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Registry No. I, 78355-34-7; II, 78355-36-9; $[(np_3)Pd(P_4)]$, 78355-37-0; $[Pt(P_3)(triphos)]BF_4$, 78355-39-2; $[Pd_2(P_3)(np_3)_2]BF_4$, 78355-41-6.

Supplementary Material Available: Listings of structure factor amplitudes (22 pages). Ordering information is given on any current masthead page.

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Preparations and X-ray Crystal Structures of Iodo-*cyclo*-heptasulfur Hexafluoroantimonate(V) and Hexafluoroarsenate(V), S_7ISbF_6 and S_7IAsF_6

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S_7IAsF_6 and S_7ISbF_6 were prepared essentially quantitatively by a variety of routes. Attempts to prepare S_8I^+ salts were unsuccessful. S_7ISbF_6 crystallizes in the orthorhombic space group $P2_12_12_1$ with $a = 11.786$ (2) Å, $b = 9.187$ (1) Å, $c = 12.400$ (3) Å, and $d_{calcd} = 2.90$ Mg m^{-3} for $Z = 4$. The structure has been determined by multiple-solution direct methods and refined by least squares to final agreement indices $R_1 = 0.046$ and $R_2 = 0.061$ for 1628 independent reflections with $I \geq 2\sigma(I)$. S_7IAsF_6 crystallizes in the triclinic space group $P\bar{1}$ with $a = 15.516$ (11) Å, $b = 11.813$ (8) Å, $c = 11.650$ (8) Å, $\alpha = 107.30$ (4)°, $\beta = 74.71$ (5)°, $\gamma = 104.62$ (5)°, and $d_{calcd} = 2.78$ Mg m^{-3} for $Z = 6$. The structure was refined to a final agreement index $R = 0.14$. The S_7I^+ cations in both salts and in $(S_7I)_4S_4(AsF_6)_6$ are essentially identical. S_7I^+ contains a seven-membered sulfur ring with a slightly twisted chair conformation, similar to that of S_7, with an exocyclic iodine, and has a geometry similar to that of S_7O. The sulfur–iodine bond length is 2.342 (3) Å and corresponds to a bond order of 1. The sulfur–sulfur distances within the ring vary from 1.906 (5) to 2.389 (4) Å. There is one short intracationic iodine–sulfur contact of 3.394 (3) Å. The geometry and bond length variations in S_7I^+ are discussed and compared with those of related systems. Some experimental observations on $S_x(AsF_6)_2$, $19 \geq x \geq 16$, are presented and the nature of these species is discussed.

Introduction

Generally any pair of main-group elements, excepting those of group 8A, form binary compounds or alloys. At one time sulfur and iodine were thought[1] to be one of the pairs of elements that were an exception to this generalization. Since then, evidence has been presented for sulfur iodides prepared at low temperatures, although they are unstable under ambient conditions. Solid S_2I_2 has been characterized at −90 °C by its infrared and electronic spectra,[2,3] and infrared evidence has been presented[4] for SI_2 isolated in an argon matrix at 9 K. An attempted preparation of SI_3^+ (cf. SeI_3^+) led instead[5] to the relatively stable S_7IMF_6 (M = As and Sb) salts, containing a binary sulfur–iodine cation, and a full account of this work is reported below. Subsequently, $[(S_7I)_2I](SbF_6)_3 \cdot 2AsF_3$[6] and $S_2I_4(AsF_6)_2$,[7] which also contain stable sulfur–iodine cations, were prepared and characterized.

The ability of sulfur to catenate is well established; however, for many years the only known sulfur rings were S_8 and S_6.[8] More recently other allotropes have been prepared,[8] and the X-ray crystal structures of S_n (n = 7,[9] 10,[10] 12,[11] 18,[8] and 20[8]) and the derivatives S_nO (n = 7,[12] 8[13]), $S_{12}O_2 \cdot 2SbCl_5 \cdot 3CS_2$,[14] and $S_8O \cdot SbCl_5$[15] have been determined. The sulfur homopolyatomic cations S_4^{2+},[16] S_8^{2+},[17] and S_{19}^{2+}[18] contain 4, 8, or two S_7 membered rings joined by S_5 chain, respectively. The radical cation S_5^+ has also been characterized by ESR spectroscopy.[19] Clearly, there is emerging a rich chemistry of sulfur rings, and S_7IMF_6, containing an S_7^+ ring, is of interest in this context. A preliminary account of this work has been reported.[5]

Experimental Section

Techniques and reagents, except those listed below, have been described in ref 20. S_8 (McArthur, precipitated), KI (Anachemia), and CaH_2 (Alfa-Ventron) were used without further purification. SO_2 (Matheson, anhydrous) was vacuum distilled onto and stored over CaH_2. SO_2ClF (Aldrich, spectrograde) was vacuum distilled onto and stored over NaF. $I_2Sb_2F_{11}$ and I_3AsF_6 were prepared according

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(1) Dasent, W. E. "Non-Existent Compounds"; Marcel Dekker: New York, 1965; p 162. Daneky, J. P. In "Sulfur in Organic and Inorganic Chemistry"; Marcel Dekker: New York, 1971; Vol. 1, p 327.

(2) Vahl, G.; Minkwitz, R. *Z. Anorg. Allg. Chem.* **1978**, *443*, 217 and references therein.

(3) Manzel, K.; Minkwitz, R. *Z. Anorg. Allg. Chem.* **1978**, *441*, 165.

(4) Feuerhahn, M.; Vahl, G. *Inorg. Nucl. Chem. Lett.* **1980**, *16*, 5.

(5) Passmore, J.; Taylor, P.; Whidden, T. K.; White, P. S. *J. Chem. Soc., Chem. Commun.* **1976**, 689.

(6) Passmore, J.; Sutherland, G.; White, P. S. *J. Chem. Soc., Chem. Commun.* **1979**, 901.

(7) Passmore, J.; Sutherland, G.; Whidden, T. K.; White, P. S. *J. Chem. Soc., Chem. Commun.* **1980**, 289.

(8) Schmidt, M. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 445 and references therein.

(9) (a) Steudel, R.; Reinhardt, R.; Schuster, F. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 715. (b) Steudel, R.; Steidel, J.; Pickardt, J.; Schuster, F. *Z. Naturforsch. B: Anorg. Chem., Org. Chem.* **1980**, *35B*, 1378.

(10) Reinhardt, R.; Steudel, R.; Schuster, F. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 57.

(11) Kutoglu, A.; Hellner, E. *Angew. Chem.* **1966**, *78*, 1021.

(12) Steudel, R.; Reinhardt, R.; Sandow, T. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 716. Steudel, R., private communication.

(13) Luger, P.; Bradaczek, H.; Steudel, R.; Rebsch, M. *Chem. Ber.* **1976**, *109*, 180.

(14) Steudel, R.; Steidel, J.; Pickhardt, J. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 325.

(15) Steudel, R.; Sandow, T.; Steidel, J. *J. Chem. Soc., Chem. Commun.* **1980**, 180.

(16) Passmore, J.; Sutherland, G.; White, P. S. *J. Chem. Soc., Chem. Commun.* **1980**, 330.

(17) Davies, C. G.; Gillespie, R. J.; Park, J. J.; Passmore, J. *Inorg. Chem.* **1971**, *10*, 2781.

(18) Burns, R. C.; Gillespie, R. J.; Sawyer, J. F. *Inorg. Chem.* **1980**, *19*, 1423.

(19) Low, H. S.; Beaudet, R. A. *J. Am. Chem. Soc.* **1976**, *98*, 3849.

(20) Passmore, J.; Taylor, P. *J. Chem. Soc., Dalton Trans.* **1976**, 804.

0020-1669/81/1320-3839$01.25/0

Table I. Weights of Products of Reactions Compared with Those Calculated for Formation of S_xIMF_6 (M = As, Sb; x = 6, 7, 8)

		wt of sol prod., g				wt of insol prod., g			
			calcd				calcd		
no.[f]	reaction[a]	exptl	S_7IMF_6	S_8IMF_6	S_6IMF_6	exptl	S_7IMF_6	S_8IMF_6	S_6IMF_6
1	excess S_8 + excess I_2 + AsF_5[b]	3.89	4.00	4.34	3.76	1.78[d]	1.79	1.55	2.03
1[c]						3.64[d]	3.80	3.49	4.10
2	excess S_8 + excess I_2 + SbF_5[b]	7.58	7.58	7.99	7.17	2.01[d]	1.96	1.55	2.37
3	$S_x(AsF_6)_2$ + excess I_2[c]					0.65[e]	0.67	0.37	0.97
3[c]		5.19	5.22	5.53	4.91	0.61[e]	0.60	0.29	0.91
3[b]		7.43	7.40	7.84	6.96	0.96[e]	0.95	0.51	1.39
4	$S_8(AsF_6)_2$ + KI[b]	1.09	1.17	1.24	1.10	0.78	0.56	0.49	0.63
4[c]		4.47	4.45	4.72	4.19	2.11	2.15	1.89	2.41
4[c]		2.56	2.46	2.60	2.31	1.20	1.26	1.11	1.41
5	I_3AsF_6 + excess S_8[b]	4.22	4.36	4.62	4.10	0.49[e]	0.47	0.21	0.73
5[c]		1.90	1.80	1.90	1.69				
5[c]						0.42[e]	0.45	0.37	0.53
5[c]						1.22[e]	1.13	0.88	1.38

[a] Refer to discussion for balanced equations. [b] Weights correspond to those for the experiment described in the text. [c] Data included here were for experiments similar to those described in the text. [d] I_2 not removed by pumping after reaction. [e] I_2 removed by pumping after reaction. [f] Refer to numbered parts of the Experimental Section for the type of reaction involved.

to ref 21 and 20, respectively. $S_8(AsF_6)_2$ was prepared as per ref 22 in SO_2 solution and purified in situ by crystallization from a 1:3 SO_2ClF/SO_2 mixture. Raman spectra were obtained at McMaster University in a spinning cell at −196 °C with a Spectra Physics Model 125 He–Ne laser (6328 Å).

Preparative Routes to S_7IMF_6 (M = As, Sb). 1. Reaction of Excess Sulfur and Iodine with Arsenic Pentafluoride. In a typical reaction AsF_5 (1.89 g, 11.1 mmol) was condensed onto S_8 (2.16 g, 8.45 mmol) and I_2 (2.23 g, 8.77 mmol) in AsF_3 (17.35 g) in a two-bulbed glass vessel incorporating a coarse sintered-glass frit and a Rotaflo valve. An intense orange-brown solution over a solid was obtained on warming to room temperature. After 72 h the solution was filtered, and refiltered five times, by condensing about half the solvent back and refiltering. A dark brown microcrystalline solid was obtained by slow evacuation to dryness with the solution at 0 °C. The weight of crystalline product and unreacted insoluble sulfur and iodine are given in Table I, and elemental analyses are given in the supplementary material.

2. Reaction of Excess Sulfur and Iodine with Antimony Pentafluoride. In a typical reaction, SbF_5 (4.67 g, 21.5 mmol) was reacted with excess S_8 (2.98 g, 11.6 mmol) and I_2 (1.89 g, 7.46 mmol) in SO_2 (7.80 g) for 2 days with stirring. The products were separated by filtration and SO_2ClF (1.45 g) was added to the solution, which was slowly (overnight) condensed back onto the insolubles, yielding a microcrystalline product. The volatiles were removed by pumping for 4 h, leaving iodine and a mixture identified by Raman spectroscopy and X-ray diffraction (powder and single-crystal ($(SbF_3)_3SbF_5$)) as S_8 and $(SbF_3)_3SbF_5$.[23] Product weights are given in Table I, and elemental analyses are given in the supplementary material.

Very large crystals (ca. 5 × 3 × 3 mm) of soluble product were obtained in a similar reaction, and a piece of one crystal was cut and mounted in the drybox and used in the subsequent X-ray diffraction analysis. The large crystals were shiny brown-black in appearance; however, small pieces, when freshly cut, appeared translucent red-orange.

3. Reaction of $S_x(AsF_6)_2$ (x = Ca. 19) with Iodine. In a typical reaction, excess S_8 (5.027 g, 20.6 mmol) was reacted with stirring with AsF_5 (3.49 g, 20.5 mmol) in SO_2 (9.21 g) for 5 h, and the resulting deep red soluble product was quantitatively filtered onto excess iodine (3.06 g, 12.0 mmol) in a previously isolated section of the apparatus and stirred for 3 days. The weight of unreacted sulfur (1.26 g, 4.92 mmol) indicated that the average stoichiometry of the red sulfur polyatomic cation was $S_{18.3}{}^{2+}$. The products were filtered through a second frit into a third bulb and evacuated to dryness, yielding a red-brown microcrystalline soluble product and elemental sulfur. If the reaction time was shorter (e.g., 12 h), the solution frothed on drying. One of these products in another reaction was found to have an X-ray powder diffraction pattern identical with those of $S_x(AsF_6)_2$ ($19 \geq x \geq 16$) although they were all of poor quality. The product weights and elemental analysis results are given in Table I and the supplementary material.

4. Reaction of $S_8(AsF_6)_2$ and KI. In one reaction $S_8(AsF_6)_2$ (1.37 g, 2.16 mmol) in SO_2 (9.7 g) was quantitatively added onto KI (0.36 g, 2.16 mmol) in a previously isolated section of the apparatus and immediately gave a red-brown solution over a finely divided precipitate. After being stirred for 2 h at room temperature, the product was filtered into a third bulb, and SO_2ClF (2.0 g) was added to facilitate crystal formation. Slow removal of the volatiles gave a good yield of orange-brown crystals. Product weights (including $KAsF_6$ and S_8 insolubles) are given in Table I. Of about 30 crystals from this and a similar reaction, only one was found suitable for single-crystal X-ray diffraction analysis.

5. Reaction of Excess Sulfur with I_3AsF_6. In a typical reaction, I_2 (2.98 g, 11.7 mmol) was reacted with a slight excess of AsF_5 (2.24 g, 13.2 mmol) in SO_2 (5.4 g), giving 4.60 g of product, corresponding to an average composition $I_{2.91}AsF_6$. This was then redissolved in SO_2 (3.76 g), washed onto sulfur (2.27 g, 8.88 mmol) in a previously isolated section of the apparatus, and stirred for 30 min at room temperature. The mixture was then quantitatively filtered into a third bulb, and the volatiles were removed, giving a crystalline soluble product and sulfur. Product weights are given in Table I, and elemental analyses are given in the supplementary material. The weight of liberated iodine (2.03 g) corresponded with that expected (2.00 g).

6. Reaction of $I_2Sb_2F_{11}$ with Excess Sulfur. $I_2Sb_2F_{11}$ (2.03 g, 2.87 mmol) and S_8 (1.78 g, 7.00 mmol) in AsF_3 (5.71 g) yielded an orange-brown solution, which on filtering yielded a noncrystalline soluble solid product (analysis is given in the supplementary material).

Stability of S_7IMF_6. Solutions of S_7IMF_6 (M = As, Sb) appeared to be stable for several weeks at room temperature, and the solids were indefinitely stable (>1 year) at −20 °C. The $AsF_6{}^-$ salt, however, was observed to decompose in the solid phase after several months at 5 °C, and more quickly (several weeks) at room temperature, as indicated by loss of crystallinity and evolution of iodine. No decomposition of the solid $SbF_6{}^-$ salt was observed at either 5 °C or room temperature in these time periods. We have also observed some decomposition of both salts on redissolution in either SO_2 or AsF_3.

Investigations into the Nature of $S_{16}(AsF_6)_2$. $S_8(AsF_6)_2$ (3.15 g, 4.97 mmol) was dissolved in SO_2 (7.8 g), transferred onto S_8 (0.96 g, 3.74 mmol) and stirred for 24 h. The sulfur completely reacted, yielding a green solution corresponding to $S_{14}(AsF_6)_2$. This was quantitatively transferred through a frit onto another aliquot of S_8 (0.16 g, 0.61 mmol), yielding a green solution of average stoichiometry $S_{15}(AsF_6)_2$ after being stirred for 24 h. Quantitative transferral across a frit onto a further aliquot of S_8 (0.16 g, 0.61 mmol) gave a red solution with no trace of green with an average stoichiometry of $S_{16.03}(AsF_6)_2$. SO_2ClF (approximately 4 g) was then added to the solution and crystals were grown over a 1-week period. Removal of

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(21) Davies, C. G.; Gillespie, R. J.; Ireland, P. R.; Sowa, J. M. *Can. J. Chem.* **1974**, *52*, 2048.

(22) Gillespie, R. J.; Passmore, J.; Ummat, P. K.; Vaidya, O. C. *Inorg. Chem.* **1971**, *10*, 1327.

(23) Passmore, J.; Nandana, W. A. S.; Swindells, N; Taylor, P.; White, P. S., unpublished results. $(SbF_3)_3SbF_5/SbF_3$ mixtures can also be products of reactions of this type, and therefore we cannot rule out SbF_3 as a product of the above reactions in addition to the observed $(SbF_3)_3SbF_5$.

Table II. Crystal Data for S_7ISbF_6 and S_7IAsF_6

	S_7ISbF_6	S_7IAsF_6
fw	587.1	540.2
D_x, calcd density, Mg m^{-3}	2.90	2.78
Z, formula units/unit cell	4	6
μ, linear abs coeff, mm^{-1}	5.48	6.13
cryst size, mm	0.36 × 0.25 × 0.26	0.34 × 0.22 × 0.05
space group	$P2_12_12_1$	$P\bar{1}$
a, Å	11.786 (2)	15.516 (11)
b, Å	9.187 (1)	11.813 (8)
c, Å	12.400 (3)	11.650 (8)
α, deg	90	107.30 (4)
β, deg	90	74.71 (5)
γ, deg	90	104.62 (5)
V, Å^3	1342	1931
temp of data collection, °C	20	20
λ (Mo Kα), Å	0.71069	0.71069
scan range, deg	$2.0 + 0.7 \tan \theta$	$2.0 + 0.7 \tan \theta$
scan rate, deg min^{-1}	$2(2\theta)$	$1(2\theta)$
maximum 2θ, deg	60	40
no. of unique reflctns	2208	3912
no. of obsd reflctns	1628	2833

the volatiles gave small orange needlelike crystals, a microcrystalline brown solid, and a crystalline yellow material, shown by Raman spectroscopy to be S_8. Elemental analysis of the bulk material fitted well for $S_{16}(AsF_6)_2$. Anal. Calcd for S_8AsF_6: S, 57.53; As, 16.85; F, 25.62. Found: S, 57.20; As, 16.61; F, 23.54.

Other reactions were carried out with large excesses of sulfur relative to S_8^{2+} or AsF_5. The amount of unreacted S_8 remaining relative to the amount of oxidizing material was used to calculate an average x (18.5) for S_x^{2+}. The results are in the supplementary material.

Attempted Identification of S_7IMF_6 Bulk Material. X-ray (Cu Kα radiation) powder photographs of several samples of S_7IAsF_6 prepared by a variety of routes (eq 1, 3, 4, and 5) showed only three strong lines (2θ = 18.20, 23.15, and 28.85°). One photograph of material obtained according to eq 1 gave these and other measurable lines. Neither intensity distribution nor the 2θ values correlated with the powder diffraction pattern calculated from single-crystal data. We were unsuccessful in obtaining a powder photograph from large ground crystals of S_7ISbF_6.

Raman spectra of S_7IAsF_6 prepared by reactions 1 and 3 were obtained at −196 °C in a spinning cell. The spectra were similar with peaks at 65, 100, 160, 200, 209, 239, 310, 335, 366, 373, 461, and 556 cm^{-1}. The spectra were poor, and peaks attributable to AsF_6^- were not observed. Various IR spectra of S_7IMF_6 were obtained showing broad peaks attributable to MF_6^-.

X-ray Crystal Structure Determinations. Data Collections. Suitable crystals, manipulated in a Vacuum Atmospheres Corp. drybox with the aid of a Wild M3 microscope of long focal length mounted outside the drybox, were sealed under dry nitrogen in rigorously dried glass capillary tubes. An initial photographic investigation was made with use of precession techniques after which the crystals were transferred to a Picker FACS I diffractometer equipped with a graphite monochromator. Pertinent crystallographic data are given in Table II.

(a) S_7ISbF_6. The diffractometer was controlled by a FORTRAN IV control program,[24] and cell parameters and an orientation matrix were refined with use of the centered coordinates of 15 reflections and their Friedel opposites. Data were collected with use of an ω–2θ scan during which a profile of the peak was accumulated in the computer. The background level was estimated by a stationary count for one-tenth of the scan time at each end of the scan. If the net intensity was significant ($I > 2\sigma(I)$), an analysis of the profile was performed to determine the limits of the peak and those parts of the scan on either side were included in the background estimate. The intensities of three standard reflections monitored every 100 reflections showed no significant deviation from their mean values.

(b) S_7IAsF_6. The diffractometer was controlled by the original Picker routines, and the cell parameters and an orientation matrix were refined with use of the coordinates of 12 well-centered reflections. Data were collected with use of an ω–2θ scan, and the backgrounds were estimated from stationary counts of 20 s at each end of the scan. Three standard reflections were monitored every 100 reflections, and it soon became apparent that the crystal was moving. The crystal was realigned whenever a significant decrease in standard intensity was observed, about every 300 reflections. All attempts to secure the crystal failed, as did numerous subsequent attempts to find another suitable single crystal.

Table III. Fractional Atomic Coordinates (×10^4) for S_7ISbF_6[a]

atom	x	y	z
I(1)	2796.4 (6)	6808.7 (8)	3798.9 (6)
S(1)	2537 (2)	4602 (3)	2888 (2)
S(2)	3888 (2)	4357 (3)	1796 (2)
S(3)	5305 (2)	5056 (3)	2522 (2)
S(4)	5717 (2)	3419 (3)	3656 (2)
S(5)	5492 (2)	4354 (4)	5062 (2)
S(6)	3690 (2)	4051 (3)	5410 (2)
S(7)	3050 (2)	2922 (3)	4276 (2)
Sb(1)	953.4 (5)	685.9 (7)	1367.1 (5)
F(1)	−6 (9)	774 (13)	2553 (7)
F(2)	1912 (8)	598 (11)	139 (6)
F(3)	2083 (10)	1655 (17)	2107 (13)
F(4)	380 (15)	2433 (16)	886 (11)
F(5)	−145 (8)	−349 (16)	587 (8)
F(6)	1559 (10)	−1048 (12)	1829 (10)

[a] Standard deviations in parentheses.

Structure Solution and Refinement. S_7ISbF_6. The solution of this structure has been previously described.[5] After correction of the data for absorption (transmission factors 0.27–0.32) the reported atomic positions were used as input to a block matrix least-squares routine, which minimized $\sum w(\Delta F)^2$ with $w = 1/(\sigma^2(F) + pF^2)$; the factor p was determined from measurements of the standards to be 0.005. Scattering factors were taken from ref 25 and were corrected for anomalous dispersion. The final values of $R = \sum|\Delta F|/\sum|F_o|$ and $R_w = (\sum w|\Delta F|^2/\sum w|F_o|^2)^{1/2}$ were 0.046 and 0.061 (0.074 and 0.070 including unobserved reflections), respectively. Final positional parameters are given in Table III, and the thermal parameters are given in the supplementary material. The program system used was that of Larsen and Gabe for the PDP 8/E computer.[26]

S_7IAsF_6. After reduction of the intensity data the structure was solved by multiple-solution direct methods using the computer program MULTAN.[27] The E map phased by the solution with the highest combined figure of merit yielded the positions of all the nonfluorine atoms. The fluorines were located by a subsequent difference synthesis. With use of unit weights and anisotropic thermal parameters for all atoms except fluorine, the structure was refined to R = 0.14. The use of anisotropic thermal parameters for the fluorines did not significantly improve the agreement, which, in view of the quality of the data, is not surprising, so the refinement was abandoned at this point. No attempt was made to correct the data for absorption. Except for bond distances and angles in Figures 3 and 4 the results have been placed in the supplementary material. The XRAY-76 suite of programs[28] were used for the refinement of this structure.

Discussion

Preparation of S_7IMF_6 (M = As and Sb). Excess sulfur and iodine react with arsenic and antimony pentafluoride in liquid SO_2 or AsF_3, essentially quantitatively according to eq 1 and 2.

$$^{14}/_{8}S_8 + I_2 + 3AsF_5 = 2S_7IAsF_6 + AsF_3 \qquad (1)$$

$$^{42}/_{8}S_8 + 3I_2 + 10SbF_5 = 6S_7ISbF_6 + (SbF_3)_3SbF_5{}^{23} \qquad (2)$$

The compositions of S_7IAsF_6 and S_7ISbF_6 are supported by elemental analyses placed in the supplementary material and

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(24) Gabe, E. J.; LePage, Y.; Grant, D. F. "A 4-Circle Diffractometer Control System Written in FORTRAN IV", private communication, 1980.

(25) Dauben, C. H.; Templeton, D. H. "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1962; Vol. IV.

(26) Larsen, A. C.; Gabe, E. J. In "Computing in Crystallography"; Schank, H., Olthof-Hazekamp, R., van Koningsveld, H., Bassi, G. C., Eds.; Delft University Press: Delft, Holland, 1978.

(27) Main, P.; Woolfson, M. M.; Germain, G. *Acta Crystallogr., Sect. A* **1971**, *A27*, 368.

(28) Stewart, J. M., Ed. Technical Report TR446; Computing Science Center, University of Maryland: College Park, MD, 1976.

product weights (Table I). The salts S_7IMF_6 (M = As, Sb) appeared to be highly crystalline and homogeneous as viewed under the microscope. One sample of S_7ISbF_6 consisted of large crystals, and a fragment of one particularly big crystal was shown to be S_7ISbF_6 by X-ray analysis. Another X-ray structural determination was carried out with use of a crystal from the product of a similar reaction with the same result and is described in the preliminary communication.[5] The S_7IAsF_6 crystals, although they usually appeared to be single and well formed, diffracted X-rays poorly. One crystal obtained from the reaction of $S_8(AsF_6)_2$ and KI (reaction 5, below) was suitable for X-ray studies and was shown to be S_7IAsF_6.

Attempts at unambiguously characterizing the bulk product of these reactions and of the reactions described below by Raman spectroscopy and X-ray powder diffraction were unsuccessful. The difficulty of making fine distinctions based on analytical results for compounds of this type is recognized. However, for 14 analyses of products from various preparative routes to S_7IMF_6, 10 fit S_7IMF_6, two S_8IAsF_6, and two S_6ISbF_6. The elemental analyses therefore reasonably support the view that S_7IMF_6 was the product in all cases. The product weights for these and other reactions, taken as a whole, support S_7IMF_6 rather than S_6IMF_6 or S_8IMF_6 (see Table I).

Crystalline S_7IAsF_6 was also prepared according to eq 3 with use of excess iodine.

$$S_x(AsF_6)_2\ (x = \text{ca. } 19) + I_2 = 2S_7IAsF_6 + ((x - 14)/8)S_8 \qquad (3)$$

The weights of S_7IAsF_6 and precipitated sulfur are both in good agreement with values calculated (see Table I) on the assumption that the reaction proceeds by eq 3. In a preliminary communication a reaction was reported between $S_{16}(AsF_6)_2$ and iodine leading to a soluble product and no precipitated sulfur. Reexamination of the data showed that the overall stoichiometry of starting material was $S_{14}(AsF_6)_2$ and not $S_{16}(AsF_6)_2$. Therefore this experiment is consistent with eq 3 and is not evidence for the formation of S_8IAsF_6 as was previously suggested. The nature of $S_x(AsF_6)_2$ (ca. $21 \geq x \geq 16$) is not completely understood;[18] however, the crystal structure of $S_{19}(AsF_6)_2$ has been determined,[18a] and the structure of S_{19}^{2+} has been shown to be that of two S_7^+ rings joined by an S_5 chain. Reactions of S_{19}^{2+} with iodine leading to S_7I^+ and sulfur are therefore readily envisaged.

Attempts to prepare S_8IAsF_6 by the reaction of I_3AsF_6 with excess sulfur and by the reaction of an exact 1:1 ratio of $S_8(AsF_6)_2$ and KI were unsuccessful. The reactions proceeded quickly and essentially quantitatively according to eq 4 and 5.

$$I_3AsF_6 + nS_8 = S_7IAsF_6 + I_2 + (n - {}^7/_8)S_8 \qquad (4)$$

$$S_8(AsF_6)_2 + KI = S_7IAsF_6 + KAsF_6 + {}^1/_8S_8 \qquad (5)$$

If S_8IAsF_6 was given by reaction 5, then sulfur would not be a product. However, it was unambiguously identified, and the weight of insoluble product ($KAsF_6 + S_8$) was in agreement with that calculated by eq 5. Presumably, S_8I^+ is the initial product of I_3^+ and S_8, and S_8^{2+} and I^-, but it rearranges to give S_7I^+ and ${}^1/_8S_8$.

S_7ISbF_6 was also prepared by the reaction of excess sulfur and $I_2Sb_2F_{11}$.

Stabilities of S_7IMF_6. Both S_7IMF_6 solids were stable at −20 °C; however, at 5 °C and room temperature S_7ISbF_6 appeared stable whereas S_7IAsF_6 decomposed slowly. Presumably decomposition was initiated by donation of F^- from AsF_6^-, consistent with the relative Lewis acidities of the salts; i.e., SbF_6^- is a poorer F^- donor than AsF_6^-.

Nonexistence of S_8IMF_6. The existence of S_8IMF_6 cannot be rigorously ruled out. It may disproportionate to S_7IMF_6 and sulfur according to eq 6.

$$S_8IMF_6(s) = S_7IMF_6(s) + {}^1/_8S_8(s) \qquad (6)$$

If it is assumed that sulfur–sulfur and sulfur–iodine bonds are of the same strength in both S_7I^+ and S_8I^+, then

$$\Delta H(\text{eq } 6) = \Delta H[{}^7\!/_8S_8 \rightarrow S_7](g) + \text{IP}[S_7(g)] - \text{IP}[S_8(g)] - {}^1\!/_8\Delta H_{\text{subl}}(S_8) + U(S_7IMF_6) - U(S_8IMF_6) = 23.8(\text{ref } 29) + 836.4(\text{ref } 30) - 872.4(\text{ref } 30) - 13.6(\text{ref } 29) - [U_{(S_8IMF_6)} - U_{(S_7IMF_6)}] \approx -26 - (\text{a small positive number})\ \text{kJ mol}^{-1}$$

Entropy also favors reaction 6 proceeding to the right. An important factor in the stability of S_7I^+ relative to S_8I^+ may be the lower ionization potential of S_7 relative to that of S_8 (see above). The ionization potential of S_5 (830 kJ mol^{-1})[30] is less than that of S_6 (868 kJ mol^{-1})[30] or S_4 (1000 kJ mol^{-1}),[30] and the radical cation S_5^+ has been detected in solution,[19] but not S_4^+ or S_6^+. The crystal structure of $S_{19}(AsF_6)_2$ shows it to have the structure S_7^+–S_5–S_7^+.[18] This suggests that the odd unipositively charged sulfur rings S_7^+ and S_5^+ (containing substituents or not) are more stable than the even-membered rings S_8^+ or S_6^+ in contrast to the situation found for neutral sulfur rings, where the even-membered rings are more stable, with the stability sequence $S_8 > S_6 > S_7 >>> S_5$ (not isolated).[31]

Nature of Red Solutions of $S_x(AsF_6)_2$, $x \geq 16$, in SO_2. In the course of our work it was found necessary to reinvestigate the nature of the material previously designated as $S_{16}(AsF_6)_2$[22] in order to understand its reaction with iodine (see eq 3 above). Blue solutions of $S_8(AsF_6)_2$ were titrated against S_8, and the solution turned red at an average stoichiometry of $S_{16}(AsF_6)_2$, consistent with previous work.[18,22] Reactions of $S_8(AsF_6)_2$ or AsF_5 with excess sulfur in SO_2 solution gave an uptake of sulfur into solution corresponding to $S_x(AsF_6)_2$, $x = 18.5$ (the average of 10 experiments, x varying between 17.4 and 20.6). Therefore, in addition to a solution of average stoichiometry $S_x(AsF_6)_2$, $x = 16$, it was demonstrated that sulfur polyatomic cations with x(average) > 16 were also formed. While this work was in progress, the X-ray structure of $S_{19}(AsF_6)_2$ was determined,[18] confirming this result. Crystallization of red solutions of average stoichiometry $S_{16}(AsF_6)_2$ gave solid S_8 and what appeared to be two other crystalline phases. The elemental analysis of the mixture fitted well for $S_{16}(AsF_6)_2$, and as one phase was S_8, the implication is that one of the other phases must contain $S_x(AsF_6)_2$, $x < 16$, possibly $S_{10}(AsF_6)_2$ analogous to the recently characterized $Se_{10}(AsF_6)_2$.[32] The species responsible for the blue color has been shown[18] to be S_5^+; the disappearance of this species at an average stoichiometry $S_{16}(AsF_6)_2$ may be fortuitous. Solutions of $S_{16}(AsF_6)_2$ will take up more sulfur, up to an average composition of ca. $S_{19}(AsF_6)_2$ presumably containing the S_7^+–S_5–S_7^+ cation. It seems reasonable to suppose that these solutions are equilibrium mixtures, containing other species in addition to S_{19}^{2+}, possibly S_7^+–S_x–S_7^+, x = 6, 4, 3, 2, and 1, as well as the observed radical cations,[18] one of which may be S_7^+, and possibly lower sulfur polyatomic cations as well [e.g., S_{10}^{2+}].

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(29) Berkowitz, J.; Marquart, J. R. *J. Chem. Phys.* **1963**, *39*, 275. Drowart, J.; Goldfinger, P.; Detry, D.; Rickert, H.; Keller, H. *Adv. Mass Spectrom.* **1968**, *4*, 499.

(30) Berkowitz, J.; Lifshitz, C. *J. Chem. Phys.* **1968**, *48*, 4346. Rosenstock, H. M.; Droxl, K.; Steiner, B. W.; Herron, J. T. *J. Phys. Chem. Ref. Data, Suppl. 1* **1977**, *6* and references therein.

(31) Steudel, R. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 655 and references therein.

(32) Burns, R. C.; Chan, W.-L.; Gillespie, R. J.; Luk, W.-C.; Sawyer, J. F.; Slim, D. R. *Inorg. Chem.* **1980**, *19*, 1432.

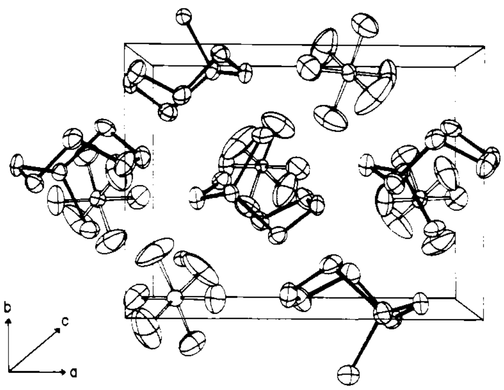


Figure 1. Contents of the S_7ISbF_6 unit cell.

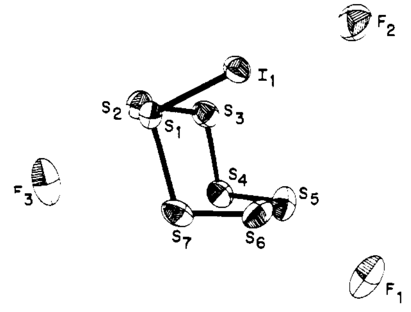


Figure 2. The S_7I^+ cation, with interionic contacts.

Table IV. Bond Distances and Significant Contacts for S_7ISbF_6 (Å)

	Bond Distances		
S(1)-I	2.342 (3)	Sb-F(1)	1.858 (9)
S(1)-S(2)	2.104 (4)	Sb-F(2)	1.897 (7)
S(2)-S(3)	2.004 (4)	Sb-F(3)	1.842 (10)
S(3)-S(4)	2.114 (4)	Sb-F(4)	1.846 (12)
S(4)-S(5)	1.963 (4)	Sb-F(5)	1.874 (10)
S(5)-S(6)	2.184 (4)	Sb-F(6)	1.836 (10)
S(6)-S(7)	1.906 (5)		
S(7)-S(1)	2.389 (4)		
	Intracationic Contacts		
I···S(6)	3.394 (3)	S(1)···S(3)	3.321 (4)
I···S(3)	3.720 (3)	S(4)···S(7)	3.268 (4)
	Interionic Contacts[a]		
I···F(2)	2.926 (9)	S(6)···F(1)	2.959 (9)
S(1)···F(3)	2.93 (1)	S(7)···F(3)	3.15 (1)
S(5)···F(1)	3.02 (1)		

[a] S···F ⩽ 3.20 Å, I···F ⩽ 3.40 Å.

Table V. Bond Angles (deg) for S_7ISbF_6

I-S(1)-S(2)	107.7 (2)	S(3)-S(4)-S(5)	104.5 (2)
I-S(1)-S(7)	100.3 (1)	S(4)-S(5)-S(6)	104.6 (2)
S(7)-S(1)-S(2)	101.7 (2)	S(5)-S(6)-S(7)	108.0 (2)
S(1)-S(2)-S(3)	107.9 (2)	S(6)-S(7)-S(1)	106.3 (2)
S(2)-S(3)-S(4)	105.2 (2)		
F(1)-Sb-F(2)	179.0 (5)	F(3)-Sb-F(4)	90.2 (9)
F(3)	91.6 (6)	F(5)	177.7 (6)
F(4)	89.7 (6)	F(6)	89.1 (7)
F(5)	90.3 (5)	F(4)-Sb-F(5)	91.4 (8)
F(6)	91.6 (6)	F(6)	178.5 (6)
F(2)-Sb-F(3)	89.3 (6)	F(5)-Sb-F(6)	89.3 (6)
F(4)	89.8 (5)		
F(5)	89.0 (5)		
F(6)	88.9 (5)		

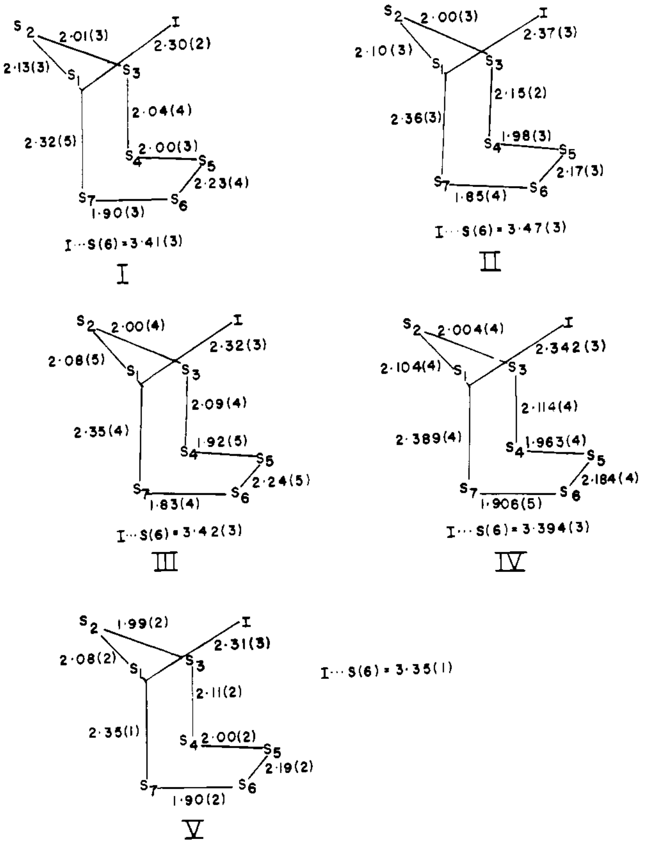


Figure 3. Comparison of the S_7I^+ bond distances in S_7IAsF_6 (I, II and III), S_7ISbF_6 (IV), and $(S_7I)_4S_4(AsF_6)_6$ (V).

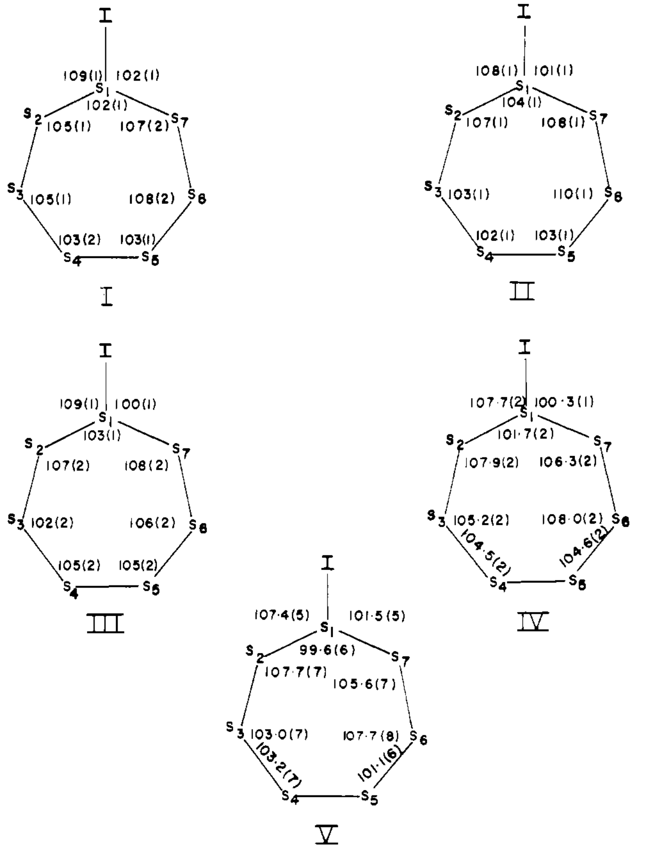


Figure 4. A comparison of the S_7I^+ bond angles in S_7IAsF_6 (I, II and III), S_7ISbF_6 (IV), and $(S_7I)_4S_4(AsF_6)_6$ (V).

Crystal Structures of S_7IMF_6 (M = As, Sb). The contents of an S_7ISbF_6 unit cell are shown in Figure 1, and the S_7I^+ cation, with interionic contacts, is illustrated in Figure 2. Appropriate bond distances and angles are given in Tables IV and V, respectively. The S_7IAsF_6 data were poor; however, three independent S_7I^+ cations were unambiguously located, and the corresponding bond distances and angles are compared

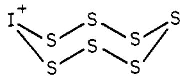
Table VI. Some Sulfur-Iodine Bond Lengths (from Ref 35)

compd	bond lengths, Å
$[(H_2N)_2CS]_2I^+I^-$	2.629
$1,4\text{-}C_4H_8S_2\cdot 2IBr$	2.687 (2)
$2Ph_3PS\cdot 3I_2$	2.69 (2)
$(PhCH_2)_2S\cdot I_2$	2.78
$1,4\text{-}C_4H_8S_2\cdot 2I_2$	2.867 (6)
$1,4\text{-}C_4H_8S_2\cdot C_2I_2$	3.27 (1)

with those of S_7I^+ in S_7ISbF_6 and in $(S_7I)_4S_4(AsF_6)_6$[16] in Figures 3 and 4. All five independent S_7I^+ cations have similar geometries, and the bond angles and distances are essentially the same if the appropriate standard deviations are taken into account. Clearly the geometry of the cation is not a consequence of crystal packing forces. In the following discussion S_7ISbF_6 results will be used, as this structure has been determined to the greatest precision. The structure of S_7ISbF_6 reported in a preliminary communication[5] is essentially the same, although less well determined.

The sulfur–iodine bond distance of 2.342 (3) Å is slightly shorter than the sum of the covalent radii of sulfur (1.04 Å) and iodine (1.33 Å) of 2.37 Å,[33] and slightly longer than that estimated[34] (2.32 Å) for the hypothetical SI_3^+ from bond distances in related species and corresponds to a bond order of 1. It is the shortest sulfur–iodine bond distance so far reported; some other sulfur–iodine distances are given in Table VI; however, in all cases they do not correspond to two-center two-electron bonds. All S_7I^+ cations have iodine–fluorine contacts [S_7ISbF_6, 2.926 (9) Å; S_7IAsF_6, 3.18 (10), 2.89 (7), and 3.05 (6) Å; $(S_7I)_4S_4(AsF_6)_6$,[16] 2.96 (2) Å] that are the strongest of the anion–cation interactions, and which are ca. 15% less than the sum of the van der Waals radii of iodine and fluorine. Like other similar iodine–fluorine contacts, the angle at iodine is approximately 180°, indicating that there is partial lone pair donation from fluorine to iodine. The fluorine atom involved in the iodine contact in S_7ISbF_6 has an antimony–fluorine bond (1.897 (7) Å) that is significantly longer than the average of the others (1.851 (4) Å).

The structure of S_7I^+ is not that of the isoelectronic TeS_7,[36] i.e., **1**. Structure **1** can be regarded as containing an I^+ unit



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and the observed structure an S_7^+ unit. It is therefore reasonable to suppose that the ease of formation of a cyclic S_7I^+ similar to TeS_7 and the observed structure is proportional to the ionization potentials of iodine and S_7, i.e., 1008 and 836 kJ mol^{-1},[30] respectively.

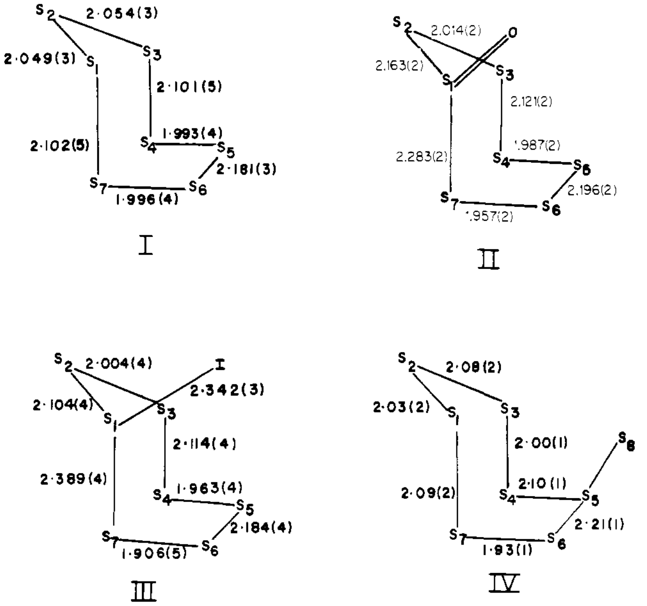

Figure 5. A comparison of the geometries of δ-S_7 (I), S_7O (II), S_7I^+ (III), and the S_7 chair in S_{19}^{2+} (IV). The bond distances given for S_7 are from ref 9a; those given in ref 9b for δ-S_7 and γ-S_7 are essentially the same.

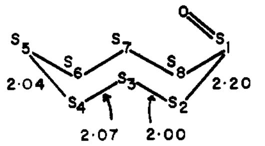

Figure 6. The geometry of S_8O.

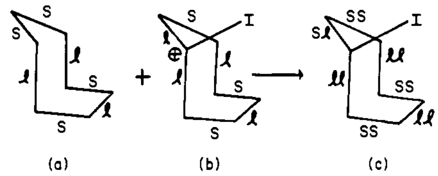

Figure 7. Estimation of bond alternations in S_7I^+: (a) bond alternations due to S_7 ring; (b) bond alternations due to $>S^+-I$; (c) resultant. *l* = long, s = short. The extent of lengthening and shortening decreases with the number of bonds from the source of perturbation.

The S_7 ring in S_7I^+ has a slightly distorted chair configuration similar to that in γ- and δ-S_7[9] and in S_7O.[12] The geometries of S_7O and S_7I^+ are very similar (see Figure 5). The dihedral angles in S_7I^+ and S_7O are similar, and a table comparing corresponding dihedral angles in S_7I^+ and S_7O is given in the supplementary material. There is marked variation of the sulfur–sulfur bond distances in both S_7I^+ and S_7O. There is also bond alternation in S_7 due to the unfavorable dihedral angle about S(5)–S(6) and in S_8O[13] (see Figure 6), which contains a partially charged three-coordinate sulfur atom. The bond alternations in S_7, and S_7O have been discussed by Steudel[9,31,37] and those in S_7, S_7O, S_7I^+, and the S_7 rings in S_{19}^{2+} by Gillespie,[18] who has also proposed a model to account for the overall geometry[38] of these molecules. To a first order of approximation, bond alternation in S_7I^+ results from a superimposition of the bond alternation in S_7 and that generated by the presence of a charged, three-coordinate S(1). The position of iodine substitution in S_7I^+ (and oxygen in S_7O) is such as to cause a maximum reinforcement of bond alternations in the ring as illustrated in Figure 7.

The bond distances and asymmetric bond alternation in S_7I^+ are approximately accounted for by this model (see Figure 7), taking into account the magnitude of the observed bond alternations in S_7 and S_8O, with the exception of S(5)–S(6). The S(1)–S(7) distance is the longest (2.389 (4) Å) and is similar in length to that in $S_2O_4^{2-}$ [31] (2.39 (1) Å), and S(7)–S(6) is the shortest (1.906 (5) Å), similar to that in $S_2(g)$[31] (1.892 Å), which has a formal bond order of 2. The valence bond

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(33) Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 3rd ed.; Interscience: Toronto, 1972.

(34) Passmore, J.; Richardson, E. K.; Whidden, T. K.; White, P. S. *Can. J. Chem.* **1980**, *58*, 851.

(35) Peach, M. E. *Int. J. Sulfur Chem.* **1973**, *8*, 151.

(36) Hawes, L. L. *Nature (London)* **1963**, *198*, 1267.

(37) Steudel, R.; Schuster, F. *J. Mol. Struct.* **1978**, *49*, 143.

(38) Gillespie, R. J. *Chem. Soc. Rev.* **1979**, *8*, 315.

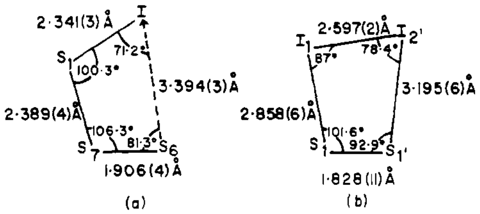
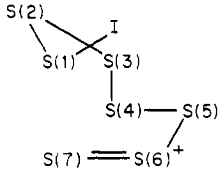


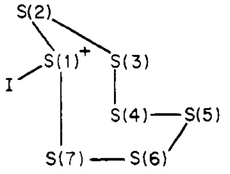
Figure 8. (a) IS(1)S(7)S(6) plane in S_7I^+. (b) S(1)I(1)I(2)′S(1)′ plane in $S_2I_4^{2+}$.

chain structure **2** may be regarded as making a significant contribution to the overall bonding in S_7I^+.



2

The IS(1)S(7)S(6) atoms lie in a plane (see the supplementary material) and the S(6)–I distance of 3.394 (3) Å is 15% less than the sum of the van der Waals radii of sulfur and iodine.[33] This contact reflects attraction (weakly bonding or electrostatic), or presumably the sterically less hindered isomer **3** would be preferred. The geometry of S_7O and S_8O and the position of substitution of the S_7 chain in S_{19}^{2+} allow similar substituent–sulfur ring interactions (see Figures 5 and 6).



3

The four sulfur atoms in the seat of the S_7 ring in S_7I^+ are essentially planar. If it is assumed[31] that the S(6) has inert 3s electrons, then it has a $3p^2$ electron pair pointing almost directly toward the iodine atom (Figure 8a). This geometry is similar to that of an S_2I_2 unit in $S_2I_4^{2+}$ [7] (Figure 8). The situations are also similar in that the angles between the IS(1)S(7)S(6) and S(7)S(6)S(5)S(4) planes (90.2°), and the two S_2I_2 units in $S_2I_4^{2+}$ (89.9°), are almost exactly 90°.

The lone pairs on S(6) and S(5) are eclipsed in S_7 and likely the most basic in the ring. Substitution occurs in this position on the S_7 chair in S_{19}^{2+} as shown in Figure 5. The S(3)S(4)S(5)S(8) atoms in S_{19}^{2+} are not planar, and the S(3)–S(8) distance is 10% less than the sum of van der Waals radii, a less significant contact than I–S(6) in S_7I^+. Differences in energy between S_7 ring conformers are likely small; possibly the weak S(6)–I and S(6)–O interactions in S_7I^+ and S_7O, although not large, play an important part in determining their geometries.

The S(6)–S(5) bond distances in S_7I^+ (2.181 (3) Å) and S_7O (2.196 (2) Å) are similar to that in S_7 (γ-S_7[9b] 2.175 (1) Å; δ-S_7 2.182 (3), 2.180 (3),[9b] and 2.184 (3) Å[9a]) whereas the predictions of the superimposition model would predict a lengthening of this bond relative to S_7. Bond alternations may in part be transmitted by increase or decrease of steric hindrance of lone pairs of the next but one sulfur atoms.[31] The lone pair on S(7) is essentially orthogonal to those on the eclipsed S(5) and S(6), and therefore, a decrease in S(7)–S(6) may not lead to much change in S(5)–S(6).

The most significant sulfur–fluorine contacts (see Figure 2 and Table VII) in S_7ISbF_6 are with S(1), S(7), S(6), and S(5); however, the shortest are with S(1), carrying a formal positive charge, and S(6), charged as per **2**.

The average sulfur–sulfur bond distance in S_7I^+ (2.094 (2) Å) is greater than that in S_7 (2.068 (2) Å). With use of suitable standards for different bond orders a rough graph of bond order vs. d_{SS} may be constructed and the approximate bond orders for each S–S bond in the rings assigned. We have found that this approach yields a higher overall bond order for the positively charged rings (i.e., S_7I^+ and S_7^+ in S_{19}^{2+}) than for S_7 and S_7O.

Acknowledgment. We wish to thank the Natural Sciences and Engineering Research Council (Canada) for financial support.

Registry No. S_7IAsF_6, 61459-17-4; S_7ISbF_6, 61459-18-5; $S_{19}(AsF_6)_2$, 72827-53-3; $S_{16}(AsF_6)_2$, 12429-04-8; AsF_5, 7784-36-3; SbF_5, 7783-70-2; S_8, 10544-50-0; I_2, 7553-56-2; $S_8(AsF_6)_2$, 33248-05-4; I_3AsF_6, 59555-19-0; $I_2Sb_2F_{11}$, 53108-64-8; KI, 7681-11-0.

Supplementary Material Available: Listings of S_7IAsF_6 and S_7ISbF_6 elemental analyses, determinations of x in S_x^{2+}, anisotropic thermal parameters for S_7ISbF_6, fractional atomic coordinates for S_7IAsF_6, anisotropic and isotropic thermal parameters for S_7IAsF_6, dihedral angles in S_7I^+ and S_7O, and calculated and observed structure factors for S_7IAsF_6 and S_7ISbF_6 (46 pages). Ordering information is given on any current masthead page.