Iodine is oxidized by peroxodisulfuryl difluoride,  $\text{S}_2\text{O}_6\text{F}_2$ , to give  $\text{I}(\text{OSO}_2\text{F})_2\text{I}$ . Crystals are orthorhombic, space group  $P2_12_12_1$ , with  $a = 5.511$  (1) Å,  $b = 12.054$  (2) Å,  $c = 13.573$  (3) Å,  $V = 901.8$  (3) Å<sup>3</sup>, and  $D_{\text{calc}} = 3.33$  g cm<sup>-3</sup> for  $Z = 4$ . The structure was solved by means of Patterson functions and refined by least squares to final agreement indices of  $R_1 = 0.0353$  and  $R_2 = 0.0374$  for 1600 independent reflections. There are three primary bonds to the central iodine, I(1),  $\text{I}(1)\text{--OSO}_2\text{F} = 2.086$  (7) and  $2.258$  (7) Å;  $\text{I}(1)\text{--I}(2) = 2.676$  (1) Å, which create a distorted T-shaped  $\text{AX}_3\text{E}_2$  geometry. The second iodine, I(2), has a primary bond to I(1) and a strong intermolecular secondary  $\text{I}(2)\text{--O}$  bond of length  $2.655$  (8) Å to one of the fluorosulfate groups that is colinear with the primary bond, giving an  $\text{AXYE}_3$  geometry about I(2). The Raman spectrum of the solid and the  $^{127}\text{I}$  Mössbauer spectrum are in full agreement with the structure found.

### Introduction

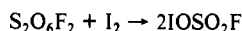
A compound claimed to be iodine(I) fluorosulfate was prepared by Aubke and Cady<sup>1</sup> by the reaction of equimolar amounts of iodine and peroxodisulfuryl difluoride. No structural information on this compound was given. In this paper we report the Raman and  $^{127}\text{I}$  Mössbauer spectra together with an X-ray single-crystal structural analysis of the product of the reaction between equimolar amounts of iodine and peroxodisulfuryl difluoride, which show that it should be formulated as  $\text{I}(\text{OSO}_2\text{F})_2\text{I}$ . A preliminary report of the crystal structure and Raman spectrum of  $\text{I}(\text{OSO}_2\text{F})_2\text{I}$  has been published previously.<sup>2</sup>

### Experimental Section

**Materials and General Procedures.** Peroxodisulfuryl difluoride,  $\text{S}_2\text{O}_6\text{F}_2$ , was prepared by the reaction of  $\text{XeF}_2$  with  $\text{HSO}_3\text{F}$ . Iodine (BDH Analytical reagent) was further purified by sublimation. The reaction was carried out in a two-bulb glass vessel equipped with a Rotoflow valve and a Teflon-coated stirring bar. Reagents were manipulated in a dry-box, under a nitrogen atmosphere, and suitable crystals for X-ray structural determination were selected in a similar box, which was equipped with a microscope, and sealed in Lindemann capillaries (0.2–0.3-mm diameter).

**Raman Spectroscopy.** Raman spectra were recorded with a Spex Industries Model 1400 spectrometer equipped with a double monochromator, an RCA C31034 phototube detector, an electrometer amplifier, and a recorder. The exciting radiation was the red 6328-Å line of a Spectra-Physics 125 He–Ne laser. The procedure followed was that described elsewhere.<sup>3</sup>

**Preparation.** When equimolar amounts of iodine and  $\text{S}_2\text{O}_6\text{F}_2$  were allowed to react at room temperature, an exothermic reaction took place and a black viscous liquid was formed:



On standing overnight at room temperature, the solution produced black crystals whose melting point (49 °C) was in good agreement with that previously reported.<sup>1</sup>

**Collection of the X-ray Data and Solution of the Structure.** Highly reactive, plate- or needle-shaped black crystals sealed in Lindemann capillaries were used to take precession photographs in order to check crystal quality and to obtain preliminary cell and symmetry information. Unit cell parameters were obtained from a least-squares refinement of the diffracting positions of 15 medium-angle reflections in the range  $20^\circ < 2\theta < 30^\circ$  recorded on a Syntex  $P2_1$  diffractometer equipped with Mo  $K\alpha$  radiation ( $\lambda = 0.71069$  Å). Intensity data were collected with graphite-monochromated radiation, by using a  $\theta(\text{crystal})\text{--}2\theta(\text{counter})$  scan, for the total of 1950 reflections with  $3^\circ < 2\theta < 50^\circ$ . The methods of selection of scan rate and initial data treatment have been described.<sup>4</sup> Lorentz, polarization, and absorption corrections ( $\psi$  scan) were applied to all reflections.<sup>5</sup> A total of 26 reflections of the 1950 collected were systematically absent and were removed from the data set. Equivalent reflections were averaged for a total of 1600 independent unique reflections. The structure was solved by routine heavy-atom methods with full-matrix least-squares refinement and with the atoms vibrating iso-

**Table I.** Summary of the Structure Determination for  $\text{I}(\text{OSO}_2\text{F})_2\text{I}$

diffractometer	Nicolet P2 <sub>1</sub>
radiation	graphite-monochromated Mo $K\alpha$ ( $\lambda = 0.71069$ Å)
syst	orthorhombic
fw	451.922
cryst size, mm	$0.2 \times 0.25 \times 0.31$
syst absences	$h00, h = 2n + 1; 0k0, k = 2n + 1; 00l, l = 2n + 1$
space group	$P2_12_12_1$ No. 19
unit cell constns: Å, deg	$a = 5.511$ (1) $b = 12.054$ (2) $c = 13.573$ (3)
$V, \text{Å}^3$	901.8 (3)
$Z$	4
$D_{\text{calc}}, \text{g}\cdot\text{cm}^{-3}$	3.33
$F(000)$	811.53 (816)
temp, °C	22
abs coeff $\mu, \text{cm}^{-1}$ ( $\mu_{\text{calc}}$ from SHELX $\text{cm}^{-1}$ )	75.3 (69.7)
max $2\theta$ , deg	50
octants	$0 \leq h \leq 6, -4 \leq k \leq 14, -16 \leq l \leq 16$
std reflns (esd)	0.6, 1 (0.014); 1, 4, 5 (0.015)
no. of reflns colld	1950
$R_{\text{merge}}$	0.012
no. of indep reflns	1600
no. of reflns with $I > 0$ used	1600
no. of params	110
final residuals: $R_1;^a R_2^a$	0.035; 0.037
final shift/error: max; av	0.001; 0.000
final diff map peaks, e Å <sup>-3</sup> : highest (location); lowest	0.96 (0.458, 0.139, 0.305°); -0.91
secondary extincn x	0.00075
weighting function	$w = (\sigma_{F^2} + 0.00116F_0^2)^{-1}$
error in observn of unit wt <sup>b</sup>	1.0654

<sup>a</sup>  $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ ;  $R_2 = (\sum w(|F_o| - |F_c|)^2 / \sum wF_o^2)^{1/2}$ . <sup>b</sup>  $S = (\sum w(|F_o| - |F_c|)^2 / (m - n))^{1/2}$ .  $m =$  number of reflections;  $n =$  number of variables. <sup>c</sup> 1.03 Å from I(1).

tropically. Subsequent Fourier maps revealed the positions of the remaining atoms and confirmed the positional assignments for the heavy ones. Further cycles of full-matrix least-squares refinement with use of anisotropic temperature factors for all atoms minimized  $\sum w(|F_o| - |F_c|)^2$ , and refinement was terminated when the maximum shift/error fell to 0.001. Final  $R_1$  and  $R_2$  were 0.0353 and 0.0374, respectively. Alter-

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**Table II.** Atomic Positional Parameters ( $\times 10^4$ ) and Temperature Factors ( $\text{\AA}^2 \times 10^3$ ) for  $\text{I}(\text{OSO}_2\text{F})_2\text{I}$ 

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}^a$
I(1)	2938.6 (11)	1793.7 (5)	3069.5 (4)	33
I(2)	4482.8 (11)	491.3 (5)	1601.0 (4)	37
S(1)	-453 (5)	3234 (2)	1674 (2)	47
S(2)	6562 (5)	1003 (2)	4887 (2)	36
O(11)	-2939 (17)	3372 (9)	1457 (8)	79
O(12)	-203 (13)	2201 (6)	2293 (5)	43
O(13)	929 (21)	4102 (8)	2041 (8)	83
O(21)	9021 (14)	812 (7)	5146 (6)	55
O(22)	6397 (14)	1288 (7)	3839 (5)	54
O(23)	5168 (17)	1686 (7)	5507 (5)	57
F(11)	841 (24)	2872 (10)	729 (6)	15
F(21)	5352 (15)	-147 (6)	4931 (6)	71

$$^a U_{\text{eq}} = \frac{1}{3}[U_{11} + U_{22} + U_{33}].$$

**Table III.** Selected Bond Lengths and Intra- and Intermolecular Distances ( $\text{\AA}$ ),<sup>a</sup> Angles (deg), and Least-Squares Mean Plane in  $\text{I}(\text{OSO}_2\text{F})_2\text{I}$ 

Distances			
I(1)-I(2)	2.676 (1)	S(1)-O(11)	1.412 (10)
I(1)-O(12)	2.086 (7)	S(1)-O(12)	1.509 (7)
I(1)-O(22)	2.258 (8)	S(1)-O(13)	1.386 (11)
I(1)···O(13)	3.305 (10)	S(1)-F(11)	1.531 (10)
I(1)···O(23)''	3.069 (8)	S(2)-O(21)	1.419 (8)
I(1)···O(23)	3.532 (7)	S(2)-O(22)	1.465 (7)
I(2)···O(12)	3.435 (7)	S(2)-O(23)	1.406 (9)
I(2)···O(22)	3.356 (7)	S(2)-F(21)	1.540 (8)
I(2)···O(21)''	2.655 (8)		
I(2)···O(13)'''	3.550 (8)		
Angles			
O(12)-I(1)-I(2)	91.5 (2)	O(13)-I(1)-I(2)	106.6 (2)
I(2)-I(1)-O(22)	85.3 (2)	O(23)-I(1)-I(2)	124.4 (1)
O(12)-I(1)-O(23)''	76.4 (3)	I(1)-I(2)-O(21)'	179.5 (2)
O(23)''-I(1)-O(22)	106.9 (2)	O(12)-I(2)-O(21)'	142.4 (2)
O(13)-I(1)-O(12)	46.4 (3)	O(21)''-I(2)-O(13)'''	83.5 (2)
O(23)-I(1)-O(22)	42.5 (2)	O(13)'''-I(2)-I(1)	96.7 (1)
O(13)-I(1)-O(23)''	66.2 (2)	O(12)-I(2)-I(1)	37.4 (1)
O(23)''-I(1)-O(23)	66.8 (2)	O(22)-I(2)-I(1)	42.1 (1)
O(13)-I(1)-O(22)	134.9 (3)	O(22)-I(2)-O(21)'	138.2 (2)
O(12)-I(1)-O(23)	140.4 (3)	O(13)'''-I(2)-O(12)	132.6 (2)
O(23)''-I(1)-I(2)	167.7 (2)	O(22)-I(2)-O(12)	79.5 (2)

Mean Plane and Deviations from It ( $\text{\AA}$ )<sup>b</sup>

I(1)\*, 0.000 (0); I(2)\*, 0.000 (0); O(12)\*, -0.003 (9); O(22)\*, -0.004 (10); O(13), 2.219 (13); O(23), -0.882 (11); O(23)'', -0.089 (9); O(21)'', -0.020 (8); O(13)''', -0.867 (14)

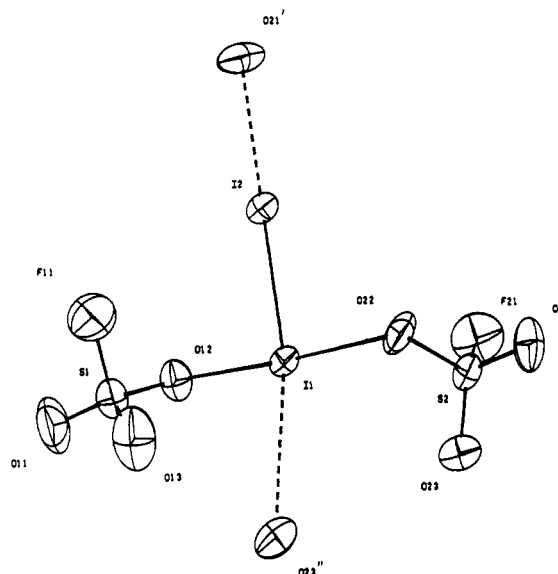
<sup>a</sup> Length of  $\text{I} \cdots \text{O} \leq 3.550 \text{\AA}$ . <sup>b</sup> Atoms defining the plane are marked with asterisks.

native refinement where coordinates *x*, *y*, *z* were replaced by  $1-x$ ,  $1-y$ , and  $1-z$  gave  $R_1 = 0.0360$  and  $R_2 = 0.0386$ , confirming the assignment for the correct hand of the structure. Corrections were made for secondary extinctions by the SHELX method.<sup>6</sup> Atomic scattering factors corrected for anomalous dispersion were taken from ref 7. Crystal data and other information related to data collection are summarized in Table I. Density was not determined because of the instability of the compound in air. Final atomic positional parameters in the asymmetric unit are given in Table II, and selected intra- and intermolecular distances and angles and a least-squares mean plane in Table III. Anisotropic thermal parameters and tables of calculated and observed structure factors may be found in the supplementary material.<sup>8</sup>

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(8) All computations were carried out on a VAX 8650 computer. Programs used for initial data treatment: Stewart, J. M. XRAY 76; Technical Report TR-446; University of Maryland: College Park, MD, 1976. Stewart, J. M.; Hall, S. R. *XTAL System of Crystallographic Programs*; University of Maryland: College Park, MD, 1983. The structure was solved with use of SHELX.<sup>6</sup> Planes were calculated with the following program: Ahmed, F. R.; Pippy, M. E. *NRC-22*; National Research Council of Canada: Ottawa, 1978. Diagrams were prepared from the program SNOOP. Davies, K. *CHEMGRAF suite: SNOOPT*; Chemical Design Ltd.: Oxford, England, 1983.



**Figure 1.** Perspective view of the molecule  $\text{I}(\text{OSO}_2\text{F})_2\text{I}$  with weakly covalently bonded oxygen atoms ( $\text{I} \cdots \text{O} < 3.1 \text{\AA}$ ). Symmetry transformations: single prime,  $1/2 - x, -y, 1/2 + z$ ; double prime,  $1/2 + x, 1/2 - y, -z$ .

As an independent check on the present structure and as confirmation that no other species were to be found in the sample prepared, several other crystals were sealed in capillaries and examined photographically. Precession photographs showed that many of the crystals were twinned or had smaller crystal intergrowth on them. However, a healthy looking crystal gave *a* and *c* parameters almost identical with those in the present structure while *b* was found to be slightly larger than twice the length of that in  $\text{I}(\text{OSO}_2\text{F})_2\text{I}$ . Furthermore, peak intensities were found to be different between the two sets of crystals. A closer examination of zero and higher layer photographs and diffractometer data revealed a monoclinic cell of  $a = 5.445 \text{\AA}$ ,  $b = 24.230 \text{\AA}$ , and  $c = 13.568 \text{\AA}$  with  $\beta = 90^\circ$  and  $V = 1790.06 \text{\AA}^3$ . This cell gave systematic absences corresponding to the space group of  $P2_1/a$  (nonconventional setting of  $P2_1/c$ ). A data set, based on this cell, was collected on the diffractometer, and the structure was solved by using the direct-methods routines of the program SHELX<sup>6</sup> and subsequent cycles of Fourier and least-squares calculations. The composition of the crystal was established as  $\text{I}(\text{OSO}_2\text{F})_2\text{I}$ , the same as that of the present structure, but with two molecules in the asymmetric unit and therefore with  $Z = 8$ . With no absorption treatment on the data and with anisotropic thermal parameters applied only to the heavy atoms, the structure was refined to an  $R_1$  index of 0.18 for 1150 independent reflections. Since the molecular structure of the  $P2_1/a$  polymorph appeared to be almost the same as that of the orthorhombic one, no further work was undertaken on this data set.

**Mössbauer Spectroscopy.** The source of 57.6-keV radiation was  $\text{Mg}_3^{127\text{m}}\text{TeO}_6$ . Details of the source preparation, irradiation, and Mössbauer spectrometer are presented elsewhere.<sup>9</sup>

Powdered absorber samples containing approximately  $0.05 \text{ g cm}^{-2}$  of  $^{127}\text{I}$  were placed neat or mixed with dry Teflon powder in 20 mm i.d. threaded Kel-F Mössbauer cells under an atmosphere of rigorously dried nitrogen. Both source and absorber were immersed in liquid helium (4.2 K) in a research cryostat manufactured by the Janis Research Corp. The velocity scale was calibrated with a standard iron foil and a  $^{57}\text{Co}/\text{Rh}$  source mounted on the reverse end of the transducer; calibration spectra were thus recorded without interruption of the drive sequence. The calibration spectra were computer-fitted to give a linear velocity scale and folding point.

Folded  $^{127}\text{I}$  spectra were fitted with the program GMFP,<sup>10</sup> which incorporates full-transmission integral procedures. The source line width was arbitrarily set at the natural line width 1.27 mm/s, the effective recoilless fraction was set equal to that of a previous source of  $\text{Ca}_3^{127\text{m}}\text{TeO}_6$ , 0.75 at 4.2 K, and the dimensionless absorber thickness,  $T_a$ , was made a variable parameter of the iterative fitting process. All isomer shifts were referenced to  $\text{K}^{127}\text{I}$  at 4.2 K.<sup>11</sup>

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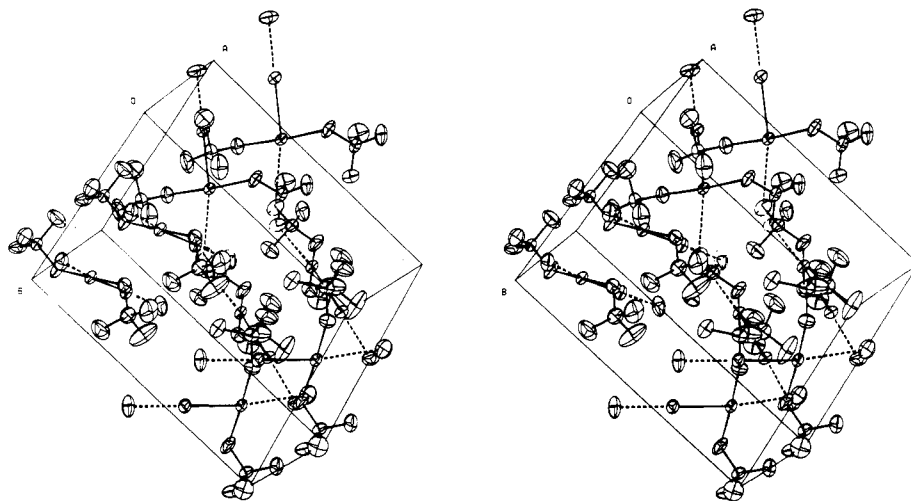


Figure 2. Stereoscopic view of the polymeric chain structure of I(OSO<sub>2</sub>F)<sub>2</sub>I.

Table IV. <sup>127</sup>I Mössbauer Data for I(OSO<sub>2</sub>F)<sub>2</sub>I and Related Species

compd	$\delta^{a,b}$	$e^2q^{127}Q_8/h^c$	$\Gamma^b$	$\eta$	$T_a^d$	ref
I(OSO <sub>2</sub> F) <sub>2</sub> I (61%)	-1.58 (6)	+2909 (36)	1.76 (9)	1.00 (3)	0.75 (4)	e
I(OSO <sub>2</sub> F) <sub>2</sub> I (39%)	-0.6 (1)	-2987 (66)	1.76 (9)	0.14 (3)		
I(O <sub>2</sub> CCH <sub>3</sub> ) <sub>3</sub>	-1.83 (3)	+3419 (16)	1.73 (8)	0.07 (3)	0.63 (2)	9
I(OSO <sub>2</sub> CF <sub>3</sub> ) <sub>3</sub>	-1.74 (3)	+3680 (14)	1.72 (7)	0.16 (1)	1.28 (4)	9
C <sub>6</sub> H <sub>5</sub> I(O <sub>2</sub> CCH <sub>3</sub> ) <sub>2</sub>	-0.87 (1)	+2507 (6)	1.53 (4)	0.79 (1)		23
I <sub>2</sub>	-0.49 (2)	-2137 (11)	1.99 (7)	0.22 (1)	0.84 (2)	21
ICl	-0.78 (4)	-2868 (20)		0.00		25
Cs[IClF]	-0.95 (5)	-3029 (36)	2.47 (17)	0.16 (3)	1.45 (7)	21
Cs[IBrF]	-0.84 (5)	-2769 (18)	2.25 (16)	0.24 (2)	1.75 (9)	21
[N(C <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> ] <sup>+</sup> [IBr <sub>2</sub> ] <sup>-</sup>	-0.67 (5)	-2695 (36)	1.95 (17)	0.19 (3)	1.21 (8)	21
[N(CH <sub>3</sub> ) <sub>4</sub> ] <sup>+</sup> [IBrCl] <sup>-</sup>	-0.73 (5)	-3048 (18)	1.58 (14)	0.00	1.5 (1)	21
[(C <sub>2</sub> H <sub>5</sub> N) <sub>2</sub> I] <sup>+</sup> [NO <sub>3</sub> ] <sup>-</sup>	-0.93 (3)	-3159 (18)	1.4 (1)	0.08 (4)	1.7 (1)	21
KI	0.00 (6)		2.23 (2)		0.28 (2)	e

<sup>a</sup> Values relative to K<sup>127</sup>I at 4.2 K. <sup>b</sup> Values in mm/s. <sup>c</sup> Values in MHz. <sup>d</sup> Dimensionless absorber thickness; see ref 10. <sup>e</sup> This work.

## Results and Discussion

**Structure.** The atomic arrangement for the I(OSO<sub>2</sub>F)<sub>2</sub>I molecule is illustrated in Figure 1. The geometry about I(1) consists of primary bonds to the oxygens O(12) and O(22) of the fluorosulfate groups of lengths 2.086 (7) and 2.258 (8) Å, respectively, and a primary bond to I(2) of length 2.676 (1) Å. The I(2)–I(1)–O(12) and I(2)–I(1)–O(22) angles are 91.5 (2) and 85.3 (2)°, respectively. A least-squares plane through atoms I(1), O(12), I(2), and O(22) passes 0.000 (0) Å from I(1), -0.003 (9) Å from O(12), 0.000 (0) Å from I(2), and -0.004 (10) Å from O(22). Thus, the primary geometry about I(1) can be described as T-shaped, AX<sub>3</sub>E<sub>2</sub>, with the two bonds to OSO<sub>2</sub>F in the axial positions and the I–I bond and the two lone pairs of electrons in the equatorial plane, as expected from the VSEPR theory.<sup>12</sup> Similar geometries have been observed, for example, for several organoiodine(III) compounds<sup>13</sup> and chlorine(III) in ClF<sub>3</sub>.<sup>14</sup> The compound can therefore be formulated as iodine(III) bis(fluorosulfate) iodide.

An additional feature of the geometry about I(1) in I(OSO<sub>2</sub>F)<sub>2</sub>I is the close contact (secondary bond<sup>17</sup>) to an oxygen atom, O(23)', which arises from a symmetry-related fluorosulfate group. This atom lies 0.089 (9) Å below the least-squares plane that is defined by atoms I(1), O(12), I(2), and O(22), is at a distance of 3.069 (8) Å from I(1), and forms a contact approximately opposite to the I(1)–I(2) primary bond with an angle O(23)'–I(1)–I(2) = 167.7 (2)°. If this contact is included, there is a distorted

square-planar AX<sub>3</sub>YE<sub>2</sub><sup>12</sup> geometry at I(1). Regular or distorted square-planar arrangements are commonly observed for iodine(III), for example in I<sub>2</sub>Cl<sub>6</sub>,<sup>14</sup> KICl<sub>4</sub>·H<sub>2</sub>O,<sup>18</sup> (SCl<sub>3</sub>)(ICl<sub>4</sub>),<sup>19</sup> and (ICl<sub>2</sub>)(AlCl<sub>4</sub>).<sup>20</sup> The nature of secondary bonding in iodine(III) compounds has previously been discussed.<sup>13</sup>

An interesting aspect of the structure is that there are two crystallographically independent fluorosulfate groups, one terminal and one bridging. The bridging oxygens join the molecules into polymeric chains, as shown in Figure 2. The geometry about I(2) consists only of a primary bond to I(1) of length 2.676 (1) Å and a strong intermolecular secondary I(2)–O(21)' bond of length 2.655 (8) Å. This intermolecular contact lies only 0.020 (8) Å below the least-squares plane defined by atoms I(1), O(12), I(2), and O(23) and forms an angle of I(1)–I(2)–O(21)' = 179.5 (2)°. If this contact is included the geometry about I(2) may be described as linear AXYE<sub>3</sub>.

The axial I–O bonds in I(OSO<sub>2</sub>F)<sub>2</sub>I (mean 2.172 (7) Å) have lengths very similar to those of the I–O bonds in the iodine(III) compounds (MeCO<sub>2</sub>)<sub>2</sub>IPh and (CHCl<sub>2</sub>CO<sub>2</sub>)<sub>2</sub>IPh (mean 2.156 (5) and 2.150 (7) Å, respectively).<sup>13</sup> There is considerable asymmetry in the I–O primary bonds in the present compound due, partly, to the steric effect induced by atom O(23) but mainly to the strong intermolecular secondary I(2)–O(21)' bond and to the weaker interaction O(23)'...I(1), all of which involve the OSO<sub>2</sub>F group with the longer primary I–O bond. The other fluorosulfate group is involved only in a very long, 3.550 (8) Å, and therefore very weak interaction through the O(13) atom. The asymmetry in (CHCl<sub>2</sub>CO<sub>2</sub>)<sub>2</sub>IPh, although less pronounced than that in I(OSO<sub>2</sub>F)<sub>2</sub>I, can also be explained in terms of the differences in the secondary bonds formed by the oxo ligands. The lengthening of

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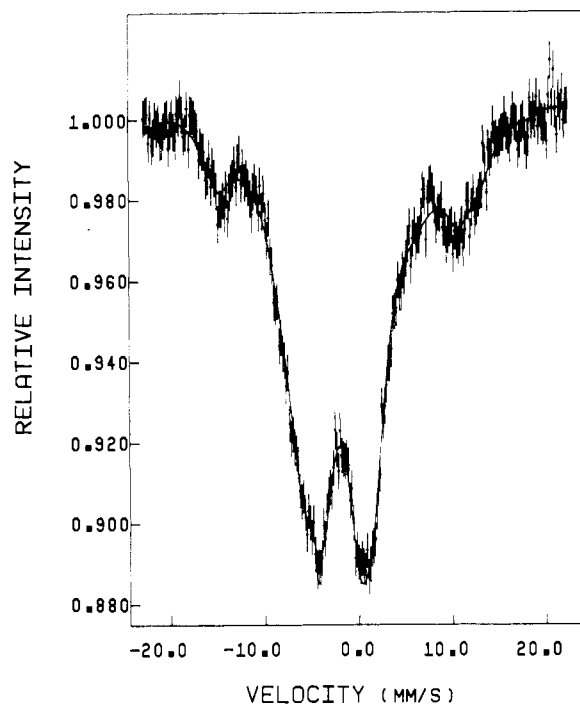


Figure 3.  $^{127}\text{I}$  Mössbauer spectrum of  $\text{I}(\text{OSO}_2\text{F})_2\text{I}$ .

the S(2)–O(21) bond in the present compound may be attributed to the strong intermolecular secondary bond with I(2).

**Mössbauer Spectroscopy.** The  $^{127}\text{I}$  Mössbauer spectrum for iodine(III) bis(fluorosulfate) iodide,  $\text{I}(\text{OSO}_2\text{F})_2\text{I}$ , is shown in Figure 3. The fitted parameters obtained from computer analysis are summarized in Table IV along with the literature data for some related iodine species. The spectrum of  $\text{I}(\text{OSO}_2\text{F})_2\text{I}$  was fitted initially to two unique iodine sites each having a contribution to the total absorption of 50%. This latter constraint was then removed resulting in a slight improvement in the value of  $\chi^2/\text{degrees of freedom}$  from 1.11 to 1.02 with a change in the relative contributions of the two sites to 61% and 39%. This effect, also observed in fitting the spectra of polyhalide anions of the type  $[\text{I}-\text{I}-\text{X}]^-$ , where the central iodine sites gave a higher contribution to the spectrum than the terminal iodine site,<sup>21</sup> is probably due to the latter site having a lower recoil-free fraction.

The first site, with a contribution of 61 (5)%, has a positive quadrupole coupling constant,  $e^2q^{127}\text{Q}_z/h$ , of 2909 (36) MHz. This site can be attributed to the iodine(III) atom, I(1). Positive quadrupole coupling constants are typical of iodine(III) compounds, since the two nonbonding pairs of electrons on the iodine nucleus are approximately axially disposed to one another along the  $z$  axis perpendicular to the molecular plane. This imposes a negative electric field gradient at the  $^{127}\text{I}$  nucleus, which in turn possesses a negative nuclear quadrupole moment,  $e^{127}\text{Q}_z$ , and hence a positive quadrupole coupling constant arises. It has been noted<sup>22</sup> that the quadrupole coupling constants observed for iodine compounds are very sensitive to changes in the primary bonding arrangement whereas changes in secondary bonding interactions have little or no effect. The magnitude of the quadrupole coupling constant for I(1) is intermediate between that reported for  $\text{I}(\text{O}_2\text{CCH}_3)_3$ <sup>9</sup> and  $\text{C}_6\text{H}_5\text{I}(\text{O}_2\text{CCH}_3)_3$ <sup>23</sup> and, when taken in conjunction with the asymmetry parameter,  $\eta$ , reflects the difference in the electronegativity of the fluorosulfate and acetate groups. The large asymmetry parameter for this site arises because the contribution to the electron density in the  $xy$  plane by the I–I bond is greater than that by the weaker bonds to the more electronegative oxygens. The electronegativity of iodine and carbon are reported as being identical,<sup>24</sup> and therefore one might expect a

Table V. I–I Bond Lengths and Stretching Frequencies (from Raman Spectra)

compd	$d(\text{I}-\text{I})$ , Å	$\nu$ , $\text{cm}^{-1}$	ref
$\text{I}_2^+(\text{Sb}_2\text{F}_{11}^-)$	2.557	238	26
$\text{I}_4^{2+}(\text{AsF}_6^-)_2$ , $\text{I}_4^{2+}(\text{SbF}_6^-)_2$ , $\text{I}_4^{2+}(\text{Sb}_4\text{F}_{20}^{2-})$	2.580 (av)	232	3
$\text{I}_2$	2.660	213	26, 27
$\text{I}_3^+(\text{AsF}_6^-)$	2.665 (av)	207	28, 29
$\text{I}(\text{OSO}_2\text{F})_2\text{I}$	2.676	197	a
$\text{I}_3\text{Cl}_2^+(\text{SbCl}_6^-)$	2.906	184	30

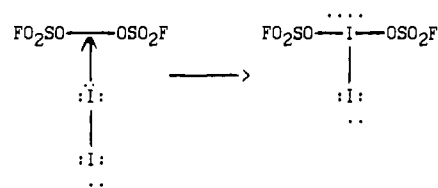
<sup>a</sup> This work.

value of  $\eta$  for I(1) to be similar to that observed for  $\text{C}_6\text{H}_5\text{I}(\text{O}_2\text{CCH}_3)_2$ ,  $\eta = 0.79$  (1).<sup>23</sup> The asymmetry parameter for I(1) however is greater,  $\eta = 1.00$  (3), and is probably a testament to the weak secondary bond formed between I(1) and O(23)'.

The second site, which makes up the remainder of the total spectrum with a contribution of 39 (5)%, is attributed to I(2). The fitted parameters for this site are very similar to those reported for other linear iodine environments (see Table IV).<sup>21,25</sup> In this case the major or  $z$  axis of the electric field gradient tensor is along the I(1)–I(2) bond with the three nonbonding pairs of electrons located in the  $xy$  plane; hence, a negative quadrupole coupling constant would be expected.  $^{127}\text{I}$  isomer shifts are relatively insensitive to changes in electron configuration, and measuring them precisely is difficult. This, in conjunction with the lack of a suitable standard before 1982,<sup>11</sup> makes comparisons between different absorbers tenuous. However, the values reported for the title compound follow the expected trends with electronegativity, as discussed above. The iodine(III) site, I(1), has a large negative isomer shift which is similar to those reported for other iodine(III) species and suggests that the bonding at I(1) is predominantly  $p$  in character with very little or no  $s$  participation.

**Raman Spectroscopy.** The Raman spectrum of the solid gave a single strong band at  $197\text{ cm}^{-1}$ , which is attributed to the I–I stretch, and this is compared in Table V with other I–I stretching frequencies and bond lengths in related iodine compounds.

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.



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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**Registry No.**  $\text{I}(\text{OSO}_2\text{F})_2\text{I}$ , 94475-78-2;  $\text{I}_2$ , 7553-56-2;  $\text{S}_2\text{O}_6\text{F}_2$ , 13709-32-5;  $^{127}\text{I}$ , 7553-56-2.

**Supplementary Material Available:** Table S1, containing anisotropic thermal parameters (1 page); a listing of final structure factor amplitudes (9 pages). Ordering information is given on any current masthead page.

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