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Contribution from the Department of Chemistry, University of New Brunswick,
Fredericton, New Brunswick, Canada E3B 6E2

Preparation and X-ray Crystal Structure of μ-Iodo-bis(4-iodo-*cyclo*-heptasulfur) Tris(hexafluoroantimonate)–Bis(arsenic trifluoride), $[(S_7I)_2I](SbF_6)_3{\cdot}2AsF_3$, and $(S_7I)_4S_4(AsF_6)_6$ Containing the Iodo-*cyclo*-heptasulfur(1+) and the Tetrasulfur(2+) Cations

JACK PASSMORE,* GEORGE SUTHERLAND, and PETER S. WHITE*

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Attempts to prepare S_5IMF_6 (M = As, Sb) led instead to crystalline $(S_7I)_4S_4(AsF_6)_6$ and $[(S_7I)_2I](SbF_6)_3{\cdot}2AsF_3$. These compounds were prepared essentially quantitatively from sulfur, iodine, and the corresponding pentafluoride in appropriate ratios. Their structures were determined by single-crystal X-ray diffractometry. $(S_7I)_4S_4(AsF_6)_6$ is tetragonal, space group $P4/n$, with $a = 19.585$ (7) Å, $c = 8.321$ (3) Å, and $Z = 2$. Data were collected for 2066 reflections with $2\theta \leq 45°$, and the structure was refined to $R = 0.106$ with use of 1307 reflections with $I \geq 3\sigma(I)$. $[(S_7I)_2I](SbF_6)_3{\cdot}2AsF_3$ is triclinic, space group $P\bar{1}$, with $a = 9.240$ (3) Å, $b = 13.321$ (6) Å, $c = 8.247$ (5) Å, $\alpha = 91.16$ (4)°, $\beta = 94.22$ (4)°, $\gamma = 111.04$ (3)°, and $Z = 1$. Data were collected for 2426 reflections with $2\theta \leq 45°$ of which 1775 had $I > 3\sigma(I)$. The structure was refined to $R = 0.118$. The structure of $[(S_7I)_2I]^{3+}$ consists of two equivalent S_7I^+ units that have geometries similar to those observed in S_7IMF_6 (M = As, Sb) and $(S_7I)_4S_4(AsF_6)_6$. They are linked via an iodine atom, which is at a center of symmetry, by a linear S(4)–I(2)–S(4) (S–I = 2.674 (7) Å) arrangement. In addition, the bridging iodine atom has a very weak contact (I(2)–S(6), 3.777 (8) Å) with each of the S_7I^+ units. The square-planar geometry of S_4^{2+} in $(S_7I)_4S_4(AsF_6)_6$ is similar to those in $S_4(AsF_6)_6{\cdot}0.6SO_2$ and $(S_7Br)_4S_4(AsF_6)_2$.

Introduction

Although S_8 is the most stable allotrope of sulfur, attempts to prepare S_8IMF_6 (M = As, Sb)[1,2] (cf. S_8O)[3] led instead to S_7IMF_6 containing the iodo-*cyclo*-heptasulfur(1+) cation (cf. S_7O).[4] Similarly, preparative and analytical evidence suggested that S_7BrMF_6 species were formed rather than S_8BrMF_6, and S_7Br^+ was unambiguously identified crystallographically in $(S_7Br)_4S_4(AsF_6)$.[5,6] The S_7^+ ring was also identified[7] in S_{19}^{2+} (S_7^+–S_5–S_7^+). We therefore attempted to prepare other iodine-substituted sulfur rings, in particular S_5ISbF_6 and S_5IAsF_6. From these reactions $[(S_7I)_2I](SbF_6)_3{\cdot}2AsF_3$ and $(S_7I)_4S_4(AsF_6)_6$ were isolated and then prepared directly. Their structures have been determined by X-ray crystallography. Preliminary accounts of this work have been published.[6,8] A full report is given below.

Experimental Section

Techniques and apparatus have been described in ref 1. The experimental weights for the reactions described below, and other similar reactions, are given in Table I.

Table I. Preparative Data

exptl sect	reactant wt			wt of sol prod., g[a]		wt of insol prod., g	
	S_8(g)	I_2(g)	MF_5(g)	obsd	calcd[b]	obsd	calcd[b]
1[c]	1.55	1.23	4.54				
1[d]	0.81	0.64	2.22	2.44	2.65	1.15	1.01
2[c]	1.93	1.72	3.10	5.90	5.74		
2[d]	1.70	1.37	2.81	5.27	5.12		
2[d]	2.26	1.79	3.83	6.36	6.72		
2[d]	1.46	1.75	2.45	4.74	4.34		
3[c]	2.04	1.01	3.12	5.25	5.30		
4[c]	1.01	0.88	2.49	3.67	3.48	0.66	0.86
4[d]	2.50	2.57	5.89	7.98	8.58	2.40	2.05
4[d]	0.92	0.81	2.21	2.95	3.15	0.83	0.77
5 A[c]	0.97	0.88	1.29	2.63	2.57		
A[d]	2.54	1.68	3.92	7.12	6.72		
A[d]	2.87	2.30	3.71	7.66	7.59		
B[c]	3.22	2.22	6.06	9.72	9.30	1.78	2.10
C[c]	2.10	2.90	4.84	7.71	8.02		
C[d]	2.48	2.85	5.84	9.54	9.48		
D[c]	1.18	1.79	3.89	4.40	5.10	1.77	1.35

[a] For AsF_5 reactions, all products are soluble, and therefore soluble weight refers to total weight. [b] Calculated on the basis of S_8 used; see Discussion for balanced equations. [c] Experiment described in text. [d] Experiment similar to that described in text.

1. Attempted Preparation of S_5ISbF_6 Leading to Single Crystals of $[(S_7I)_2I](SbF_6)_3{\cdot}2AsF_3$. Antimony pentafluoride, SbF_5 (4.54 g, 21.0 mmol), was condensed onto a mixture of S_8 (1.55 g, 6.07 mmol) and I_2 (1.23 g, 4.86 mmol) in AsF_3 (11.20 g). After 1 week, the solution was filtered, and the volatile material was slowly condensed back across the frit by holding the bulb containing the less soluble material at 0 °C, resulting in a highly crystalline product. Subsequent similar refiltrations gave a soluble product of greatly decreased crystallinity and a change in color of the filtered solution from red to blue-green. Therefore, all material was transferred back across the frit and the solution filtered just once. The solvent was slowly removed, as above, until the soluble red-orange crystals were just dry, as prolonged pumping led to a powder. Crystals were mounted in glass capillaries in the drybox and subsequently identified as $[(S_7I)_2I](SbF_6)_3{\cdot}2AsF_3$ by X-ray crystallography. The less soluble product contained a mixture of an unidentified insoluble antimony fluoride and blue crystals with the appearance and solubility characteristics of $S_8(Sb_2F_{11})_2$, both heavily contaminated with a red soluble material. An elemental analysis of the soluble product gave the following results. Anal. Calcd for $S_{14}I_3Sb_3As_2F_{24}$: S, 24.93; I, 21.14; Sb, 20.28; As, 8.32; F, 25.32. Found: S, 25.90, 25.77; I, 25.43; Sb, 22.14; As, 5.59, 5.71; F, 25.10.

2. Attempted Preparation of S_5IAsF_6 Leading to Single Crystals of $(S_7I)_4S_4(AsF_6)_6$. Arsenic pentafluoride (3.10 g, 18.2 mmol) was condensed onto a mixture of S_8 (1.93 g, 7.55 mmol) and I_2 (1.72 g, 6.77 mmol) in SO_2 (6.53 g). After 24 h a brown solution over brown shiny needlelike crystals was obtained. The crystals were separated from the supernatant by filtration and washed twice with ca. 1 cm³ of recondensed solvent, yielding a brown solution. Removal of the volatile material gave crystals on both sides of the frit. Crystals suitable for single-crystal X-ray diffraction studies were obtained from both products and identified as $(S_7I)_4S_4(AsF_6)_6$. X-ray powder diffraction

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photographs of both the more, and less, soluble products were identical with each other and with those obtained from other similar preparations.

3. Preparation of $(S_7I)_4S_4(AsF_6)_6$. Arsenic pentafluoride (3.12 g, 18.4 mmol) was condensed onto a mixture of S_8 (2.04 g, 7.95 mmol) and I_2 (1.01 g, 3.98 mmol) in SO_2 (4.47 g). Removal of the volatile material after 24 h gave small brown needlelike crystals that were identical in appearance with those prepared above (section 2) and were shown to be $(S_7I)_4S_4(AsF_6)_6$. The X-ray powder photograph was also identical with that obtained from the preparation in section 2.

Crystalline $(S_7I)_4S_4(AsF_6)_6$ showed no signs of decomposition on storage at room temperature for several weeks or on redissolution in dry SO_2.

4. Preparation of $[(S_7I)_2I](SbF_6)_3 \cdot xAsF_3$ ($x \leq 2$). Antimony pentafluoride (2.49 g, 11.5 mmol) was reacted with S_8 (1.01 g, 3.96 mmol) and I_2 (0.88 g, 3.47 mmol) in AsF_3 (11.82 g) for 3 days with stirring. A brown solution containing solids was obtained. The products were separated by filtration and the volatile material removed. The dry microcrystalline soluble product slowly (ca. 0.1 g per day) lost AsF_3 and I_2 on prolonged pumping with loss of crystallinity. The insoluble product from a similar reaction was shown to contain $(SbF_3)_3 \cdot SbF_5$[9] by single-crystal X-ray precession photography and Raman spectroscopy.

5. Attempted Preparations. (A) S_6IAsF_6. Arsenic pentafluoride (1.29 g, 7.60 mmol) was condensed onto a mixture of S_8 (0.97 g, 3.78 mmol) and I_2 (0.88 g, 3.47 mmol) in SO_2ClF (4.21 g) and SO_2 (1.90 g). After 24 h the solution was filtered once and pumped to dryness. The less soluble product was a microcrystalline red-brown solid, shown to contain $(S_7I)_4S_4(AsF_6)_6$ by X-ray powder photography. The more soluble product was an unidentified brown solid.

(B) S_6ISbF_6. Antimony pentafluoride (6.06 g, 28.0 mmol) was condensed onto a mixture of S_8 (3.22 g, 12.6 mmol) and I_2 (2.22 g, 8.75 mmol) in SO_2 (7.0 g). The soluble and insoluble materials were quantitatively separated after 24 h, and SO_2ClF was (1.55 g) added to facilitate crystal growth. Slow removal of the volatile material to constant weight yielded large dark brown crystals and a lighter colored brown powder as the soluble product. The insoluble product was an unidentified white powder. One of the dark brown crystals was identified as S_7ISbF_6 by X-ray precession photography.

(C) $S_7I_2(AsF_6)_2$. Arsenic pentafluoride (4.84 g, 28.5 mmol) was condensed onto a mixture of S_8 (2.10 g, 8.22 mmol) and I_2 (2.90 g, 11.4 mmol) in SO_2 (16.00 g). The mixture was occasionally agitated over a 3-day period and a green-brown solution over a dark brown crystalline material. The more soluble material was removed by filtration, leaving shiny dark brown crystals, which were washed with recondensed solvent as described above (section 2). The volatile material was then removed.

A single crystal of the less soluble material from a similar reaction was examined by X-ray precession photography and identified as $S_2I_4(AsF_6)_2$.[10] The more soluble product was an unidentified brown solid.

(D) $S_7I_2(SbF_6)_2$. Antimony pentafluoride (3.89 g, 17.9 mmol) was condensed onto a mixture of S_8 (1.18 g, 4.60 mmol) and I_2 (1.79 g, 7.06 mmol) in AsF_3 (16.00 g). Quantitative separation of the soluble and insoluble products was followed by slow removal of the volatile material with the vessel held at 0 °C. The soluble product was an unidentified brown powder containing several shiny black iodine crystals. The Raman spectrum of the crystalline insoluble product was identical with that of $(SbF_3)_3SbF_5$.[9]

Table II. Crystal Data for $[(S_7I)_2I](SbF_6)_3 \cdot 2AsF_3$ and $(S_7I)_4S_4(AsF_6)_6$

	$[(S_7I)_2I](SbF_6)_3 \cdot 2AsF_3$	$(S_7I)_4S_4(AsF_6)_6$
fw	1800.6	2666.9
D_x, calcd density, Mg m^{-3}	3.17	2.77
Z, formula units/unit cell	1	2
μ, linear abs coeff, mm^{-1}	7.35	6.37
cryst size, mm	0.11 × 0.06 × 0.17	0.05 × 0.22 × 0.35
space group	$P\bar{1}$	$P4/n$
a, Å	9.240 (3)	19.585 (7)
b, Å	13.321 (6)	19.585 (7)
c, Å	8.247 (5)	8.321 (3)
α, deg	91.16 (4)	
β, deg	94.22 (4)	
γ, deg	111.04 (3)	
V, Å^3	943	3191
temp of data collection, °C	20	20
λ(Mo Kα), Å	0.71069	0.71069
scan range, deg	2	2
scan rate, deg min^{-1}	2(2θ)	1(2θ)
max 2θ, deg	45	45
no. of unique reflctns	2426	2066
no. of obsd reflctns	1775	1307
R	0.118	0.106
R_w	0.175	0.125

Table III. Fractional Atomic Coordinates (Esd's) × 10^4 for $[(S_7I)_2I](SbF_6)_3 \cdot 2AsF_3$

atom	x	y	z
Sb(1)	0	0	0
Sb(2)	1202 (2)	3372 (1)	4631 (2)
As(1)	2362 (4)	55 (3)	4908 (4)
I(1)	6130 (2)	3771 (1)	2818 (2)
I(2)	0	$^1/_2$	0
S(1)	4112 (7)	2418 (5)	1296 (8)
S(2)	5385 (8)	1339 (5)	381 (11)
S(3)	7542 (8)	2078 (6)	951 (10)
S(4)	8485 (9)	2978 (5)	8814 (11)
S(5)	6647 (14)	2926 (8)	7354 (12)
S(6)	5763 (9)	3997 (7)	8397 (11)
S(7)	3689 (9)	3070 (7)	9082 (12)
F(11)	2087 (23)	252 (17)	−87 (24)
F(12)	9643 (22)	8581 (16)	448 (23)
F(13)	255 (37)	363 (27)	2253 (37)
F(21)	1149 (30)	3105 (22)	2434 (31)
F(22)	8715 (28)	6296 (21)	3119 (28)
F(23)	9293 (50)	3416 (35)	4536 (48)
F(24)	3031 (46)	3176 (31)	5111 (47)
F(25)	2338 (37)	4791 (28)	4226 (37)
F(26)	104 (48)	1969 (33)	4907 (47)
F(31)	2911 (37)	9306 (25)	3528 (38)
F(32)	3911 (30)	1177 (21)	4339 (29)
F(33)	6711 (45)	227 (33)	3514 (45)

X-ray Crystal Structures of $[(S_7I)_2](SbF_6)_3 \cdot 2AsF_3$ and $(S_7I)_4S_4(AsF_6)_6$. A number of crystals of each compound were mounted under dry N_2 in rigorously dried glass capillaries as previously described.[11,12] Suitable crystals for single-crystal data collection were then selected by a preliminary photographic survey. Precession photographs were used to determine the diffraction symmetry and approximate cell dimensions, after which the crystals were transferred to a Picker FACS-I four-circle diffractometer equipped with a molybdenum tube (λ(Mo Kα) = 0.71069 Å) and a graphite monochromator.

$[(S_7I)_2I](SbF_6)_3 \cdot 2AsF_3$. The initial photographic survey showed this crystal to be triclinic. Cell dimensions and an orientation matrix were refined with use of the centered settings of 14 Friedel pairs of reflections with 30° $\leq 2\theta \leq$ 40°. Intensity data were collected with an ω–2θ scan with backgrounds estimated from a standing count at each end of the scan. Three reference reflections, which were monitored every 100 reflections, showed no significant deviation from their mean values throughout the data collection. Of the 2426 unique reflections with $2\theta \leq 45°$, 1775 were considered observed ($I_{obsd} > 3\sigma(I_{obsd})$) and used in the subsequent calculations. After normalization the structure was solved by direct methods using a version of MULTAN modified[13] for the PDP8/A minicomputer with the assumption of space

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(9) The reduction product of antimony pentafluoride in the presence of an excess of iodine or phosphorus trifluoride under conditions similar to those of these experiments is either $(SbF_3)_3SbF_5$ or a mixture of $(SbF_3)_3SbF_5$ and SbF_3: Passmore, J.; Nandana, W. A. S.; Swindells, N.; Taylor, P.; White, P. S., unpublished results.

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Table IV. Fractional Atomic Coordinates (Esd's) × 10^4 for $(S_7I)_4S_4(AsF_6)_6$

atom	*x*	*y*	*z*
I(1)	5622 (2)	6556 (2)	2448 (3)
S(1)	4547 (5)	6729 (5)	3529 (11)
S(2)	4746 (6)	7660 (5)	5242 (13)
S(3)	5704 (6)	7804 (6)	5201 (19)
S(4)	6160 (7)	7146 (6)	7034 (17)
S(5)	5360 (7)	6635 (8)	7912 (12)
S(6)	5796 (6)	9728 (6)	6335 (14)
S(7)	4385 (5)	5907 (6)	5231 (16)
S(8)	1811 (4)	7699 (4)	−3 (14)
As(1)	8563 (2)	374 (2)	82 (5)
F(11)	9354 (16)	479 (32)	−208 (62)
F(12)	8331 (16)	919 (17)	−1414 (37)
F(13)	8502 (20)	−312 (23)	−1029 (51)
F(14)	8726 (20)	−107 (16)	1645 (35)
F(15)	7733 (25)	291 (15)	282 (56)
F(16)	8507 (20)	1080 (27)	1246 (48)
As(2)[a]	$^1/_4$	$^3/_4$	$^1/_2$
F(21)[a]	3065 (28)	7204 (37)	3869 (64)
F(22)[a]	2162 (41)	6907 (29)	3865 (71)
As(3)	$^1/_4$	$^1/_4$	8576 (10)
F(31)	$^1/_4$	$^1/_4$	6478 (70)
F(32)	$^1/_4$	$^1/_4$	10665 (45)
F(33)	2943 (11)	3207 (10)	8572 (32)

[a] Disordered AsF_6^- on a $\bar{4}$ site. Each of the fluorine positions has occupancy $^3/_4$.

group $P\bar{1}$. At this point an absorption correction was included and the structure refined by block-matrix least squares. The thermal parameters of the fluorines were refined isotropically and those of all other atoms anisotropically to a final agreement factor of $R = 0.12$ ($R_w = 0.17$). The scattering factors were taken from ref 14 and were corrected for anomalous dispersion. The function minimized was $\sum w(\Delta|F|)^2$ in which $w_{hkl} = 1/(\sigma(F_{hkl})^2 + pF_{hkl}^2)$; a value of 0.005 was calculated for p from the statistics of the reference reflections. An analysis of $w(\Delta|F|)^2$ as functions of F and sin θ showed no significant trend. An attempt was made to refine the structure in the acentric space group $P1$, but this did not significantly improve the agreement and was abandoned. When the fluorine thermal parameters were allowed to vary anisotropically, no significant improvement in the refinement was observed; however, extremely high values were observed for some of the thermal parameters, which seems to indicate a libration of the anions that the conventional thermal factor expression cannot adequately describe. The crystal data are summarized in Table II, and the atomic coordinates are given in Table III.

$(S_7I)_4S_4(AsF_6)_6$. An initial photographic survey with a precession camera showed this compound to be tetragonal, belonging to space group $P4/n$. After alignment on the diffractometer with the settings for 12 centered reflections with $30 \leq 2\theta \leq 45°$, data were collected as above. Of the 2066 possible unique reflections for $2\theta \leq 45°$, 1307 were considered observed ($I_{obsd} \geq 3\sigma(I_{obsd})$) and included in the subsequent calculations. The structure was solved by direct methods using the MULTAN system,[15] and after correction for absorption the structure was refined by least squares[16] to a final $R = 0.106$ ($R_w = 0.125$). Scattering factors were taken from ref 14 and corrected for anomalous dispersion; the quantity minimized was $\sum w(\Delta|F|)^2$ with $w = 1/(\sigma(F_{obsd})^2 + 0.005F_{obsd}^2)$. Crystal data are given in Table II and fractional atomic coordinates in Table IV.

In both of these structures the thermal parameters of the fluorines were abnormally large in the directions perpendicular to the As–F bond, indicating that there is some orientational disorder of the AsF_6^- anion that cannot be accommodated by the conventional thermal ellipsoid approximation. This is not a major problem as it is the cations that are the principal interest of the investigation; however, the inability of the model to adequately describe the entire structure, a quite common phenomenon in such compounds, results in R factors that are somewhat larger than normally encountered.

Discussion

Preparation of $(S_7I)_4S_4(AsF_6)_6$. The title compound was prepared essentially quantitatively according to eq 1.

$$4S_8 + 2I_2 + 9AsF_5 \xrightarrow{SO_2} (S_7I)_4S_4(AsF_6)_6 + 3AsF_3 \qquad (1)$$

X-ray powder photographs of this material were relatively poor, but the observed lines and intensities were not inconsistent with those calculated on the basis of single-crystal diffractometer data. It is therefore likely that the bulk of the material is $(S_7I)_4S_4(AsF_6)_6$, as also indicated by the experimental product weight (Table I) and the highly crystalline nature of the product.

It is noteworthy that AsF_5 alone will not[17,18] oxidize S_8 to S_4^{2+}, and since the salt contained S_4^{2+}, it was postulated that the halogen (iodine) was facilitating its formation. We subsequently prepared $S_4(AsF_6)_2$ quantitatively from sulfur and arsenic pentafluoride in SO_2 solution with the addition of small quantities of iodine or bromine.[6,18]

Stabilities of $(S_7I)_4S_4(AsF_6)_6$ and S_7IAsF_6. We have found that $(S_7I)_4S_4(AsF_6)_6$ is thermally more stable than S_7IAsF_6. This may in part be due to the higher lattice energy of the former (which contains the dipositive S_4^{2+} cation). There are fewer and longer[19] S_7I^+–AsF_6^- contacts in the S_4^{2+}-containing salt than in S_7IAsF_6. It therefore appears that the more electrophilic S_4^{2+} cation induces a lesser tendency for AsF_6^- to donate fluoride ions to S_7I^+, which may be the initial step in decomposition of S_7IAsF_6.

Preparation of $[(S_7I)_2I](SbF_6)_3{\cdot}xAsF_3$ ($x \leq 2$). The stoichiometric preparation of the title compound was carried out according to eq 2. The soluble product lost AsF_3 and I_2 on prolonged pumping, accounting for the low yields in some reactions (Table II).

$$^{28}/_8S_8 + 3I_2 + 10SbF_5 \xrightarrow{AsF_3} 2[(S_7I)_2I](SbF_6)_3{\cdot}xAsF_3 + (SbF_3)_3{\cdot}SbF_5{}^{9} \qquad (2)$$

A more crystalline product was obtained from attempted preparations of S_5ISbF_6 (eq 5), in which there was present an excess of SbF_5 relative to that in eq 3. Isolation of $[(S_7I)_2I](SbF_6)_3{\cdot}2AsF_3$ was possible in these reactions due to its greater solubility in AsF_3 than other mixture components. It is possible that $[(S_7I)_2I](SbF_6)_3{\cdot}2AsF_3$ is in equilibrium with other products, e.g., those indicated in eq 3. Iodine monofluoride disproportionates under ambient conditions. The equilibrium may be displaced to the right on pumping and formation of $[(S_7I)_2I](SbF_6)_3$ favored by excess SbF_5.

$$[(S_7I)_2I](SbF_6)_3{\cdot}2AsF_3 \rightleftarrows 2S_7ISbF_6 + \text{“}ISbF_6\text{”} \text{ (or } {}^1/_2I_2FSb_2F_{11}\text{, cf. } Cl_2FAsF_6{}^{20}\text{)} + 2AsF_3 \qquad (3)$$

$$\text{“}ISbF_6\text{”} \rightleftarrows \text{“}IF\text{”} + SbF_5 \qquad (3a)$$

$$I_2FSb_2F_{11} \rightleftarrows \text{“}ISb_2F_{11}\text{”} + IF \qquad (3b)$$

$$\text{“}ISb_2F_{11}\text{”} \rightleftarrows \text{“}IF\text{”} + 2SbF_5 \qquad (3c)$$

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

(18) Murchie, M.; Passmore, J.; Sutherland, G., unpublished results.

(19) $(S_7I)_4S_4(AsF_6)_6$: three contacts per S_7I^+, I···F = 2.96 (2) Å, S···F(average of two) = 3.12 Å. $3S_7IAsF_6$: five contacts per S_7I^+, I···F(average of three) = 3.04 Å, S···F(average of twelve) = 2.98 Å, for contacts less than 3.20 Å.

(20) Gillespie, R. J.; Morton, M. J. *Inorg. Chem.* **1970**, *9*, 811.

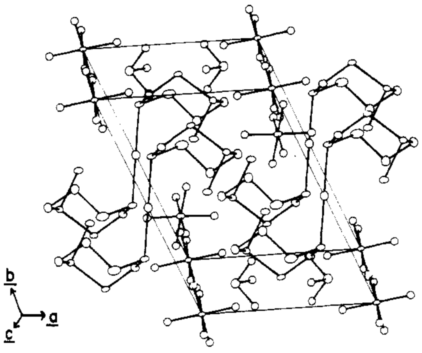

Figure 1. Crystal packing in $[(S_7I)_2I](SbF_6)_3{\cdot}2AsF_3$.

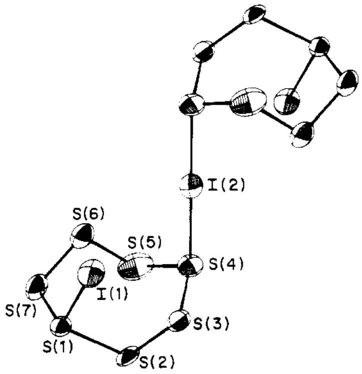

Figure 2. Structure of $[(S_7I)_2I]^{3+}$.

Attempted Preparations of S_xMF_6 (M = As, Sb; x = 5, 6) and $S_7I_2(MF_6)_2$. Preparations of the title compounds were attempted according to eq 4–9.

$$^{5}/_{4}S_8 + I_2 + 3AsF_5 \underset{AsF_3}{\overset{SO_2\text{ or}}{\not\twoheadrightarrow}} 2S_5IAsF_6 + AsF_3 \qquad (4)$$

$$^{5}/_{4}S_8 + I_2 + 4SbF_5 \overset{AsF_3}{\not\twoheadrightarrow} 2S_5ISbF_6 + SbF_3SbF_5 \qquad (5)$$

$$^{3}/_{2}S_8 + I_2 + 3AsF_5 \overset{SO_2}{\not\twoheadrightarrow} 2S_6IAsF_6 + AsF_3 \qquad (6)$$

$$^{9}/_{2}S_8 + 3I_2 + 10SbF_5 \overset{SO_2}{\not\twoheadrightarrow} 6S_6ISbF_6 + (SbF_3)_3SbF_5 \qquad (7)$$

$$^{7}/_{8}S_8 + I_2 + 3AsF_5 \overset{SO_2}{\not\twoheadrightarrow} S_7I_2(AsF_6)_2 + AsF_3 \qquad (8)$$

$$^{21}/_{8}S_8 + 3I_2 + 10SbF_5 \overset{SO_2}{\not\twoheadrightarrow} 3S_7I_2(SbF_6)_2 + (SbF_3)_3SbF_5 \qquad (9)$$

The products were mixtures with average stoichiometries indicated by the appropriate equation. It is possible that, if these species are formed at all, they may disproportionate, e.g., as illustrated in eq 10–12.

$$11S_5IAsF_5 \rightarrow (S_7I)_4S_4(AsF_6)_2{}^{21a} + S_2I_4(AsF_6)_2 + 3S_7IAsF_6 \qquad (10)$$

$$22S_6IAsF_6 \rightarrow (S_7I)_4S_4(AsF_6)_6{}^{21a} + S_2I_4(AsF_6)_2 + 14S_7IAsF_6 \qquad (11)$$

$$5S_7I_2(AsF_6)_2 \rightarrow 2S_2I_4(AsF_6)_2{}^{21a} + 2S_{8.5}(AsF_6)_2{}^{21b} + 2S_7IAsF_6 \qquad (12)$$

Table V. Interatomic Distances (Å) in $[(S_7I)_2I](SbF_6)_3{\cdot}2AsF_3{}^{a}$

	Cation Distances		
I(1)-S(1)	2.335 (6)	S(7)-S(1)	2.108 (12)
S(1)-S(2)	2.306 (10)	S(1)-S(6)	3.302 (12)
S(2)-S(3)	1.897 (10)	S(2)-S(5)	3.307 (14)
S(3)-S(4)	2.205 (13)	I(1)-S(3)	3.381 (9)
S(4)-S(5)	1.988 (15)	I(2)-S(6)	3.777 (8)
S(5)-S(6)	2.081 (14)	I(1)-I(2)	4.248 (3)
S(6)-S(7)	2.001 (13)	I(2)-S(4)	2.674 (7)
	AsF_3 with Long Contacts		
As(1)-F(31)	1.72 (3)	As(1)-F(13)	2.96 (3)
As(1)-F(32)	1.76 (3)	As(1)-F(13)′	3.40 (3)
As(1)-F(33)	1.63 (4)	As(1)-F(26)	2.86 (4)
	Interionic Contacts[b]		
I(1)-F(25)	2.99 (3)	S(4)-F(22)	3.01 (3)
I(1)-F(22)	3.35 (3)	S(4)-F(12)	3.19 (2)
I(1)-F(23)	3.34 (5)	S(5)-F(25)	3.18 (4)
S(1)-F(11)	2.97 (2)	S(6)-F(25)	3.00 (3)
S(1)-F(32)	3.01 (3)	S(7)-F(12)	3.13 (2)
S(2)-F(11)	2.86 (2)	S(7)-F(22)	3.12 (3)
S(3)-F(33)	3.20 (4)		

[a] Standard deviations are in parentheses. [b] $S\cdots F \leqslant 3.20$ Å, $I\cdots F \leqslant 3.40$ Å.

Table VI. Bond Angles (Deg) in $[(S_7I)_2I](SbF_6)_3{\cdot}2AsF_3{}^{a}$

	Cation		
I(1)-S(1)-S(2)	101.6 (3)	S(3)-S(4)-I(2)	104.5 (4)
I(1)-S(1)-S(7)	107.2 (4)	I(2)-S(4)-S(5)	109.2 (4)
S(7)-S(1)-S(2)	99.5 (5)	S(4)-S(5)-S(6)	106.5 (5)
S(1)-S(2)-S(3)	107.1 (4)	S(5)-S(6)-S(7)	104.9 (6)
S(2)-S(3)-S(4)	106.3 (5)	S(6)-S(7)-S(1)	106.9 (4)
S(3)-S(4)-S(5)	105.8 (5)	S(4)-I(2)-S(4)′	180
	AsF_3 with Long Contacts		
F(31)-As(1)-F(32)	87 (1)	F(13)′-As(1)-F(32)	135 (1)
F(31)-As(1)-F(33)	96 (1)	F(13)′-As(1)-F(33)	78 (1)
F(32)-As(1)-F(33)	97 (1)	F(26)-As(1)-F(31)	81 (1)
F(13)-As(1)-F(31)	88 (1)	F(26)-As(1)-F(32)	166 (1)
F(13)-As(1)-F(32)	91 (1)	F(26)-As(1)-F(33)	89 (2)
F(13)-As(1)-F(33)	171 (2)	F(26)-As(1)-F(13)	83 (1)
F(13)-As(1)-F(13)′	94 (1)	F(26)-As(1)-F(13)′	58 (1)
F(13)′-As(1)-F(31)	138 (1)		

[a] Standard deviations are in parentheses.

Disproportionation of S_xISbF_6 (x = 5, 6) to mixtures that include S_7ISbF_6 (x = 6) and $[(S_7I)_2I][SbF_6]$, $2AsF_3$, and $S_8(Sb_2F_{11})$ (x = 5) may be envisaged. Disproportionation of $S_7I_2(SbF_6)_2$ to products including $(S_7I)_2I(SbF_6)_3$ (cf. eq 3) is also possible. Different products are obtained in similar reactions using AsF_5 and SbF_5. This may be attributable to the differences in the two pentafluorides; i.e., SbF_5 is a stronger acceptor and oxidizing agent (as per eq 13) and forms complex

$$3MF_5(g) + 2e^- \rightarrow 2MF_6^-(g) + MF_3(g) \qquad (13)$$

anions (e.g., $Sb_2F_{11}^-$) and a variety of $(SbF_3)_x{\cdot}SbF_5$ reduced products.[9,22] Arsenic pentafluoride, on the other hand, at room temperature, forms only AsF_6^- and the single reduced product AsF_3.

Although the substituted ring species S_nO (n = 5–8)[23-27] have been reported, the only analogous iodide we have isolated is S_7I^+. Similarly, although S_7O_2[28] and the diiodine-substituted S_7 ring in $[(S_7I)_2I]^{3+}$ are known, we were unable to prepare $S_7I_2(MF_6)_2$. The latter is expected to be more electrophilic than $[(S_7I)_2I]^{3+}$ and therefore may more readily disproportionate.

Structure of $[(S_7I)_2I](SbF_6)_3{\cdot}2AsF_3$. The crystal packing of $[(S_7I)_2I](SbF_6)_3{\cdot}2AsF_3$ is illustrated in Figure 1, the

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(21) (a) Unambiguously identified in the reaction mixtures. (b) This is an average stoichiometry for the sulfur cation and may be a mixture of $S_8{}^{2+}$ and a higher polyatomic cation, e.g., $S_{19}{}^{2+}$.[1,7]

(22) $SbF_3{\cdot}SbF_5$: Gillespie, R. J.; Slim, D. R.; Vekris, E. *J. Chem. Soc. A* **1971**, 971. $6SbF_3{\cdot}5SbF_5$: Edwards, A. J.; Slim, D. R. *J. Chem. Soc., Chem. Commun.* **1974**, 178. $5SbF_3{\cdot}3SbF_5$: Nandana, W. A. S.; Passmore, J.; White, P. S.; Wong, C.-M., unpublished results. $2SbF_3{\cdot}SbF_5$: Edwards, A. J., private communication.

(23) (a) Genz, W.; Schenk, P. W. *Z. Anorg. Allg. Chem.* **1970**, *379*, 300. (b) Steudel, R.; Steidel, J. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 134.

(24) Steudel, R.; Sandow, T. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 772.

(25) Steudel, R.; Rebsch, M. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 302.

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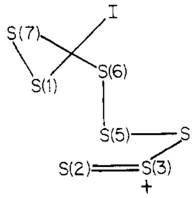
$[(S_7I)_2I]^{3+}$ cation is given in Figure 2, bond distances and angles in the cation and AsF_3 are presented in Tables V and VI, and those associated with SbF_6^- are deposited as supplementary material. The closest I···F and S···F contacts are 2.99 (3) and 2.86 (2) Å, respectively, indicating that the structure is essentially ionic.

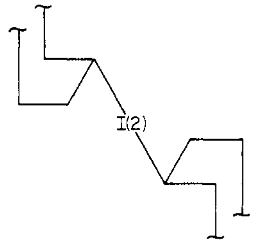
The structure of the $[(S_7I)_2I]^{3+}$ cation consists of two S_7I^+ units joined by a linear S–I–S bond. The two S_7I^+ rings are related by an inversion center at I(2) and are therefore identical.

The S_7I^+ unit in $[(S_7I)_2I]^{3+}$ is very similar in geometry to the S_7I^+ cations in S_7IAsF_6[2] and S_7ISbF_6,[1,2] with minor differences. The position of the I(1) substituent is the same as that in S_7I^+, and the second substituent (I(2)) is in a position similar to that of the sulfur substituent of the S_7 chair conformer in $S_{19}(AsF_6)_2$.[7] The lone pairs on S(3) and S(4) are eclipsed in S_7I^+ and therefore likely the most basic. The S(3) lone pair is expected to be less basic than that on S(4) due to a contribution from valence bond structure **1**.[1] It is therefore reasonable that the I(2) adds to S(4), as observed.



1

Corresponding torsional angles in $[(S_7I)_2I]^{3+}$ and S_7I^+ are very similar except those associated with S(4), in $[(S_7I)_2I]^{3+}$, which is joined to the substituent I(2), not present in S_7I^+. Torsional angles in S_7I^+, $[(S_7I)_2I]^{3+}$, and S_7 (chair) in S_{19}^{2+} have been deposited as supplementary material. More significant differences in corresponding torsional angles are observed between $[(S_7I)_2I]^{3+}$ and the S_7 chair in S_{19}^{2+}. This is probably due to the lack of an S(1) substituent in the latter. Gillespie[30] has recently derived the shapes of S_7, S_7O, and S_7I^+ species, based on a cube. In both S_7I^+ and $[(S_7I)_2I]^{3+}$, relatively good planes can be computed for I(1)S(1)S(2)S(3), S(1)S(2)S(5)S(6), and S(2)S(3)S(4)S(5) (maximum deviations from least-squares planes are 0.09, 0.08, and 0.10 Å, respectively, for $[(S_7I)_2I]^{3+}$). Angles between these planes are given in Table VII. The other three sides of the "cube" involving I(2), i.e., I(1)S(3)S(4)I(2), I(1)S(1)S(6)I(2), and I(2)S(4)S(5)S(6), are much less planar with maximum deviations from least-squares planes of 0.5, 0.5, and 0.3 Å, respectively. Support for Gillespie's model lies in the fact that I(2) is endo to the ring, suggestive of some sort of weak attractive interaction (I(2)···S(6) = 3.777 (8) Å (sum of van der Waals radii 4.0 Å)). Otherwise, the less sterically hindered isomer **2** would presumably be formed.



2

The other reported disubstituted S_7 ring, S_7O_2, has been prepared and a structure[31] proposed on the basis of its Raman spectrum. The structure of $S_{12}O_2$ containing the disubstituted S_{12} ring in $S_{12}O_2 \cdot 2SbCl_5 \cdot 3CS_2$ has been determined.[32]

Table VII. Comparison of Angles (Deg) between Planes in S_7I^+ and $[(S_7I)_2I]^{3+}$

plane[a]	S_7I^+	$[(S_7I)_2I]^{3+}$	plane[a]	S_7I^+	$[(S_7I)_2I]^{3+}$
1–2	90.21	92.4	2–3	106.2	108.2
1–3	103.3	103.5			

[a] Planes: 1 = I(1)S(1)S(2)S(3); 2 = S(2)S(3)S(4)S(5); 3 = S(1)S(2)S(5)S(6).

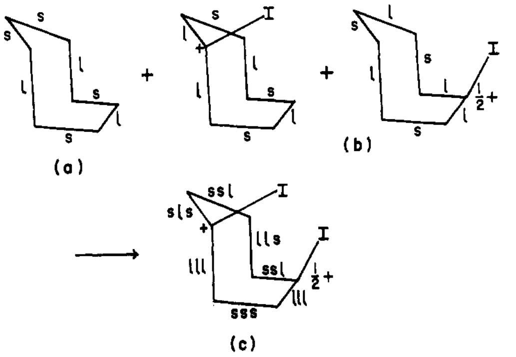


Figure 3. Estimation of bond alternations in $[(S_7I)_2I]^{3+}$: (a) alternation due to the S_7 ring; (b) alternation due to S^+–I; (c) resultant, l = long, s = short. The extent of lengthening and shortening decreases with the number of bonds from the source of perturbation.

The sulfur–sulfur bond distances in the S_7 chair conformation in S_7, S_{19}^{2+}, S_7I^+, and $[(S_7I)_2I]^{3+}$ are compared in Table VIII. Alternations in $[(S_7I)_2I]^{3+}$ may be viewed as a summation of the alternations imposed by substitution of the S_7 ring at S(1) and S(4) as illustrated in Figure 3. The effect of iodine substitution at S(4) is reasonably less pronounced than that at S(1), as the formal charge on S(4) is half that on S(1). Alternatively, the bond distances in the S_7 ring in $[(S_7I)_2I]^{3+}$ may be regarded as approximately the summation of those in the S_7 chair in S_{19}^{2+} and S_7I^+ (see Table VIII). All but one of the $[(S_7I)_2I]^{3+}$ bond distances support the additivity of bond alternations (Figure 3). The shorter S(1)–S(2) bond in $[(S_7I)_2I]^{3+}$ relative to that in S_7I^+ (2.306 (10) vs. 2.389 (4) Å) is not predicted by this model.

The S(1)–I(1) bond distance in $[(S_7I)_2I]^{3+}$ of 2.335 (7) Å is similar to that in S_7I^+ [2.342 (3),[1] 2.314 (8) Å (in $(S_7I)_4S_4(AsF_6)_6$)] and is slightly shorter than the sum of the covalent radii (2.37 Å).

The linear S(4)–I(2)–S(4) bond has a sulfur–iodine distance of 2.674 (7) Å, similar to that in the $[(H_2N)_2CS]_2I^+$ ion (2.63 Å), *N*-(methylthio)caprolactam-iodine(1/1) (2.688 (2) Å), and other related species[33] and substantially longer than the S(1)–I(1) bond distance (2.335 (7) Å). The structure may be regarded as two S_7I^+ units donating electrons through S(4) to I^+, thereby giving the bridging iodine a linear AX_2E_3[34] type configuration.

The I(1)I(2)I(1)′ unit is linear as in I_3^-; however, the I(1)–I(2) contact is very long (4.247 (3) Å), suggesting negligible interaction. There is a long I(2)–S(6) contact of 3.777 (8) Å, which may be indicative of a weak attractive interaction. I(1)S(1)S(2)S(3) is approximately planar, and the short I-

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(30) Gillespie, R. J. *Chem. Soc. Rev.* **1979**, *8*, 315 and references cited therein.

(31) Steudel, R.; Sandow, T. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 611.

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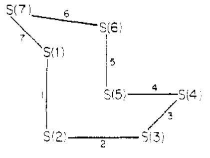
Table VIII. Comparison of the Geometries of the S_7 Rings of Chair Conformation in S_7, S_{19}^{2+}, S_7I^+, and $[(S_7I)_2I]^{3+}$

	1[d]	2	3	4	5	6	7
S_7[a]	2.102 (5)	1.996 (4)	2.181 (3)	1.993 (4)	2.101 (5)	2.054 (3)	2.049 (3)
S_7 (chair) in S_{19}^{2+} [b]	2.09 (2)	1.93 (1)	2.21 (1)	2.10 (1)	2.00 (1)	2.08 (2)	2.03 (2)
S_7I^+ [c]	2.389 (4)	1.906 (5)	2.184 (4)	1.963 (4)	2.114 (4)	2.004 (4)	2.104 (4)
$[(S_7I)_2I]^{3+}$	2.306 (10)	1.897 (10)	2.205 (13)	1.988 (15)	2.081 (14)	2.001 (13)	2.108 (12)

[a] The bond distances given are for δ-S_7 from ref 29. [b] Reference 7. [c] S_7I^+ in S_7ISbF_6 from ref 1. [d] Bonds are defined as per **3**; distances are given in angstroms.



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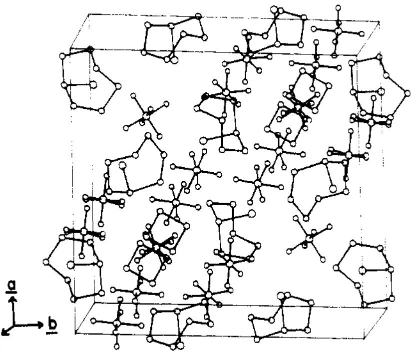

Figure 4. Crystal packing in $(S_7I)_4S_4(AsF_6)_6$.

(1)–S(3) distance (3.381 (9) Å) likely implies an attractive interaction.[1]

The strongest anion–cation contact is between I(1) and F(25) (2.99 (3) Å) and is very approximately linear (S(1)–I(1)–F(25) = 155.3 (6)°) (cf. S_7ISbF_6;[1] I···F = 2.925 (9) Å, corresponding angle = 174.2 (2)°]. The shortest I(2)–F contact is at 3.57 (2) Å, greater than the sum of the van der Waals radii of I and F (3.50 Å).

There are several sulfur–fluorine contacts, the strongest of which is S(2)–F(11) (2.86 (2) Å) (see Table V), in contrast to S_7ISbF_6, which has its strongest S–F contact to S(1), (2.93 (1) Å). However, there are two contacts to S(1) in $[(S_7I)_2I]^{3+}$ at 2.97 (2) and 3.01 (3) Å, which may represent interaction equal to or greater than one contact to S(2) at 2.86 (2) Å. There are also more S–F contacts less than 3.20 Å in $[(S_7I)_2I]^{3+}$ (9) than in S_7I^+ (4), consistent with the greater positive character of the S_7 ring in $[(S_7I)_2I]^{3+}$.

The SbF_6^- anions are essentially octahedral with an average Sb–F length of 1.845 Å and average F–Sb–F angle of 90.0°.

The AsF_3 molecule has a mean As–F bond distance of 1.70 Å and F–As–F angle of 93.1°. These values may be compared with values of 1.706 (2) Å and 96.2 (2)° from a gas-phase electron diffraction study for AsF_3[35] and 1.69 (2) Å and 92 (1)° for AsF_3 in $Te_6(AsF_6)_4{\cdot}2AsF_3$.[36] Thus the bond distances are the same within experimental error while the bond angles of the AsF_3 molecules in the salts are the same but significantly less than the gas-phase value as discussed by Gillespie et al.[36] and Passmore et al.[37] Three long As–F contacts of 2.96 (3), 3.40 (3), and 2.85 (4) Å complete the very approximate octahedron about the arsenic atom (see Table V).

Structure of $(S_7I)_4S_4(AsF_6)_6$. The crystal packing in $(S_7I)_4S_4(AsF_6)_6$ is given in Figure 4, and Tables IX and X list appropriate bond distances and angles in the cations; AsF_6^- bond distances and angles are deposited as supplementary material. The structure may be regarded as consisting of essentially discrete S_7I^+ and S_4^{2+} cations, and AsF_6^- anions, with relatively weak anion–cation contacts. The structure of the one crystallographically unique S_7I^+ unit is essentially identical with that in S_7ISbF_6, when the appropriate standard deviations are taken into consideration, and has been discussed previously.[1,2]

Table IX. Interatomic Distances (Å) in $(S_7I)_4S_4(AsF_6)_6$[a]

	S_7I^+ Distances		
I(1)–S(1)	2.314 (9)	S(4)–S(5)	2.00 (2)
S(1)–S(2)	2.34 (1)	S(5)–S(6)	2.11 (2)
S(2)–S(3)	1.89 (2)	S(6)–S(7)	1.99 (2)
S(3)–S(4)	2.19 (2)	S(7)–S(1)	2.08 (1)
	S_4^{2+} Distance		
S(8)–S(8)′	1.98 (1)		
	Interionic Contacts[b]		
I(1)–F(33)	2.96 (2)	S(8)–F(12)	2.96 (3)
I(1)–F(14)	3.18 (3)	S(8)–F(12)′	2.91 (3)
S(1)–F(21)	3.06 (6)	S(8)–F(16)	2.95 (5)
S(5)–F(11)	3.18 (4)	S(8)–F(16)′	2.68 (4)
S(8)–F(11)	3.10 (5)		

[a] Standard deviations are in parentheses. [b] S···F ⩽ 3.20 Å, I···F ⩽ 3.40 Å.

Table X. Bond Angles (Deg) in $(S_7I)_4S_4(AsF_6)_6$[a]

	S_7I^+		
I(1)–S(1)–S(2)	101.4 (4)	S(5)–S(6)–S(7)	103.0 (7)
S(1)–S(2)–S(3)	105.5 (7)	S(6)–S(7)–S(1)	107.7 (6)
S(2)–S(3)–S(4)	107.7 (8)	S(7)–S(1)–S(2)	99.6 (6)
S(3)–S(4)–S(5)	101.1 (6)	S(7)–S(1)–I(1)	107.4 (5)
S(4)–S(5)–S(6)	103.1 (7)		
	S_4^{2+}		
S(8)′–S(8)–S(8)″	90.0 (5)		

[a] Standard deviations in parentheses.

The S_4^{2+} unit is centered at ($^1/_4$, $^3/_4$, 0), and although it has symmetry $\bar{4}$ it is essentially planar with equal sulfur–sulfur bond distances of 1.985 (13) Å, which are equivalent to those in $S_4(AsF_6)_2{\cdot}0.62SO_2$[6] (2.015 (3), 2.013 (3) Å). The anion–cation contacts to S_4^{2+} in $(S_7I)_4S_4(AsF_6)_6$ are the strongest in the compound (see Table IX), consistent with the greater positive charge per sulfur atom relative to that in S_7I^+. The shortest S–F contacts for S_4^{2+} are not in the plane of the ring in contrast to those in $S_4(AsF_6)_2{\cdot}0.62SO_2$ and most other Se_4^{2+}- and Te_4^{2+}-containing salts.[38,39] A detailed description of anion–cation contacts in $S_4(AsF_6)_2{\cdot}0.62SO_2$ and $(S_7I)_4S_4$-

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$(AsF_6)_6$ and in Se_4^{2+}- and Te_4^{2+}-containing salts has been recently published.[40]

The S_4^{2+} units are arranged in a stack along the fourfold inversion axis separated by AsF_6^- ions, which are disordered. The most satisfactory description of these was with an As at $(^1/_4, ^3/_4, ^1/_2)$ surrounded by eight fluorine positions each with $^3/_4$ occupancy.

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Registry No. $(S_7I)_4S_4(AsF_6)_6$, 74823-90-8; $[(S_7I)_2I](SbF_6)_3{\cdot}2AsF_3$, 73381-83-6; SbF_5, 7783-70-2; AsF_5, 7784-36-3; S_8, 10544-50-0; I_2, 7553-56-2.

Supplementary Material Available: Tables of calculated and observed structure factors and isotropic and anisotropic thermal parameters for $[(S_7I)_2I](SbF_6)_3{\cdot}2AsF_3$ and $(S_7I)_4S_4(AsF_6)_2$, bond distances and angles for SbF_6^- in $[(S_7I)_2I](SbF_6)_3{\cdot}2AsF_3$, bond distances and angles for AsF_6^- in $(S_7I)_4S_4(AsF_6)_6$, and torsional angles in S_7I^+, $[(S_7I)_2I]^{3+}$, and the S_7 chair in S_{19}^{2+} (32 pages). Ordering information is given on any current masthead page.

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Contribution from the Chemistry Department,
University College, Belfield, Dublin 4, Ireland

MO Theory of Organometallic Compounds. 16.[1] Perturbation Theory of the Reactivity of Metal Carbonyl Complexes

DAVID A. BROWN,* JOSEPH P. CHESTER, and NOEL J. FITZPATRICK

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The perturbation theory of reactivity has been applied to the nucleophilic substitution and addition reactions of a series of metal carbonyl complexes, $AM(CO)_3$, A = C_6H_6Cr, C_5H_5Mn, C_4H_4Fe, or C_3H_5Co, and $[BFe(CO)_3]^+$, B = C_5H_5, C_6H_7, or C_7H_9, by both hard and soft reagents. For $C_6H_6Cr(CO)_3$ and $C_5H_5Mn(CO)_3$, attack by a hard nucleophile is predicted in the order metal > carbonyl > ring and the reverse for soft nucleophiles in polar solvents. In the cationic series, attack by a hard nucleophile may occur at either metal or carbonyl, while for a soft nucleophile, initial metal attack is predicted with a change to ring attack as solvent polarity increases.

Introduction

One of the most challenging problems facing theoretical inorganic chemistry is the development of structure–reactivity correlations of a degree of sophistication and success comparable to those used so widely in mechanistic organic chemistry.[2] Even in the case of simple substitution reactions of organometallic systems, it is still very difficult to predict a priori whether, for example, carbonyl substitution of a metal carbonyl complex will occur by an S_N1 dissociative or S_N2 associative mechanism.[3] In the former case, it is reasonable to assume that calculations of ground-state properties such as metal–carbon overlap populations using semiempirical MO methods should give a reasonable indication of relative reactivities. Such attempts at structure–reactivity correlations have proved quite successful in series of closely related molecules, for example, the metal carbonyl halides $M(CO)_5X$ (M = Mn, Re; X = Cl, Br, I).[4] In the case of nucleophilic addition to organo–transition-metal complexes, rules based on simple Hückel theory considerations of the HOMO of the polyene fragment have been applied to a wide range of complexes.[5] However, in general for associative S_N2 substitution reactions similar correlations are much less successful since explicit account is now required of the interaction between the nucleophile and substrate and thus of calculations of transition-state energies. Such calculations are still impracticable or prohibitively expensive for the large molecules under discussion, and consequently attempts to rationalize associative mechanisms have concentrated on correlations with various reactivity indices. For example, the site of attack of a nucleophile in an associative substitution reaction of a metal carbonyl complex might be expected to correlate with calculated charge densities. However, INDO calculations[6,7] for $[C_6H_7Fe(CO)_3]^+$ and $[C_7H_6XCr(CO)_3]^+$ showed the best correlation between bond index values and the effect of coordination on reactivity; however, the site of nucleophilic attack did not correlate with any electronic parameter in the latter case. If the interaction between the attacking nucleophile and substrate is frontier controlled, that is, if it is dominated by the interaction of the highest occupied orbital (HOMO) of the nucleophile with the lowest unoccupied orbital (LUMO) of the substrate, then, for a given nucleophile, correlation between reactivity and the frontier electron density (P_A^{LUMO}) at a given atom A, the site of attack of the substrate, should be observed. We have shown previously that such correlation does occur in both (a) the neutral $AM(CO)_3$ series (A = C_6H_6Cr, C_5H_5Mn, C_4H_4Fe, C_3H_5Co or C_2H_4Ni) and (b) the cationic series $[BFe(CO)_3]^+$ (B = C_5H_5, C_6H_7, or C_7H_9).[8] For example, in the $AM(CO)_3$ series, the values of P_M^{LUMO} increase in the series $C_2 \rightarrow C_6$ with the reverse trend in $P_{C(O)}^{LUMO}$ in accord with the facile S_N1 carbonyl substitution of the cobalt complex compared to the relative inertness of the chromium complex. In contrast, the cationic series gives the sequence $P_M^{LUMO} > P_{C(O)}^{LUMO} > P_{C(ring)}^{LUMO}$, indicating metal attack as the most common initial step. This agrees with evidence of metal attack by some nucleophiles but not apparently where ring adducts are obtained as the final products; however, care must be exercized in discussions of reaction mechanisms based simply on the nature of the final products.

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