peak profile analysis, Lorentz and polarization corrections; ORFLS (Busing, Martin, and Levy), structure factor calculations and full-matrix least-squares refinement; ABSCOR, a locally written ψ-scan-based absorption correction calculation; ORTEP (Johnson).

Solution and Refinement of the Structure of $(NEt_4)_2$(5). Atoms were located by use of heavy-atom methods. All calculations were performed on the VAX 3100 computer of the J. D. McCullough X-ray Crystallography Laboratory. All carboranyl hydrogens were included in located positions. All methyl and methylene hydrogens were included in calculated positions in structure factor calculations (C–H = 1.0 Å), with an assigned *u* value of 0.06 (carboranyl), 0.10 (THF), or 0.08, 0.10, or 0.11 (cation) Å². H parameters were not refined. Scattering factors for H were obtained from Stewart and co-workers,[33] and those for other atoms were taken from ref 34. Anomalous dispersion terms were applied to the scattering of Eu. The largest peak on a final difference electron density map was 1.0 e Å^{-3}.

Acknowledgment. We thank the National Science Foundation (Grant CHE-88-06179) for the support of this work.

Supplementary Material Available: Tables of crystallographic data collection, atom coordinates, bond distances and angles, torsion angles, and positional and thermal parameters for **4** and $(NEt_4)_2$(**5**) (14 pages); tables of observed and calculated structure factors for **4** and $(NEt_4)_2$(**5**) (34 pages). Ordering information is given on any current masthead page.

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

Preparation, Characterization, and X-ray Crystal Structures of $S_2I_4(MF_6)_2$ (M = As, Sb) and the Electronic Structure of the Highly π-Bonded Eclipsed Disulfur Tetraiodine(2+) Cation: Thermodynamic Considerations and the Nonexistence of SI_3AsF_6(s)

Michael P. Murchie, James P. Johnson, Jack Passmore,* George W. Sutherland, Mahmoud Tajik, Thomas K. Whidden, Peter S. White,*[,1] and Friedrich Grein

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Crystalline $S_2I_4(AsF_6)_2$ was prepared quantitatively by the reaction of stoichiometric amounts of S_8, I_2, and AsF_5, in liquid SO_2, and in reactions designed to give SI_3AsF_6(s). It was also a product of reactions designed to give various other related sulfur–iodine cations. Crystalline $S_2I_4(SbF_6)_2$ was prepared essentially quantitatively by the reaction of stoichiometric amounts of S_8, I_2, and SbF_5, designed to give $S_2I_4(SbF_6)_2$ and $5SbF_3{\cdot}3SbF_5$. Crystal data for $S_2I_4(AsF_6)_2$: monoclinic, space group $C2/c$ (No. 15), a = 9.650 (2) Å, b = 12.874 (2) Å, c = 13.644 (1) Å, β = 93.79 (2)°, Z = 4, R = 0.049 (R_w = 0.054) for 948 significant reflections. Crystal data for $S_2I_4(SbF_6)_2$: orthorhombic, space group $Cmcm$ (No. 63), a = 9.850 (4) Å, b = 13.067 (9) Å, c = 13.782 (9) Å, Z = 4, R = 0.051 (R_w = 0.058) for 568 significant reflections. The $S_2I_4(MF_6)_2$ salt consist of $S_2I_4^{2+}$ and MF_6^- [M = As, Sb] with weak cation–anion interactions. The $S_2I_4^{2+}$ cations have distorted right-triangular-prismatic structures, with symmetry C_2 (AsF_6^-) and C_{2v} (SbF_6^-). Each cation consists of two quadrilateral S_2I_2 units joined at the common S–S bond, with interplanar angles of 89.8 (1)° (AsF_6^-) and 91.3 (1)° (SbF_6^-). The S–S distances of 1.818 (10) Å (SbF_6^-) and 1.843 (6) Å (AsF_6^-) are the shortest reported for an isolated compound and correspond to bond orders of 2.7 and 2.4, respectively. The I–I bonds are 2.571 (2) Å (SbF_6^-) and 2.5987 (17) Å (AsF_6^-), corresponding to bond orders 1.4 and 1.3. The S–I bond distances are 2.993 (4) Å (SbF_6^-) and 2.860 (4) and 3.178 (4) Å (AsF_6^-). A simple model for the bonding in $S_2I_4^{2+}$ is proposed in which an S_2 unit is bonded to two I_2^+ units by two mutually perpendicular four-center–two-electron π^*–π^* bonds, with some charge redistribution resulting in a +0.33 charge on each of the six atoms. This model is supported by quantum-mechanical STO-3G ab initio calculations on rectangular Cl_4^{2+}, as a two dimensional model of the bonding in $S_2I_4^{2+}$, and calculations on $O_2Cl_4^{2+}$ of suitable geometry. The enthalpy of the formation of $S_2I_4(AsF_6)_2$(s) from corresponding amounts of S_8, I_2, and AsF_5 is estimated by a simple model to be much more favorable than that of $2SI_3AsF_6$(s). In addition, the enthalpy of disproportionation of the hypothetical $2SI_3AsF_6$(s) to $S_2I_4(AsF_6)_2$(s) and I_2(s) is estimated to be substantially exothermic and the enthalpy of isomerization of the observed π-bonded $S_2I_4^{2+}$ to the classical σ-bonded $I_2S^+S^+I_2$ is also estimated to be endothermic.

Introduction

Binary compounds of sulfur and iodine were at one time unknown.[2,3] Since then, the formation of S_2I_2 and SI_2 have been demonstrated[4-6] but not binary selenium iodides.[7] However, SeI_6^{2-} has been known for some time,[8] and more recently we have prepared SeI_3MF_6 (M = As, Sb),[9,10] containing SeI_3^+. In fact salts of all possible chalcogen trihalide cations, $M'X_3^+$ (M' = S, Se, Te; X = I, Br, Cl, F) have all been prepared and characterized,[10] with the exception of SI_3^+. There seemed no obvious reason why SI_3MF_6 should not have been preparable by similar routes. However, all our attempts to prepare SI_3AsF_6(s) by a wide variety of routes, including those using an excess of iodine, led to $S_2I_4(AsF_6)_2$(s) and I_2(s). Reactions in which larger amounts of sulfur were present led to our discovery of S_7IMF_6,[11] $(S_7I)_2I(SbF_6)_3{\cdot}2AsF_3$,[12a,b] and $(S_7I)_4S_4(AsF_6)_6$.[12a,c] In this paper we give a full account of the various reactions that lead to $S_2I_4(MF_6)_2$(s), and account for the greater stability of $S_2I_4(AsF_6)_2$(s) and I_2(s), relative to 2 $SI_3(AsF_6)_2$(s).

$S_2I_4^{2+}$ has a distorted right-triangular-prismatic structure, the only known example of this type, very different from the isoelectronic classically σ-bonded *trans*-P_2I_4(s).[13a] It contains the shortest sulfur–sulfur bond distance [1.843 (6) Å (AsF_6^-), 1.818

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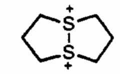
(10) Å (SbF_6^-)], so far observed in an isolated compound, corresponding to bond orders of 2.4 and 2.7, respectively. It is the clearest example of a species containing a S=S bond, the subject of extensive investigations.[13b] In addition, the S–S bond would appear to have the highest bond order of any bond between atoms of heavier ($n \geq 3$) main-group elements in an isolated compound. The overall geometry of $S_2I_4^{2+}$ implies that it consists of a $S_2^{0.66+}$ ion and two $I_2^{0.66+}$ ions weakly bonded via two mutually perpendicular four-center–two-electron $\pi^*-\pi^*$ bonds, and contains 3σ and 2π bonds, maximizing π-bond formation. It is a three-dimensional equivalent of rectangular I_4^{2+} [14] that contains two $I_2^{\bullet+}$ weakly bonded by a four-center–two-electron $\pi^*-\pi^*$ bond. The preference of $S_2I_4^{2+}$ for π-bond formation is reminiscent of compounds containing only second-row elements, e.g. O_2, NO, N_2O, and N_2, and contrasts with $np\pi-np\pi$-bonded ($n \geq 3$) compounds of groups 14 and 15 that are kinetically stabilized by bulky groups.[15] Thermodynamically stable π bonds and clusterlike structures are also found in the homopolyatomic cations of groups 16 and 17,[16] the related $Se_2I_4^{2+}$,[17] and many other sulfur and selenium iodine and bromine cations.[18]

$S_2I_4^{2+}$ is related to a general class[19a] of dication that contains two adjacent positively charged atoms of the same element (e.g. **1**,[19b] $\rangle N^+-N^+\langle$) that is of considerable current interest.[19a] A preliminary account of $S_2I_4(AsF_6)_2$ has been published.[20] A full account of $S_2I_4(MF_6)_2$ is given below.



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Experimental Section

Apparatus and techniques, except those referred to below, have been previously described.[21,22] Precipitated S_8 (Fisher), I_2(BDH), and AsF_5 (Ozark-Mahoning) were used without further purification. Antimony pentafluoride (Ozark-Mahoning) was distilled in vacuo three or four times prior to use. Arsenic trifluoride (Ozark-Mahoning) and SO_2 (Matheson) were distilled onto and stored over NaF and CaH_2, respectively. Chlorine (Matheson) and Br_2 (Fisher) were stored over P_2O_5. The reagents $S_4(AsF_6)_2 0.6SO_2$ and $S_4(Sb_2F_{11})_2$ were prepared as previously described.[12c,23-25]

Air-sensitive nonvolatile solids were manipulated in a Vacuum Atmospheres Corp. Dri-Lab glovebox equipped with a Dri-Train (HE-493).[26] Infrared spectra were obtained on a Perkin-Elmer 683 spectrometer in the range from 4000 to 200 cm^{-1}. Infrared spectra of solids were obtained as fine powders between AgCl plates. Raman spectra were obtained using a Spex Ramalab spectrometer and a Spectra Physics Model 164 2W argon ion laser (5145 Å). X-ray powder diffraction photographs were obtained using a Philips Debye–Scherrer powder camera with Straumanis loading and nickel-filtered Cu Kα radiation. Elemental analyses were carried out by Beller Mikroanalytisches Laboratorium, Göttingen, Germany.

Preparation of $S_2I_4(AsF_6)_2$. In a typical reaction a slight excess of I_2, (relative to the amount required by eq 1 was added to S_8 (0.25 g, 0.98 mmol) in one of the bulbs of a two-bulbed vessel incorporating a coarse-sintered glass frit, and two Teflon-in-glass (J. Young) valves. The vessel was evacuated until the weight of I_2 (2.00 g, 7.88 mmol) was reduced to almost the exact amount (1.98 g) according to eq 1 and the corresponding weight of S_8. SO_2 (6.67 g) and AsF_5 (2.12 g, 12.48 mmol) were condensed onto the mixture, which on warming to room temperature became a dark red-brown solution. A black microcrystalline solid under the red-brown solution formed after 1 day. The solution was filtered once into the second bulb. Crystalline black material was obtained by slowly condensing the solvent (SO_2/AsF_3) back into the first bulb by cooling it with running tap water (ca. 12 °C) overnight. The volatile material was removed under a dynamic vacuum (30–45 min). The total weight of product in both bulbs was 3.74 g (calculated weight for $S_2I_4(AsF_6)_2$ based on S_8 is 3.71 g). The X-ray powder diffraction photographs of the crystalline solids in both bulbs were identical and consistent with the $S_2I_4(AsF_6)_2$ single crystal data. Anal. Calcd (found) for SI_2AsF_6: S, 6.75 (6.61); I, 53.46 (53.55); As, 15.78 (15.59); F, 24.01 (23.97).

IR of the black soluble product: 813 vw, 732 sh, 693 vs, 673 sh, and 395 m cm^{-1}, indicative of a distorted AsF_6^- anion.[27] Attempts to obtain Raman spectra of $S_2I_4(AsF_6)_2$ as a solid and in SO_2 solution at room temperature and −196 °C (with and without spinning) were unsuccessful. The solubility of $S_2I_4(AsF_6)_2$ in SO_2 and AsF_3 is ca. 0.023 and 0.14 g/g of solvent, respectively. Finely ground $S_2I_4(AsF_6)_2$ (0.16 g), subjected to a dynamic vacuum at room temperature, lost 2.36 mg/h over a 70-h period. The remaining solid showed it contained only $S_2I_4(AsF_6)_2$ (X-ray powder photograph). Samples were stored at −20 °C for >1 year without noticeable decomposition. Magnetic susceptibility measurements on solid $S_2I_4(AsF_6)_2$ gave the values (Gouy method) of μ_{eff} (μ_B) at room temperature of 0.51, 0.77, 1.14, and 1.17. A solution in AsF_3 gave a value of 0.88 μ_B based on the assumption that $S_2I_4^{2+}$ retains its identity in solution. Experimental results are included with the supplementary data.

Attempted Preparation of SI_3AsF_6 in the Solid State and in Solution and Various Other Sulfur–Iodine-Containing Cations That Led to $S_2I_4(AsF_6)_2(s)$. (a) $SI_3AsF_6(s)$. Arsenic pentafluoride (2.38 g) was condensed onto a mixture of S_8 (0.29 g) and an excess of I_2 (4.49 g) in SO_2 (10.32 g). After 1 day an intense red brown solution over a black solid was obtained. The volatiles were quickly removed giving 0.91 g of precipitate and 5.47 g of filtrate. $S_2I_4(AsF_6)_2$ (X-ray powder diffraction) and iodine (white color in Tesla discharge, characteristic volatility) were detected in both products. Removal of I_2 on prolonged evacuation led to a total product weight corresponding to $S_2I_4(AsF_6)_2$. $S_2I_4(AsF_6)_2(s)$ was also produced quantitatively and found in both precipitates and filtrates (X-ray powder diffraction) from stoichiometric amounts of S_8, I_2, and AsF_5 and from reactions of $S_2I_4(AsF_6)_2$ with a stoichiometric amount of I_2 and an excess of I_2. Detailed information is included with the supplementary data.

(b) SI_3AsF_6 in Solution. It was noticed that the apparent solubility of $S_2I_4(AsF_6)_2$ in sulfur dioxide increased dramatically as iodine was added. Therefore a series of experiments were conducted in which solutions of $S_2I_4(AsF_6)_2$ and I_2 were prepared in various ratios. $S_2I_4(AsF_6)_2$ and I_2 in the molar ratios 1:0.5, 1:0.75, 1:1.0, and 1:2.08 gave solubilities (g/g of SO_2) of 0.14, 0.22, 0.25, and 0.36 and S:I ratios in the filtrate of 1:4.05, 1:4.05, 1:4.1, and 1:4.5. The solubilities are significantly higher than that of solid I_2 in SO_2 (0.0050), or $S_2I_4(AsF_6)_2$ in SO_2 (0.023) or AsF_3 (0.14). $S_2I_4(AsF_6)_2(s)$ was detected (X-ray powder photographs) in both the precipitates and filtrates. The S:I ratios were established by removal of I_2 under a dynamic vacuum of a portion of each filtrate. $S_2I_4(AsF_6)_2(s)$ slowly loses I_2 (2.4 mg/h) under these conditions. A chemical analysis of the filtrate of the 1:2.08 sample gave the following analysis: S, 1.0; I, 4.7; As, 2.0; F, 6.0. Data for these reactions and parallel reactions starting from S_8, I_2, and AsF_5 are included with the supplementary data.

(c) Other Sulfur–Iodine-Containing Cations. Reactions of S_8, I_2, and AsF_5 designed to give the AsF_6^- salts of $S_4I_4^{2+}$, $S_4I_4^{4+}$, S_2I^+, and a mixture of S_4^{2+} and $4I_2^+$, all gave products that included $S_2I_4(AsF_6)_2$ (X-ray powder and/or X-ray precession photographs of single crystals). Crystals of $S_2I_4(AsF_6)_2$, from which X-ray data were measured, were obtained

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from the attempted preparation of S_2IAsF_6 from $S_4(AsF_6)_2$ and I_2. $S_2I_4(AsF_6)_2$(s) was also obtained from a reaction of $S_4(AsF_6)_2$ and excess I_2 designed to give $S_4I_4(AsF_6)_2$, from reactions of $S_2I_4(AsF_6)_2$ with X_2 (X = Cl, Br) designed to give SI_2XAsF_6, and in reactions designed to give SI_2BrAsF_6, $SIBr_2AsF_6$, and $S_2I_2Br_2(AsF_6)_2$ from appropriate amounts of S_8, X_2, and AsF_5. SX_3AsF_6 were also identified in the chlorine and bromine reactions. Full descriptions of these reactions with corresponding data are included with the supplementary material.

Preparation of $S_2I_4(SbF_6)_2$. In a typical reaction S_8 (0.169 g, 0.63 mmol) and I_2 (1.29 g, 5.06 mmol) were placed into one bulb of a two-bulb vessel, fitted with two valves, and were isolated by closing one of the valves. Antimony pentafluoride was condensed into the second bulb, until the correct amount indicated by eq 2 (1.85 g, 8.52 mmol) had been transferred. Sulfur dioxide (13.63 g) was condensed onto the SbF_5, and the resulting solution was poured onto the S_8–I_2 mixture. An intense red-brown solution over a pale white precipitate was formed after 5 min. The solution was filtered, and the soluble product was completely extracted from the insoluble white precipitate by condensing ca. 2 mL of SO_2 back onto the precipitate and refiltering (six times). The volatile materials were removed by evacuation under dynamic vacuum, leaving a beige-white powder, $(SbF_3)_5(SbF_5)_3$ (X-ray powder diffraction[28]) (0.61 g; calculated for $(SbF_3)_5(SbF_5)_3$, 0.73 g) and a black microcrystalline solid (2.66 g; calculated for $S_2I_4(SbF_6)_2$, 2.47 g). Attempts to obtain Raman spectra of the insoluble white solid and black soluble solid were unsuccessful. Anal. Calcd (found) for the black soluble solid (SI_2SbF_6): S, 6.13 (5.72); I, 48.66 (47.18); Sb, 23.37 (25.93); F, 21.84 (21.3). Anal. Found for a soluble solid from a similar reaction: S, 6.02; I, 46.70; Sb, 26.87; F, 19.7. IR (737 w, 710 w, 657 vs and 580 w cm^{-1}) spectroscopy indicated distorted SbF_6^-.[27,29] Magnetic susceptibility measurements for solid $S_2I_4(SbF_6)_2$ gave μ_{eff} (μ_B) at room temperature of 0.80 (Gouy method), 0.85, and 1.02 (Faraday method). Experimental data are included with the supplementary data. The $S_2I_4(SbF_6)_2$ was sealed in glass sample tubes and stored at −20 °C with no visible signs of decomposition after 1 year.

Single crystals of $S_2I_4(SbF_6)_2$, from which X-ray diffraction data were obtained, were produced from the attempted preparation of $S_2ISb_2F_{11}$. $S_4(Sb_2F_{11})_2$ (1.36 g, 1.32 mmol) and I_2 (0.33 g, 1.31 mmol) were reacted in SO_2 (3.05 g), yielding an intense red-brown solution. After 1 day the solution was filtered into the second bulb, leaving a very small amount of a white insoluble solid, which was washed 2–3 times with ca. 1 mL of SO_2. The second bulb was cooled and SO_2 slowly (15–20 h) condensed into the first, yielding a highly crystalline black solid. The volatile materials were removed, leaving a white insoluble solid containing the S_4^{2+} cation[12,30] and an unidentified complex Sb(V), Sb(III) fluorine-containing species (Raman), and a soluble black solid (total product weight 1.66 g). Several single crystals of the black solid were shown to be $S_2I_4(SbF_6)_2$ by X-ray diffraction.

Table I. Crystallographic Data for $S_2I_4(MF_6)_2$ (M = As, Sb)

chem formula	$[S_2I_4][AsF_6]_2$	$[S_2I_4][SbF_6]_2$
fw	949.76	1043.42
space group	*C*2/*c* (No. 15)	*Cmcm* (No. 63)
a, Å	9.650 (2)	9.850 (4)
b, Å	12.874 (2)	13.067 (9)
c, Å	13.644 (2)	13.782 (9)
β, deg	93.79 (2)	
V, Å^3	1694 (1)	1774 (1)
Z	4	4
ρ_{calc}, g cm^{-3}	3.721	3.904
λ(Mo Kα), Å	0.710 69	0.710 69
μ, cm^{-1}	118.8	102.25
temp, K	298	298
R^a (incl unobsd reflcns)	0.049 (0.093)	0.051 (0.102)
R_w^b (incl unobsd reflcns)	0.054 (0.072)	0.058 (0.082)

[a] $R = [\sum|\Delta F|/\sum|F|]$. [b] $R_w = [(\sum w|\Delta F|^2/\sum w|F|^2)^{1/2}]$.

Attempted Preparations of $S_2I_4(Sb_2F_{11})_2$. Various attempts to prepare $S_2I_4(Sb_2F_{11})_2$ by the reaction of S_8, I_2, and SbF_5[31a] and $S_2I_4(AsF_6)_2$ with an excess of SbF_5[31b] led to mixtures containing S_4^{2+} and I_2^+ (or I_4^{2+} depending on the anion).

X-ray Crystallographic Analysis. Suitable crystals were mounted in capillary tubes and sealed under an atmosphere of dry nitrogen as previously described.[22] A preliminary X-ray photographic survey was made to determine diffraction symmetry and approximate cell dimensions. The crystals were then mounted on a Picker FACS-I diffractometer equipped with Mo Kα radiation and controlled by the NRC DIFRAC control program.[36] Intensity data were collected using an ω–2θ scan. Background intensity was measured by a standing count at either end of the scan, and if the peak was significant, profile analysis was used to improve the estimate. Final cell parameters were obtained by a least-squares fit to the accurately centered coordinates of 12 reflections and their Friedel opposites. Three standard reflections were measured every 200 reflections throughout the intensity data collection; in both structures, only minor long term deviations in intensities were observed, and corrections were applied to the data.

The structures were solved using the MULTAN[37] direct methods routine. Subsequent calculations were performed using the NRCVAX[38] and SHELX-76[39] program packages. It was not possible to obtain an analytical absorption correction because of the irregular shapes of the crystals. Instead a spherical absorption correction was applied, and subsequently the empirical DIFABS routine of Walker and Stuart[40a] was used. Scattering factors were taken from ref 40b and corrected for anomalous dispersion. The pertinent crystallographic data are given in Table I, and a more complete listing is included with the supplementary data.

$S_2I_4(AsF_6)_2$. This structure was originally reported in ref 20 with a less accurate absorption correction based on an approximate crystal shape. After the application of a DIFABS[40a] absorption correction, it became apparent that there was disorder at both anion positions. This was modeled by assuming an ideal octahedral geometry for the anions with As–F bond distances of 1.68 Å. Two such groups were placed at each anion position and refined as rigid groups using SHELX-76[39] with their total occupancies constrained to be unity. After the relative occupancies were determined, the fluorine atoms were assigned isotropic thermal parameters. Final atomic parameters are given in Table II, and thermal parameters and structure factor tables have been deposited as supplementary material.

$S_2I_4(SbF_6)_2$. The structure was initially solved in space group *Cmcm* with the *E* map giving the sulfur, iodine, and antimony positions. The

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(31) (a) Antimony pentafluoride (1.90 g, 8.77 mmol) was condensed onto a mixture of S_8 (0.11 g, 0.41 mmol) and I_2 (0.80 g, 3.15 mmol) in SO_2 (6.21 g). A dark red-brown solution over a dark solid was formed on warming to room temperature. After 2 days the solution was filtered into the second bulb, and the remaining soluble product in the first bulb was extracted with SO_2 (>10 times with ca. 2 mL of SO_2) until the insoluble solid appeared white. The volatile materials were removed, leaving a white insoluble solid containing S_4^{2+}[23,24,30] and an unidentified complex antimony(V) fluoride counteranion conceivably similar to that in $(Se_1S_3)_2(Sb_4F_{17})(SbF_6)_3$ and other complex Sb(III)-containing salts,[32] and a black soluble solid (total weight 2.81 g). A sample of the black soluble solid (1.80 g) was redissolved in AsF_3 (12.11 g), forming an intense red-brown solution over a small quantity of white precipitate. Crystals were obtained from the soluble solution, one of which was identified as $I_4(Sb_3F_{14})(SbF_6)$[14] (X-ray precession photography). (b) In one reaction SbF_5 (2.89 g, 13.31 mmol) was condensed onto a mixture of $S_2I_4(AsF_6)_2$ (1.47 g, 1.57 mmol) in SO_2 (7.86 g) giving an intense red-brown solution over a dark solid on warming to room temperature. After 6 days, the solution was filtered into the second bulb, and the remaining soluble product was extracted from the insoluble white precipitate as described above. The solvent was slowly condensed (ca. 5 days) from the second bulb onto the insoluble white solid, leaving a black crystalline solid. The volatile materials were removed. The insoluble white solid was identified as β-$(SbF_3)_6(SbF_5)_5$ (Raman)[33] and the soluble black solid was identified as containing $Sb_2F_{11}^-$[28,34] (IR) and $I_2Sb_2F_{11}$[35] (X-ray precision photography). Anal. For soluble black solid found: S, 3.38; I, 24.88; Sb, 38.57; F, 32.8. Calcd for a 1:4 mixture of $S_4(Sb_2F_{11})_2$ and $I_2Sb_2F_{11}$: S, 3.32; I, 26.31; Sb, 37.87; F, 32.50.

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Table II. Fractional Atomic Coordinates with Standard Deviations in Parentheses for $S_2I_4(AsF_6)_2$

atom	*x*/*a*	*y*/*b*	*z*/*c*	B_{iso},[b] Å^2	occupancy[a]
S(1)	0.4043 (3)	0.1888 (3)	0.2465 (3)	3.24 (14)	1.00
I(1)	0.35087 (9)	0.34129 (9)	0.39165 (8)	4.2 (5)	1.00
I(2)	0.38171 (11)	0.36477 (9)	0.08288 (8)	4.7 (5)	1.00
As(1)	0.00000	0.1797 (2)	0.25000	3.2 (4)	1.00
F(1)	0.10546 (1)	0.10220 (2)	0.18960 (1)	5.9 (5)	0.49
F(2)	0.10838 (1)	0.27994 (2)	0.23640 (1)	6.2 (5)	0.49
F(3)	0.08700 (1)	0.14856 (2)	0.35653 (1)	9.32 (8)	0.49
F(1A)	0.09512 (1)	0.20664 (2)	0.35434 (1)	6.2 (5)	0.51
F(2A)	0.09967 (1)	0.07514 (2)	0.23258 (1)	7.3 (6)	0.51
F(3A)	0.10704 (1)	0.25297 (2)	0.18680 (1)	6.2 (5)	0.51
As(2)	0.00000	0.50000	0.00000	3.1 (3)	1.00
F(4)	0.14045 (1)	0.55784 (1)	0.05504 (1)	6.5 (4)	0.62
F(5)	0.08376 (1)	0.38552 (1)	0.00464 (1)	7.0 (4)	0.62
F(6)	0.06079 (1)	0.52409 (1)	−0.11015 (1)	7.3 (5)	0.62
F(4A)	0.08806 (1)	0.48149 (1)	0.10881 (1)	7.97 (8)	0.38
F(5A)	0.07762 (1)	0.61589 (1)	−0.01059 (1)	8.13 (8)	0.38
F(6A)	0.12905 (1)	0.44294 (1)	−0.05685 (1)	6.4 (6)	0.38

[a] Both anions are disordered and were modeled by superimposed rigid bodies, hence the abnormally low esd's for the fluorines. [b] B_{iso} is the mean of the principal axes of the thermal ellipsoid.

Table III. Fractional Atomic Coordinates with Standard Deviations in Parentheses for $S_2I_4(SbF_6)_2$

atom	*x*/*a*	*y*/*b*	*z*/*c*	B_{iso},[b] Å^2	occupancy[a]
S(1)	0.0923 (5)	0.1942 (4)	0.5000	4.63 (22)	1.00
I(1)	0.13048 (11)	0.35303 (11)	0.40408 (9)	6.7 (5)	1.00
Sb(1)	0.50000	0.18408 (17)	0.25000	4.41 (22)	1.00
F(1)	0.38960 (1)	0.15109 (17)	0.35678 (1)	7.90 (11)	0.25
F(2)	0.38909 (1)	0.10389 (17)	0.16914 (1)	9.55 (14)	0.25
F(3)	0.39074 (1)	0.29889 (17)	0.22416 (1)	6.47 (9)	0.25
F(1A)	0.61040 (1)	0.21710 (17)	0.14322 (1)	6.40 (8)	0.25
F(2A)	0.60925 (1)	0.06932 (17)	0.27583 (1)	9.40 (12)	0.25
F(3A)	0.61089 (1)	0.26431 (17)	0.33086 (1)	4.6 (6)	0.25
Sb(2)	0.00000	0.00000	0.50000	4.4 (4)	1.00
F(4)	−0.08940 (1)	0.12712 (1)	0.49935 (1)	5.4 (6)	0.25
F(5)	0.14445 (1)	0.05733 (1)	0.42930 (1)	5.0 (7)	0.25
F(6)	0.08703 (1)	0.03544 (1)	0.61667 (1)	8.21 (13)	0.25
F(4A)	−0.11864 (1)	0.10110 (1)	0.45281 (1)	6.79 (10)	0.25
F(5A)	0.10117 (1)	0.00754 (1)	0.38454 (1)	6.24 (9)	0.25
F(6A)	0.11006 (1)	0.10209 (1)	0.55526 (1)	9.55 (13)	0.25

[a] Both anions are disordered and were modeled by superimposed rigid bodies, hence the abnormally low esd's for the fluorines. [b] B_{iso} in the mean of the principal axes of the thermal ellipsoid.

two antimony atoms were found to be at sites with symmetries 2/*m* and *mm*; however, peaks in the difference synthesis did not correspond to the expected fluorine positions. Refinement of the structure was therefore undertaken in the three possible space groups, *Cmcm*, *Cmc*2$_1$ and *C*2*cm*. In the space group *Cmcm* the two SbF_6^- anions were each modeled by two idealized octahedral groups with the Sb–F distance of 1.88 Å. The final *R* indices for *Cmcm*, *Cmc*2$_1$, and *C*2*cm* were 0.051, 0.055, and 0.057 for 49, 57, and 59 parameters respectively, indicating that the *Cmcm* disorder model was the best fit to the data. In addition, the cation bond distances in the lower symmetry space groups were all within 3σ of those for *Cmcm*. Final atomic coordinates are given in Table III, and thermal parameters and structure factor tables have been deposited as supplementary material.

Results and Discussion

Preparation of Crystalline $S_2I_4(AsF_6)_2$. Crystalline $S_2I_4(AsF_6)_2$ was prepared quantitatively by the reaction of elemental sulfur, iodine and arsenic pentafluoride according to eq 1.

$$\tfrac{1}{4}S_8 + 2I_2 + 3AsF_5 \xrightarrow{\text{liquid } SO_2} S_2I_4(AsF_6)_2 + AsF_3 \quad (1)$$

The weight of the solid product $S_2I_4(AsF_6)_2$ was in good agreement with that calculated according to eq 1, and the elemental analyses are in excellent agreement with the given formation. The product appeared crystalline and homogeneous when viewed under a microscope, and the X-ray powder diffraction photograph of the bulk material was consistent with the single-crystal data. Rather surprisingly, a number of reactions all designed to give SI_3AsF_6(s) gave instead $S_2I_4(AsF_6)_2$(s) and I_2(s). In addition, reactions designed to give the more highly oxidized $S_4I_4(AsF_6)_4$ and $S_4I_8(AsF_6)_6$ [or $S_4(AsF_6)_2$ and $4I_2AsF_6$] gave instead $S_2I_4(AsF_6)_2$(s) as a product. Thus reaction 1 also proceeded quantitatively either with an excess of iodine or with an excess of AsF_5. However, we recommend the use of a slight excess of iodine and AsF_5. Solid $S_2I_4(AsF_6)_2$ was also identified as a product of reactions designed to give $S_4I_4(AsF_6)_2$, and $S_2I(AsF_6)_2$. Attempts to prepare chlorine and bromine derivatives of SI_3AsF_6 gave instead $S_2I_4(AsF_6)_2$ (all cases) and SX_3AsF_6 [X = Cl, Br]. This implies not only that SI_3AsF_6(s) is thermodynamically unstable with respect to $S_2I_4(AsF_6)_2$(s) and I_2(s) (see below) but that $SI_xX_{3-x}AsF_6$(s) (x = 1, 2) are also unstable with respect to products that include $S_2I_4(AsF_6)_2$(s) and I_2(s). They may disproportionate as shown in eqs 2 and 3. In addition attempts to

$$6SIX_2AsF_6(s) \rightarrow S_2I_4(AsF_6)_2(s) + I_2(s) + 4SX_3AsF_6(s) \quad (2)$$

$$6SI_2XAsF_6(s) \rightarrow 2S_2I_4(AsF_6)_2(s) + 2I_2(s) + 2SX_3AsF_6(s) \quad (3)$$

prepare $S_2I_2Br_2(AsF_6)_2$(s) led instead to $S_2I_4(AsF_6)_2$(s) and SBr_3AsF_6(s). All these observations imply a surprisingly high thermodynamic stability for $S_2I_4(AsF_6)_2$(s).

Preparation of Crystalline $S_2I_4(SbF_6)_2$. Highly crystalline $S_2I_4(SbF_6)_2$ was prepared by the reaction of sulfur and iodine with SbF_5 in liquid sulfur dioxide, possibly according to eq 4.

$$\tfrac{5}{4}S_8 + 10I_2 + 18SbF_5 \xrightarrow{\text{liquid } SO_2} 5S_2I_4(AsF_6)_2 + 5SbF_3\cdot 3SbF_5 \quad (4)$$

The reduced antimony fluoride was insoluble and therefore separated from the slightly soluble $S_2I_4(SbF_6)_2$. The X-ray powder photograph of the insoluble product was very similar to that of $5SbF_3\cdot 3SbF_5$,[28] and it was therefore assigned as such, although we could not rule out the possibility of the presence of other related but noncrystalline reduced products, e.g. $3SbF_3{\cdot}SbF_5$.[41] The elemental analyses were high for antimony and low for sulfur, fluorine, and iodine relative to the calculated values, and the experimental weights of soluble (2.66 g) and insoluble (0.61 g) products were higher (2.47 g) and lower (0.73 g), respectively, than those expected from eq 2. This suggested that some $5SbF_3{\cdot}3SbF_5$ passed through the glass frit and was present as an impurity in the $S_2I_4(SbF_6)_2$, although the $S_2I_4(SbF_6)_2$ appeared to be crystalline and homogeneous when viewed under the microscope.

Crystals of $S_2I_4(SbF_6)_2$ were also obtained from the reaction of $S_4(Sb_2F_{11})_2$,[23,24] and elemental iodine design to give $S_2ISb_2F_{11}$. Reactions designed to give $S_2I_4(Sb_2F_{11})_2$ gave products that included S_4^{2+}, I_2^+, or I_4^{2+} depending on the anion. This implies that $S_2I_4(Sb_2F_{11})_2$ does not exist, and that the SbF_5 of the $Sb_2F_{11}^-$ anion oxidizes the cation to S_4^{2+} and I_2^+. Thus, in this system SbF_5 is a significantly stronger oxidizer than AsF_5.

Magnetic Susceptibility of $S_2I_4(MF_6)_2$ (M = As, Sb). Both solid $S_2I_4(MF_6)_2$ salts might be expected to be completely diamagnetic. However, both salts are slightly paramagnetic with average effective magnetic moments (μ_B) of ca. 0.9 for $S_2I_4(AsF_6)_2$ and $S_2I_4(SbF_6)_2$. Similar room-temperature values have been found for the related salts $I_4(AsF_6)_2$[14,23] (0.98), $(S_3N_2)_2(AsF_6)_2$ (0.69),[42,43] and $(Se_2N_2S)_2(AsF_6)_2$ (0.88).[43,44] All three salts contain related cations that consist of monomers containing one unpaired electron in π^* orbitals that are weakly linked forming π^*–π^*-bonded dimers. The paramagnetism may be intrinsic and can be attributed to temperature-independent paramagnetism,[45,46] some surface decomposition (giving paramagnetic species on the surface), small quantities of paramagnetic species (e.g. I_2^+) distributed throughout the bulk material, or combinations of all the above.[47a] The value of 0.9 μ_B for $S_2I_4(AsF_6)_2$ in AsF_3 solution suggests that, if dissociation of $S_2I_4(AsF_6)_2$ to paramagnetic species occurs at all in solution, it is not extensive.[47b]

X-ray Crystal Structures of $S_2I_4(MF_6)_2$. The structure of $S_2I_4(AsF_6)_2$ reported previously[20] has been subject to further refinement using[40a] an improved absorption correction. The use of DIFABS permitted correction for an irregularly shaped crystal with ill-defined faces. As a result of this correction, it became apparent that a disorder model for the anion was necessary. Abnormal thermal parameters had indicated disorder, but the form was not readily apparent. This refinement confirmed the distortion of the cation reported previously.

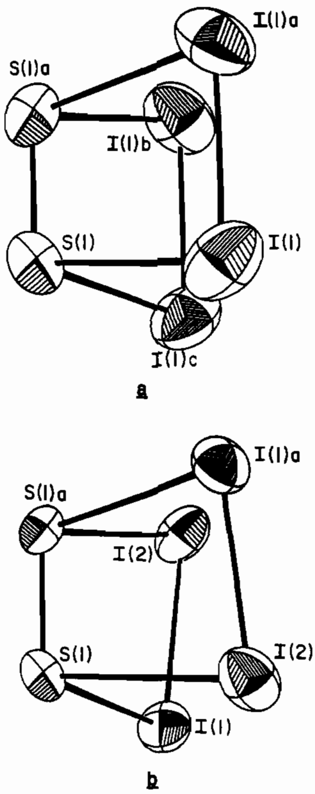

Figure 1. ORTEP plot of the $S_2I_4^{2+}$ cation in (a, top) $S_2I_4(SbF_6)_2$ and (b, bottom) $S_2I_4(AsF_6)_2$.

Table IV. Bond Distances (Å) and Angles (deg) for $S_2I_4(MF_6)_2$ (M = As, Sb), with Estimated Standard Deviations in Parentheses

	$S_2I_4(AsF_6)_2$[a]		
S(1)–S(1)a	1.843 (6)	I(1)–I(2)	2.5987 (15)
S(1)–I(1)	2.860 (4)	I(1)–I(2)a	4.2537 (17)
S(1)–I(2)a	3.178 (4)		
I(1)–S(1)–I(2)a	89.43 (11)	I(2)–I(1)–I(2)a	89.44 (4)
I(1)–S(1)–S(1)a	100.96 (19)	I(2)–I(1)–S(1)	87.11 (7)
I(2a)–S(1)–S(1)a	93.35 (19)	I(2)a–I(1)–S(1)	48.34 (8)
		I(1)–I(2)–I(1)a	89.61 (4)
		I(1)–I(2)–S(1)a	78.56 (7)
		I(1)a–I(2)–S(1)a	42.24 (7)
	$S_2I_4(SbF_6)_2$[b]		
S(1)–S(1)a	1.818 (10)	I(1)–I(1)a	2.571 (2)
S(1)–I(1)	2.993 (4)	I(1)–I(1)c	4.247 (4)
I(1)–S(1)–I(1)c	90.38 (16)	S(1)–I(1)–I(1)a	82.77 (10)
I(1)–S(1)–S(1)a	97.23 (19)	S(1)–I(1)–I(1)c	44.81 (8)
		I(1)a–I(1)–I(1)c	90.00

[a] All As–F bonds were fixed at 1.68 Å. Symmetry operation a = $1 - x, y, {}^1/_2 - z$. [b] All Sb–F bonds were fixed at 1.88 Å. Symmetry Operations: (a) $-x, y, z$; (b) $-x, y, {}^1/_2 - z$ (c) $x, y, {}^1/_2 - z$.

The X-ray structure determination of $S_2I_4(SbF_6)_2$ was undertaken to provide further insight into the distortion of the $S_2I_4^{2+}$ cation observed in $S_2I_4(AsF_6)_2$. This investigation was hindered by the salt crystallizing in a form that could be described by space groups *Cmcm*, *Cmc*2$_1$ or *C*2*cm*. In *Cmcm* the cation would have symmetry *m*2*m* and would be undistorted. However, in order to describe the structure adequately, the SbF_6^- anions would have to be disordered. Such disorder could well be the result of the correct space group being of lower symmetry, *Cmc*2$_1$ or *C*2*cm*, in which case the cation would have lower symmetry and would exhibit some distortion from *m*2*m*. If the true space group were *Cmcm* this distortion would be an artifact introduced by including highly correlated parameters in the least-squares refinements. Several steps were taken to determine the correct space group. A full sphere of data was collected to ensure that the absorption correction did not produce any spurious results. The structure was solved and refined completely in each possible space group with full account being taken of any apparent disorder. The result was that even though the *Cmcm* structure was described by fewer

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(47) (a) It is also possible that more suitable values of the diamagnetic correction terms would reduce the value of the observed effective magnetic moment. The paramagnetism of $S_2I_4(MF_6)_2$ varied considerably from sample to sample (0.5–1.17 μ_B for M = As) suggesting that the extent of grinding, and thus surface area, also could be a factor in determining the overall paramagnetism. (b) Similar magnetic results are also found for $Se_2I_4(AsF_6)_2$, i.e. very weakly paramagnetic in the solid state, and in solution.[17]

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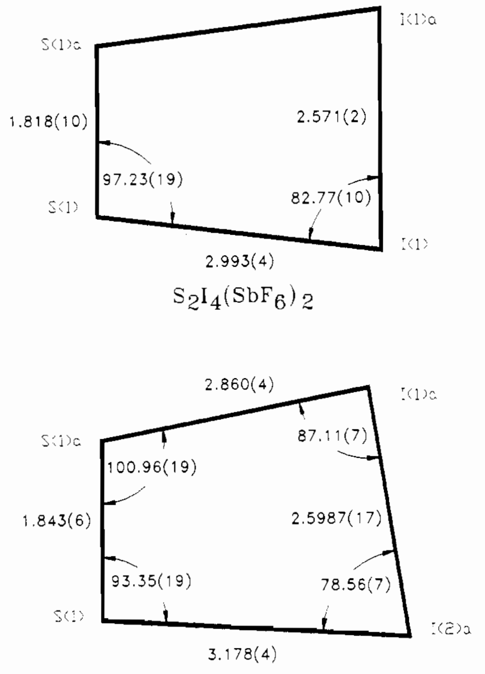

Figure 2. S_2I_2 Planar S_2I_2 Units in $S_2I_4(MF_6)_2$.

parameters it gave significantly lower agreement factors. In addition, the lower symmetry models, although showing the expected distortion of the cation, had bond lengths and angles that were within 3σ of the undistorted *Cmcm* model.

Both $S_2I_4^{2+}$ cations are shown in Figure 1, and corresponding bond distances and angles given in Table IV. Stereoviews of the packing in the unit cells of $S_2I_4(MF_6)_2$ (M = As, Sb) are included with the supplementary material.

Structures of the Distorted Right-Triangular-Prismatic $S_2I_4^{2+}$ Cations in $S_2I_4(MF_6)_2$. The $S_2I_4^{2+}$ cation has C_2 and C_{2v} symmetry in the AsF_6^- and SbF_6^- salts, respectively. Each cation consists of two planar quadrilateral S_2I_2 units (see Figures 1 and 2) joined at the common S–S bond with interplanar angles of 89.8 (1)° [S(1)a–S(1)–I(2)a–I(1)a and S(1)a–S(1)–I(1)–I(2), AsF_6^-] and 91.3 (1)° [S(1)a–I(1)a–S(1)–I(1) and S(1)a–S(1)–I(1)b–I(1)c, SbF_6^-]. The S_2I_2 units in $S_2I_4(SbF_6)_2$ are crystallographically planar, with the S–S bond parallel to the I–I bonds (Figures 1 and 2). The corresponding S_2I_2 units in $S_2I_4(AsF_6)_2$ are essentially planar with an I(2)a–S(1)–S(1)a–I(1)a torsional angle of –1.2 (1)° and with the S–S bond not parallel to the I–I bonds. Thus the overall geometry of both the $S_2I_4^{2+}$ cations is that of a distorted right triangular prism and is, as far as we are aware, the only example of this chemical entity. The major distortions from ideal right-triangular-prismatic geometry arise, in both salts, from the different lengths of S_2 and I_2 and, in addition in the AsF_6^- salt, from the different lengths of S(1)a–I(1)a (2.860 (4) Å) and S(1)–I(2)a (3.178 (4) Å). Although the $S_2I_4^{2+}$ cation is more distorted in the AsF_6^- salt, the dihedral angles between the two planes containing the triangular SI_2 faces are very similar, 20.0 (4)° [AsF_6^-, S(1)a–I(1)a–I(2) and S(1)–I(1)–I(2)a] and 21.0 (2)° [SbF_6^-, S(1)a–I(1)a–I(1)b and S(1)–I(1)–I(1)c], and the I(1)a–I(2)a–I(2)–I(1) face is almost rectangular (angle I(2)–I(1)–I(2)a, 89.44 (4)°; angle I(1)a–I(2)–I(1), 89.61 (4)°; $\sum$ angles = 358.1°). In the SbF_6^- salt, the I(1)–I(1)a–I(1)b–I(1)c face is crystallographically rectangular. In addition, equivalent or average bond distances and angles are almost identical (see Table V). However, all the bonding distances are slightly shorter in the SbF_6^- salt. This is consistent with the weaker basicity of SbF_6^- and less donation of charge into empty antibonding orbitals in $S_2I_4^{2+}$, which weakens the effective net bonding within the cation. It is reasonable to presume that the energy difference between the two geometries is very small and that the more ideal symmetric C_{2v} geometry of $S_2I_4^{2+}$ in $S_2I_4(SbF_6)_2$ more nearly represents the dication present in an ideal totally ionic environment.

Table V. Comparison of Equivalent $S_2I_4^{2+}$ Bond Distances (Å) and Angles (deg) in $S_2I_4(SbF_6)_2$ and $S_2I_4(AsF_6)_2$

	SbF_6^-	AsF_6^-
S–S distance	1.818 (10)	1.843 (6)
I–I	2.571 (2)	2.5987 (17)
S–I	2.993 (4)	3.019 (4)[a]
I–I[d]	4.247 (4)	4.2537 (15)
S–S–I angle	97.23 (19)	97.16 (19)[b]
S–I–I	82.77 (10)	82.84 (7)[c]
I–S–I	90.38 (16)	89.43 (11)

[a] Average S(1)a–I(1)a and S(1)–I(2)a. [b] Average of I(1)a–S(1)a–S(1) and S(1)a–S(1)–I(2)a angles. [c] Average of S(1)–I(2)a–I(1)a and I(2)a–I(1)a–S(1)a angles. [d] Nonbonded distance across the face containing all four iodine atoms.

Table VI. Comparison of Bond Distances in $S_2I_4(MF_6)_2$ (M = As, Sb) with Those in Related Compounds

	bond dist, Å (bond order)			
compd	S–S[a]	I–I[c]	S–I[d]	refs
$S_2I_4(AsF_6)_2$	1.843 (2.4)	2.599 (1.3)	2.862 (0.1)	this work
			3.180 (0.0)	
$S_2I_4(SbF_6)_2$	1.818 (2.7)	2.571 (1.4)	2.993 (0.1)	this work
S_8	2.048 (1.0)			49
$S_2(X^3\Sigma g^-)$	1.8894 (2.0)			50
$S_2^+(X^2\pi g)$	1.824 (2.6)			51
S_2F_2	1.888 (2.0)			52
SSF_2	1.86 (2.3)			52
S_2O	1.892 (2.0)			52
$I_2(g)$		2.666 (1.0)		53
I_5AsF_6		2.645 (1.1)		54
		2.895 (0.4)		
$I_4(AsF_6)_2$		2.587 (1.3)		14a
		3.256 (0.1)		
$I_2Sb_2F_{11}$		2.557 (1.5)		35
$[(S_7I)_2I][SbF_6]_3$[b]	1.897 (1.9)		2.335 (1.1)	12
	2.306 (0.3)		2.674 (0.3)	
S_7ISbF_6[b]	1.906 (1.9)		2.342 (1.1)	11
	2.389 (0.2)			
$(C_6H_5)_3CSI$			2.406 (0.8)	55
$(C_4H_{12}S)_2(CF_3SO_3)_2$	2.124 (0.7)			19b

[a] Bond orders were estimated using a variation of Pauling's[48] bond distance–bond order relationship, $D(n') = D_1 - 0.526 \log n'$, where n' is the bond order, $D(n')$ is the observed bond length and D_1 is the S–S single bond distance observed in S_8[49] (i.e. 2.048 Å). The constant 0.526 was determined by assuming that the bond order in $S_2[X^3\Sigma g^-]$ (bond distance = 1.8894 Å) is 2.0. [b] Both the shortest and longest S–S bond distances are reported. There are significant bond distance alternations in the ring. [c] Iodine–iodine bond orders were estimated using the relationship $D(n') = D_1 - 0.619 \log n'$. The constant, 0.619, was determined by assuming that the bond order in $I_2Sb_2F_{11}$ (bond distance is 2.557 Å[35]) is 1.5 and by using the I–I single bond distance observed in $I_2(g)$ (2.666 Å). [d] Sulfur–iodine bond orders were estimated using the relationship $D(n') = D_1 - 0.572 \log n'$. The constant, 0.572, is the average of the constants used in the S–S and I–I relationships. The value for D_1 (2.357 Å) was estimated as the sum of half the S–S (2.048 Å) and I–I (2.666 Å) single-bond distances.

Evidence for Two π Bonds per $S_2I_4^{2+}$. The S–S, I–I, and S–I distances in $S_2I_4(MF_6)_2$ are compared with those in some related compounds in Table VI. The S–S distances of 1.818 (10) Å (SbF_6^-) and 1.843 (6) Å (AsF_6^-) are by far the shortest so far reported in an isolated compound, and correspond to bond orders of 2.7 and 2.4, respectively. The I–I bond distances of 2.571 (2) Å (SbF_6^-) and 2.5987 (17) Å (AsF_6^-) correspond to bond orders of 1.4 and 1.3. In contrast the S–I bond distances of 2.993 (4) Å (SbF_6^-) and 2.860 (4) and 3.178 (4) Å [average 3.019 (4) Å] (AsF_6^-) have very low bond orders of 0.1 (SbF_6^-) and 0.1 (average AsF_6^-). These bond distances are in the range 2.60–3.73 Å[56,57,58]

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(57) (a) Freeman, F.; Ziller, J. W.; Po, H. N.; Keindl, M. C. *J. Am. Chem. Soc.* **1988**, *110*, 2586. (b) Nosco, D. L.; Heeg, M. J.; Glick, M. D.; Elder, R. C.; Deutsch, E. *J. Am. Chem. Soc.* **1980**, *102*, 7786. (c) Snow, M. R.; McDonald, J.; Basolo, F.; Ibers, J. A. *J. Am. Chem. Soc.* **1972**, *94*, 2528. (d) Cordes, A. W.; Craig, S. L.; Condren, M. S.; Oakley, R. T.; Reed, R. W. *Acta Crystallogr.* **1986**, *C42*, 922. (e) Herbstein, F. H.; Schwotzer, W. *J. Am. Chem. Soc.* **1984**, *106*, 2367.

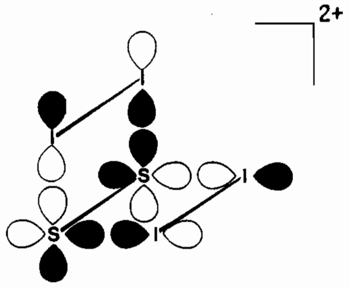
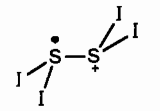


Figure 3. Two mutually perpendicular four-center–two-electron $\pi^*-\pi^*$ bonds in $S_2I_4^{2+}$.

observed for S–I bonds in sulfur–iodine charge-transfer complexes. Thus $S_2I_4^{2+}$ can reasonably be considered to contain an S_2 unit of bond order 2.33 and two I_2 units of bond order 1.33, held together by a weak interaction, with a total π-bond order of 2. $S_2I_4^{2+}$ is not sterically constrained from adopting the alternative classical σ bonded isomeric structure **2**, resembling the isoelectronic P_2I_4,[13] or the eclipsed structure **3**, which is a rotomer of **2**, or can be derived from the dication of 1,5-dithiacyclooctane (**1**)[19b] by replacement of the organic substituents by iodine. The S–S distance in **1** is 2.124 (3) Å (average); i.e., it is a normal S–S bond that has undergone some lengthening, presumably due to electrostatic repulsions.



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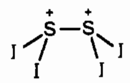

3

$S_2I_4^{2+}$ is the most highly $np\pi-np\pi$-bonded ($n \geq 3$) species reported. It is therefore the most unambiguous exception to date to the "double-bond rule" that states[15b] "Elements with a valence principal quantum number of three or greater will not participate in π bonding." In fact all the participating atoms have principal quantum numbers of 3 or greater, and the π bonds can be regarded as being formed at the expense of σ bonds of the isomeric classically σ-bonded isomer. It is also thermodynamically stable to addition of I_2.

A Simple Model for the Bonding in $S_2I_4^{2+}$. To a first order of approximation the bonding in $S_2I_4^{2+}$ may be viewed as arising from overlap of the two unpaired electrons in the mutually orthogonal π^* orbitals of $S_2(X^3\Sigma_g^-)$ with each of the two unpaired electrons in the π^* orbitals of I_2^+, as illustrated in Figure 3. The S_2 unit is therefore bonded to two I_2^+ units by two orthogonal mutually perpendicular four-center–two-electron $\pi^*-\pi^*$ bonds, consistent with the 90° dihedral angle between the two S_2I_2 planes and the long S–I distances. The ionization energies of S_2(g), 9.40 ± 0.05 eV, and I_2(g), 9.3995 ± 0.10012 eV, are essentially the same.[59] Therefore +0.66 charge is expected to reside on each dimer unit, or +0.33 charge on each atom. This equidistribution of charge can be realized by movement of electrons in the $\pi^*-\pi^*$ orbitals from S_2 toward the two I_2^+ ions. The resultant $S_2^{0.66+}$ ion and two $I_2^{0.66+}$ ions would have bond orders of 2.33 and 1.33, respectively, consistent with the observed bond distances and derived empirical bond orders. $S_2I_4^{2+}$ can be regarded as a three-dimensional counterpart of the two-dimensional I_4^{2+},[14] which contains two I_2^+ ions weakly bound by a four-center–two-electron $\pi^*-\pi^*$ bond (see Figure 4).

Electronic Structures of Cl_4^{2+} and $O_2Cl_4^{2+}$, Models for I_4^{2+} and $S_2I_4^{2+}$. In order to understand more fully the nature of the bonding in $S_2I_4^{2+}$, we carried out ab initio RHF, STO-3G calculations[60] using the GAUSSIAN 82 and 86[61,62] computer programs on Cl_4^{2+} and $O_2Cl_4^{2+}$. These cations are assumed to provide reasonable models for I_4^{2+} and $S_2I_4^{2+}$. An optimized rectangular geometry of Cl_4^{2+} was obtained[63] at −1 140 319.1 kcal·mol⁻¹, with a shorter Cl–Cl

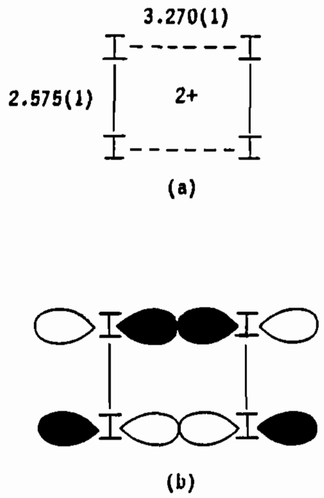

Figure 4. (a) Structure of I_4^{2+} in $I_4(AsF_6)_2$, with distances in Å. (b) Four-center–two-electron $\pi^*-\pi^*$ bond in I_4^{2+}.

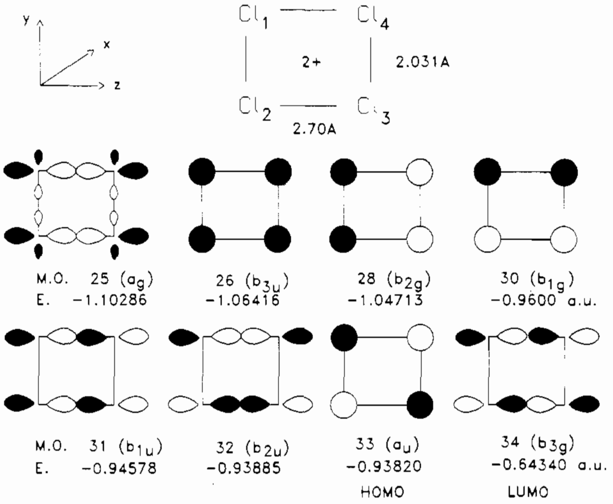

Figure 5. π MO's in Cl_4^{2+}.

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(58) (a) Burford, N.; Chivers, T.; Hojo, M.; Laidlaw, W. G.; Richardson, J. F.; Trsic, M. *Inorg. Chem.* **1985**, *24*, 709. (b) Chivers, T.; Rao, M. N. S.; Richardson, J. F. *J. Chem. Soc., Chem. Commun.* **1983**, 700.

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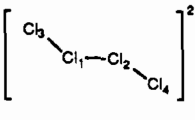
(63) (a) The related optimised rectangular geometry at the 4-31G level gave R(Cl–Cl) = 2.116 and 2.824 Å, at E = 1 151 358.1 kcal·mol⁻¹. However, when the constraint that the geometry be restricted to rectangular was removed, a chainlike geometry was obtained.



STO-3G optimized parameters $R(Cl_1-Cl_2)$ = 2.147, $R(Cl_1-Cl_3)$ = $R(Cl_2-Cl_4)$ = 2.07 Å. $\angle Cl_3Cl_1Cl_2 = \angle Cl_1Cl_2Cl_4$ = 106.5°, ϕ(dihedral) = 148.8° at E = −1 140 356.6 kcal·mol⁻¹. 4-31G optimized parameters: $R(Cl_1-Cl_2)$ = 2.245 Å, $R(Cl_2-Cl_3) = R(Cl_2-Cl_4)$ = 2.367 Å, $\angle Cl_3Cl_1Cl_2 = \angle Cl_1Cl_2Cl_4$ = 105.5°, ϕ(dihedral) = 173.6° at E = −1 151 397.9 kcal·mol⁻¹. Another recent calculation[64] for Cl_4^{2+} also gave a bent geometry on full optimization. Whether or not Cl_4^{2+}(g) has a different geometry from that observed for I_4^{2+} in the solid state still remains to be resolved.

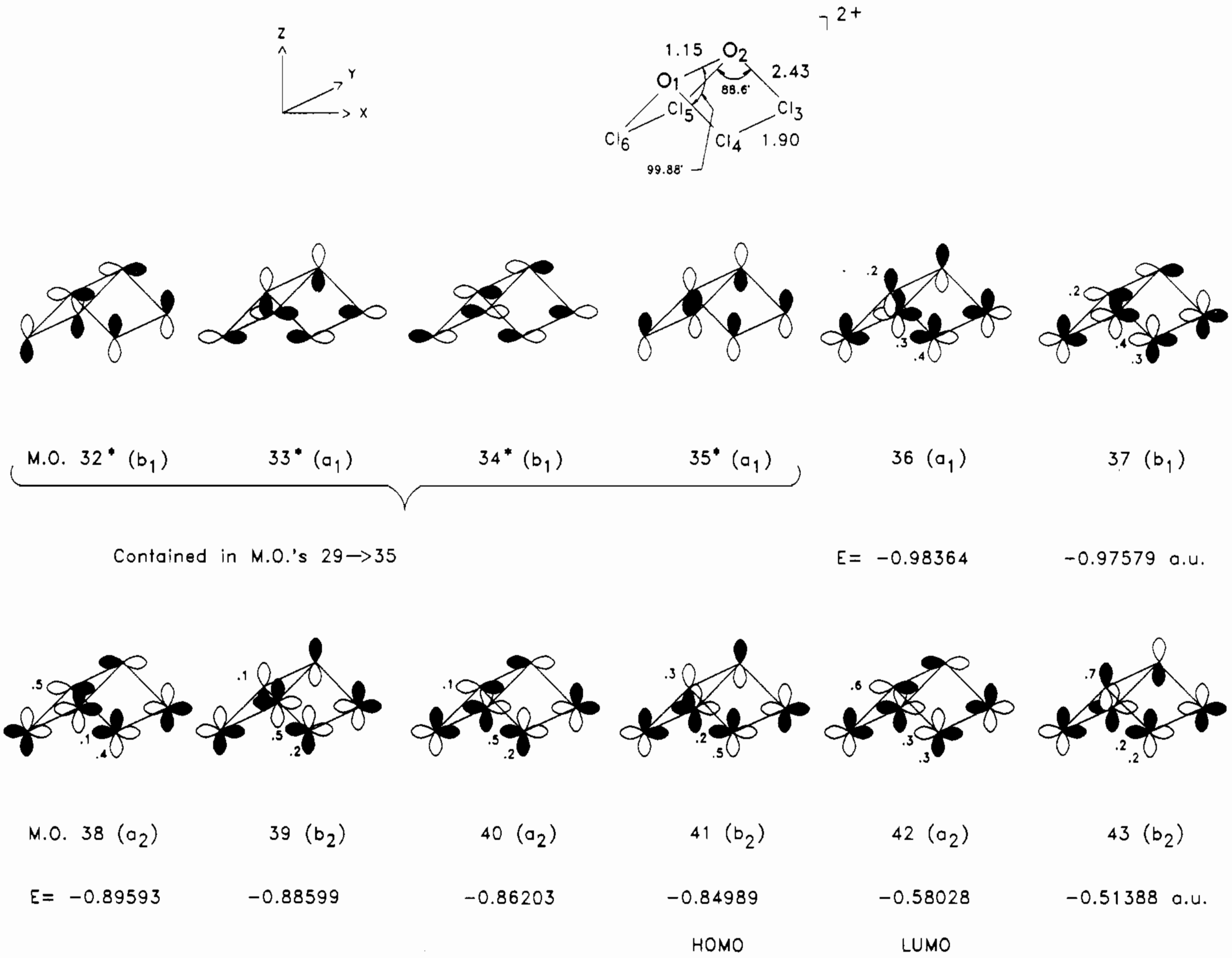


Figure 6. π MO's in $O_2Cl_4^{2+}$.

distance of 2.031 Å and a longer Cl–Cl distance of 2.700 Å. The $O_2Cl_4^{2+}$ calculation was carried out at a fixed configuration (given in Figure 6) that reflects the observed geometry of $S_2I_4^{2+}$.

Cl_4^{2+}. The eight MO's of Cl_4^{2+}, which are built from π and π^* MO's of the two dimer units, are illustrated in Figure 5. The symmetry designations (D_{2h}) are also included. There are four in-plane MO's ($\pi + \pi$, $\pi - \pi$, $\pi^* + \pi^*$, $\pi^* - \pi^*$) and four corresponding out-of-plane MO's. They are numbered according to increasing orbital energy within the set of all Cl_4^{2+} MO's. Note that MO's 27 and 29 are not included; both are MO's that have σ bonds within the dimers. The filled interdimer bonding MO's 25, 26, and 30 are matched by filled MO's with corresponding interdimer antibonding combinations (MO's 31, 28, and 33). However, MO 32 (the HOMO – 1), is matched by the LUMO (MO 34), and therefore, to a first order of approximation, the HOMO – 1 is responsible for the bonding between the Cl_2^+ dimer units in rectangular Cl_4^{2+}. The MO's 25, 26, 28, and 31 are all π bonding within the dimer region, with antibonding counterparts in MO's 30, 32, 33, and 34. All of these MO's are filled except MO 34, the LUMO, and therefore, to a first order of approximation there is one net intradimer π bond per Cl_4^{2+} or 0.5 π bond per Cl_2^+. The same situation applies to Cl_2^+, which has one half-π-bond relative to Cl_2. Thus this analysis supports the simple bonding model proposed for I_4^{2+} in which two I_2^+ ions are weakly linked by a two-center–two-electron π^*–π^* bond (Figure 4). Theoretical calculations have shown that similar sulfur-based four-center–two-electron π^*–π^* bonds[65] are also present in (cis-$H_2S_2^{\bullet+})_2$[66] of suitable geometry as a model for ($\overline{SNSNS}^{\bullet+})_2$,[43,67] ($CF_3\overline{CNSSN}^{\bullet})_2$,[68] and ($C_6H_4S_2N^{\bullet})_2$.[69] An account of these and other related π^*–π^* bonds is included in ref 16.

$O_2Cl_4^{2+}$. $O_2Cl_4^{2+}$ has C_{2v} symmetry, and consists of the three dimer units O_1–O_2, Cl_3–Cl_4, and Cl_5–Cl_6 (see Figure 6). Each individual dimer has two π and two π^* orbitals, giving a total of 12 orbitals. Approximate linear combinations of these π and π^* orbitals give rise to three a_1, three a_2, three b_1, and three b_2 MO's for $O_2Cl_4^{2+}$ (also allowing for the inclusion of 2s and $2p_y$ atomic orbitals). For the MO's denoted by 32*–35*, there is heavy σ mixing. They are contained in the original MO's 29–35. For the other MO's, 36–43, there is only light σ mixing.

In Figure 7 positive and negative linear combinations of MO's from Figure 6 are shown such that the interdimer π orbitals are

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(64) Li, Y.; Wang, X.; Jensen, F.; Houk, K. N.; Olah, G. A. *J. Am. Chem. Soc.* **1990**, *112*, 3922.

(65) Gleiter has described[66] the bond joining the two radical cations in cis-$(H_2S_2^+)_2$ as a four-center–six-electron bond. The related bond in Cl_4^{2+} may also be described in this way as contributions from MO's 26, 28, 30, and 33 not only are very small but also formally cancel one another out, leaving only the filled MO's 25, 31, and 32 contributing to the bond in the interdimer region. However MO 25 is formally cancelled by MO 31, and for simplicity we refer to interdimer bonds of this sort as four-center–two-electron π^*–π^* bonds. At less than equilibrium interdimer distances the importance of MO's 25 and 31 rapidly increases and account for the very long interdimer equilibrium bond length in Cl_4^{2+}.

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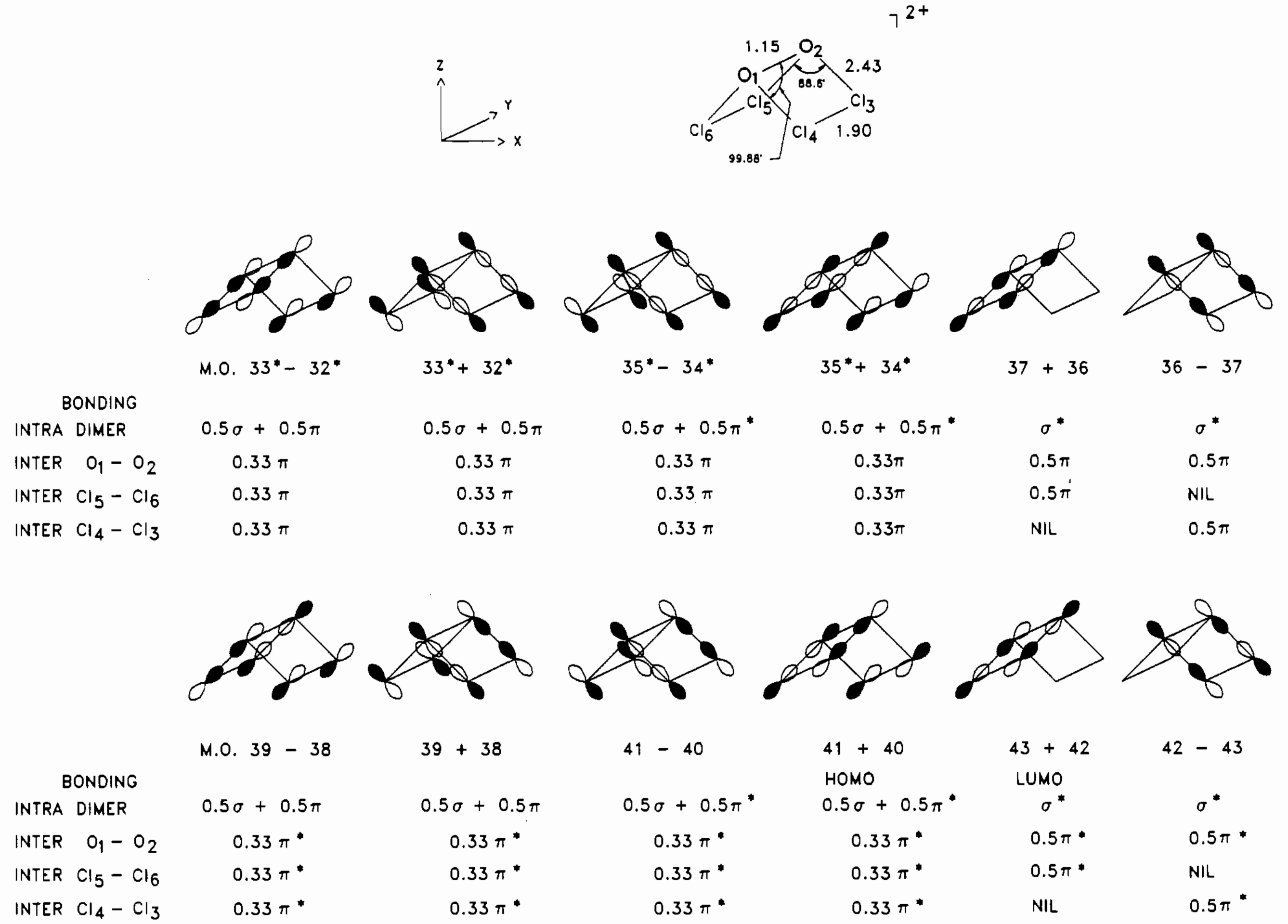
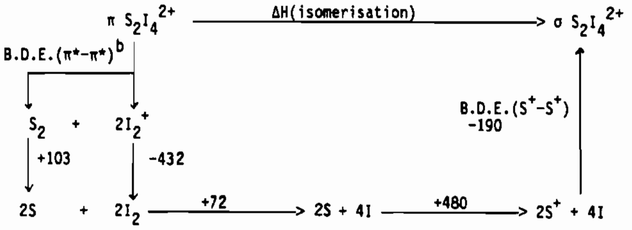


BONDING	M.O. 33* − 32*	33* + 32*	35* − 34*	35* + 34*	37 + 36	36 − 37
INTRA DIMER	0.5σ + 0.5π	0.5σ + 0.5π	0.5σ + 0.5π*	0.5σ + 0.5π*	σ*	σ*
INTER O_1 − O_2	0.33 π	0.33 π	0.33 π	0.33π	0.5π	0.5π
INTER Cl_5 − Cl_6	0.33 π	0.33 π	0.33 π	0.33π	0.5π	NIL
INTER Cl_4 − Cl_3	0.33 π	0.33 π	0.33 π	0.33π	NIL	0.5π

BONDING	M.O. 39 − 38	39 + 38	41 − 40	41 + 40 HOMO	43 + 42 LUMO	42 − 43
INTRA DIMER	0.5σ + 0.5π	0.5σ + 0.5π	0.5σ + 0.5π*	0.5σ + 0.5π*	σ*	σ*
INTER O_1 − O_2	0.33 π*	0.33 π*	0.33 π*	0.33 π*	0.5π*	0.5π*
INTER Cl_5 − Cl_6	0.33 π*	0.33 π*	0.33 π*	0.33 π*	0.5π*	NIL
INTER Cl_4 − Cl_3	0.33 π*	0.33 π*	0.33 π*	0.33 π*	NIL	0.5π*

Figure 7. Idealized π-$O_2Cl_4^{2+}$ MO's, perpendicular to and in the O_2Cl_2 planes.

Scheme I. Estimate[a] of the Relative Energies of σ- and π-Bonded $S_2I_4^{2+}$



ΔH (isomerisation) = + 33 + B.D.E.(π*−π*) − B.D.E.(S^+−S^+)

[a] All species in the gas phase, thermodynamic values, and estimations (in kcal·mol^{-1}) are given in Table VII. [b] The value of BDE (π*−π*) leading to S_2^+ + I_2^+ + I_2 is essentially the same as that given in the scheme, as IE(S_2) = 215.8 kcal·mol^{-1} is almost identical to IE(I_2) = 216 kcal·mol^{-1}.

rotated by 45° and are therefore directed in one of the O_2Cl_2 planes (σ) or perpendicular to it (π). (The angle between the two planes is close to 90°.) The assumption has been made that the minor contributions on the chlorine atoms in MO's 38 ($3p_x$), 39 ($3p_z$), 40 ($3p_z$), and 41 ($3p_x$) (Figure 6) can be ignored, and the remaining coefficients of equivalent pairs are made equal. Thus the MO's of Figure 7 are idealized and are no longer symmetry orbitals. For each MO of Figure 7 the number of intradimer and interdimer σ and π bonds are given. The net bonding between dimer units is two σ bonds, or one σ bond per O_2Cl_2 unit, and they are of the π*−π* type and arise from the four highest filled MO's. Within the dimer units there are two resulting π bonds represented by MO 36 + 37 and MO 36 − 37. There is an O–O π bond, and half a π bond for each Cl–Cl unit. Therefore, the O–O bond order is 2, and the Cl–Cl dimer bond order is 1.5, in accordance with a neutral O_2 interacting with two $Cl_2^{\bullet+}$ units. The calculated charges on $O_2Cl_4^{2+}$ are divided almost evenly between all six atoms: 0.356 for oxygen and 0.322 for each chlorine. Thus this semiquantitative treatment of $O_2Cl_4^{2+}$ gives a description of the electronic structure that is in agreement with that given by the simple MO model for $S_2I_4^{2+}$ (see above).

Greater Thermodynamic Stability of the Observed π $S_2I_4^{2+}$ Relative to the σ-Bonded Isomer (3). The Δ*H*(isomerization) (in kcal·mol^{-1}) of π-$S_2I_4^{2+}$ to the σ-bonded isomer is given from Scheme I by eq 5.

$$\Delta H(\text{isomerization}) = 33 + \mathrm{BDE}(\pi^*\text{–}\pi^*) - \mathrm{BDE}(S^+\text{–}S^+) \quad (5)$$

π-$S_2I_4^{2+}$ contains two mutually orthogonal π*−π* bonds. Related species have one π*−π* bond with corresponding dissociation energies of 0–10 kcal·mol^{-1}.[16,70] The repulsion energy associated with the two positively charged sulfur atoms is likely to be large[71] and the corresponding BDE(S^+–S^+) is reasonably less than 33 kcal·mol^{-1}. (cf. BDE(S–S) in S_2F_{10}[72a] of 23 kcal·

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(70) (a) A value of BDE(π*−π*) of 10 ± 2 kcal·mol^{-1} was determined for I_4^{2+} in HSO_3F solution assuming $2I_1^+$ dimerized to I_4^{2+} on lowering of the temperature.[70b] However, further work has shown[14a] that I_4^{2+} (as the SO_3F^- salt) as well as being in equilibrium with $2I_2^+$ appears to undergo disproportionation to I_3^+ and "I^{+}". Therefore the thermodynamics of the system needs to be reevaluated. Energies of a range of related π*−π* bonds vary between 0 and 10 kcal·mol^{-1}.[16] (b) Gillespie, R. J.; Milne, J. B.; Morton, M. J. *Inorg. Chem.* **1968**, *7*, 2221.

(71) (a) The electrostatic repulsion energy (kcal·mol^{-1}) may be estimated[71b] using the point charge model

$$E_{rep} = 333q_1q_2/d$$

where *d* is the distance (Å) between the two positive charges q_1 and q_2. (b) Liebman, J. F. In *Molecular Structure and Energetics 3*; Liebman, J. F., Greenberg, A., Eds.; VCH: Deerfield Beach, FL, 1986.

Table VII. Thermodynamic Data[a]

	ΔH, kcal·mol^{-1}	footnotes or refs
$SI_3^+(g) + AsF_6^-(g) \rightarrow SI_3AsF_6(s)$	−124	*b*
$S_2I_4^{2+}(g) + 2AsF_6(g) \rightarrow S_2I_4(AsF_6)_2(s)$	−333	*c*
$SI_3^+(g) \rightarrow S^+(g) + 3I(g)$	142	*d*
$I_2(s) \rightarrow I_2(g)$	15	59
$I_2(g) \rightarrow 2I(g)$	36	59
$I_2(g) \rightarrow I_2^+(g) + e^-$	216	59
$S_2(g) \rightarrow 2S(g)$	+103	73
$S(g) \rightarrow S^+(g) + e^-$	+240	59
$3AsF_5(g) \rightarrow 2AsF_6^-(g) + AsF_3(g)$	−233	59, 74, 77
$AsF_3(l) \rightarrow AsF_3(g)$	+8.5	59
$S_2(g) \rightarrow S_2^+(g)$	215.8	59
$^1/_8S_8(s) \rightarrow S(g)$	66.6	59

[a] Thermodynamic quantitites and estimates of unknown quantities given in ref 10. [b] Crystal lattice energies of 1.1 salts are estimated from the expression[77] $\Delta H = (556.3(\text{molecular volume})^{-1/3} + 26.3)$ kcal·mol^{-1}, and in addition an extra 10 kcal·mol^{-1} has been added to account for the greater dispersion energies expected in these salts relative to simple 1:1 salts, e.g. NaCl. The volume of the hypothetical SI_3AsF_6 was estimated to be 7 Å^3 less than that (265 Å^3) of SeI_3AsF_6[10] i.e. 258 Å^3. [c] The crystal lattice energy of $S_2I_4(AsF_6)_2$ is estimated as 329 kcal·mol^{-1} by the Kapustinskii equation,[73]

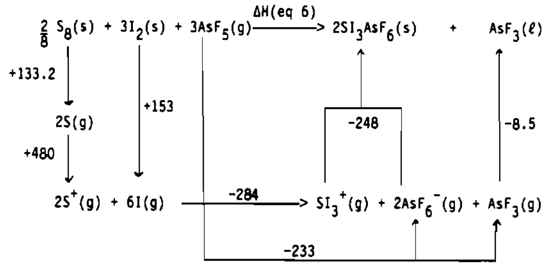
$$U = \frac{290.4\nu\, z^+z^-}{r_0}\left[1 - \frac{0.345}{r_0}\right]$$

where r_0 is the shortest distance between the center of the cation to the center of the anion (4.923 Å). As U for a 2:1 salt has $\nu = 3$, $z^+ = 2$, and $z^- = 1$, then U(2:1 salt) may be approximately equal to $3U$(1:1 salt). The lattice energy of the 1:1 salt was calculated using the Bartlett approach above with a volume of $S_2I_4AsF_6$ of 423.5 Å, i.e. the volume of $S_2I_4(AsF_6)_2$ ((423.5 Å^3) minus the volume of AsF_6^- (105 Å^3))[22]. This leads to a value $U = -333$ kcal·mol^{-1}. The value of U for $(SF_3)_2GeF_6$ estimated by this approach is 384 kcal·mol^{-1}, very similar to the value of 381 kcal·mol^{-1} calculated using a rigorous treatment.[77] [d] The same approach is used as in ref 10 where it is assumed that M-(hal)$_3^+$ [M = S, Se; hal = Br, I] bond energies are similar to those in M(hal)$_2$ as all M(hal)$_3^+$ bond lengths are either essentially equal to or estimated to be equal to those in M(hal)$_2$. The S^+–I bond energy in SI_3^+ is therefore made equal to that estimated for SI_2 by Sanderson.[78] This can be regarded as a lower limit for this bond energy. Using a similar approach, the energetics of M(hal)$_4$AsF$_6$, M(hal)$_4$PF$_6$, and M(hal)$_4$Al(hal)$_4$ (hal = Cl, Br, I; M = P, As) systems have also been successfully modeled.[79]

mol^{-1}). Therefore the estimate of ΔH(isomerization) from this simple treatment is reasonably positive. Included in the +33 kcal·mol^{-1} contribution to ΔH(isomerization) is the difference between the ionization energies of $2I_2(g)$ and that of $2S(g)$, which is 48 kcal·mol^{-1}. Therefore the energy associated with the positive charge localization on the sulfur atoms in σ-$S_2I_4^{2+}$ (3), relative to the delocalized charge in π-$S_2I_4^{2+}$, and the low S^+–S^+ and S^+–I bond dissociation energies in σ-bonded $S_2I_4^{2+}$ largely account for the existence of the observed π-bonded $S_2I_4^{2+}$ in $S_2I_4(AsF_6)$ and the existence of its thermodynamically stable π bonds.

Many of the homopolyatomic cations of groups 16 and 17[16] and related bromo- and iodosulfur and -selenium cations[18] also adopt cagelike structures in which positive charge is delocalized, contain $np\pi$–$np\pi$ ($n \geq 3$) thermodynamically stable bonds, and have unstable σ-bonded isomers in which the dipositive positive charge is localized on adjacently bonded atoms.[16-18,72b]

Scheme II. Estimate[a] of the Enthalpy, Entropy, and Free Energy of Formation of $SI_3AsF_6(s)$ from Sulfur, Iodine, and AsF_5 According to Equation 6



$$\Delta H(\text{eq } 6) \simeq -7 \text{ kcal. mol}^{-1} \tag{6}$$

$$\frac{2}{8} S_8(s) + 3I_2(s) + 3AsF_5(g) \longrightarrow 2SI_3AsF_6(s) + AsF_3(\ell)$$

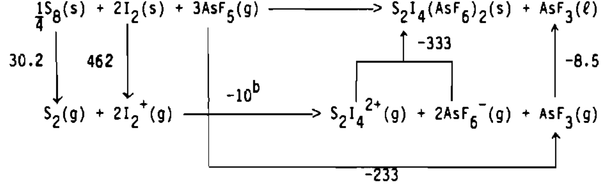
$$S°(\text{cal. } k^{-1}\text{mol}^{-1})\ \frac{2}{8}\,103^b + 3\text{x}27.8^b + 3\text{x}78^b \qquad +2\text{x}113.5^c + 43.3^d$$

$$\Delta S \simeq -73 \text{ cal. } k^{-1}\text{mol}^{-1} \quad T\Delta S(\text{at } 293°\text{K}) \simeq -21.4 \text{ kcal. mol}^{-1}$$

$$\Delta G \simeq +14 \text{ kcal. mol}^{-1} \text{ (at } 293°\text{K)}$$

[a] Thermodynamic values and estimations are given in Table VII. All values are in kcal·mol^{-1}. [b] Reference 73. [c] For A^+B^- salts, Bartlett has shown[74] that $S° = 0.44V_m$, when V_m = molar volume in Å^3 and $S°$ is kcal·mol^{-1}·K^{-1}. The molar volume of SI_3AsF_6 is estimated[10] as 258 Å^3. [d] Reference 75.

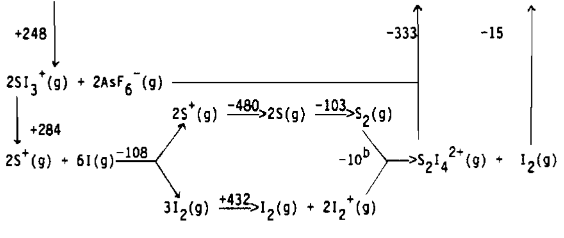
Scheme III. Estimate[a] of the Enthalpy of Formation of $S_2I_4(AsF_6)_2$ from Sulfur Iodine and Arsenic Pentafluoride According to Equation 7



$$\Delta H(\text{eq } 7) \simeq -92 \text{ kcal. mol}^{-1} \tag{7}$$

[a] Thermodynamic values and estimates are given in Table VII. All values are given in kcal·mol^{-1}. [b] The π^*–π^* bond strength in $S_2I_4^{2+}$. Values of dissociation energies of related π^*–π^* bonds vary between 0 and 10 kcal·mol^{-1}.[16,17] $S_2I_4^{2+}$ contains two such sets of bonds, so here we have roughly estimated an arbitrary value of 10 kcal·mol^{-1}.

Scheme IV. Estimate[a] of the Enthalpy of Dissociation of $2SI_3AsF_6(s)$ to $S_2I_4(AsF_6)_2(s)$ and $I_2(s)$



$$\Delta H(\text{eq } 8) \simeq -85 \text{ kcal. mol}^{-1} \tag{8}$$

[a] Corresponding values of the thermodynamic data are given in Table VII. All values are in kcal·mol^{-1}. [b] See footnote *b*, Scheme III.

Energetics and the Nonexistence of $SI_3AsF_6(s)$. All attempts to prepare $SI_3AsF_6(s)$ led instead to mixtures of $S_2I_4(AsF_6)_2(s)$ and $I_2(s)$. However, the average composition of the solutes given on dissolving mixtures of $S_2I_4(AsF_6)_2(s)$ and $I_2(s)$ in SO_2 was SI_4AsF_6 for ratios of $S_2I_4(AsF_6)_2(s)$ and I_2 up to 1:2 and $SI_{4.5}As_6$ for 1:2. On removal of the solvent $S_2I_4(AsF_6)_2(s)$ and $I_2(s)$ were obtained. The enthalpy and free energy change at 273 K of the formation of $2SI_3AsF_6(s)$ from stoichiometric amounts of sulfur, iodine, and arsenic pentafluoride according to eq 6 in Scheme II are estimated as ca. −7 and +14 kcal·mol^{-1}, respectively. (The

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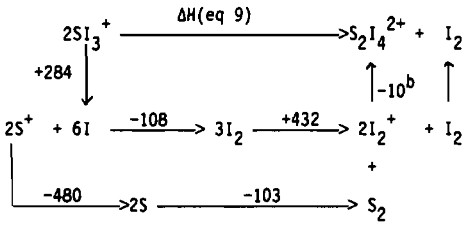
(72) (a) Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*; Pergamon Press: Elmsford, NY, 1984; see references therein. (b) Nandana, W. A. S.; Passmore, J.; White, P. S.; Wong, C.-M. *Inorg. Chem.* **1989**, *28*, 3320.

(73) Johnson, D. A. *Some Thermodynamics of Inorganic Chemistry*, 2nd ed.; Cambridge University Press: Ithaca, NY, 1982.

(74) Richardson, T. J.; Tanzella, F. L.; Bartlett, N. *J. Am. Chem. Soc.* **1986**, *108*, 4937.

(75) O'Hare, P. A. G.; Hubbard, W. N. *J. Phys. Chem.* **1965**, *69*, 4358.

Scheme V. Estimation[a] of the Gas-Phase Dissociation of $2SI_3^+$ into $S_2I_4^{2+}$ and I_2



$$\Delta H(\text{eq } 9) = +15 \text{ kcal. mol}^{-1} \quad (9)$$

[a] All species are in the gas phase. Estimates and thermodynamic values are given in Table VII. All values are in kcal·mol⁻¹. [b] See footnote *b*, Scheme III.

enthalpy of formation of SeI_3AsF_6 by an analogous route is estimated[10] as −24[76] kcal·mol⁻¹.) In contrast, the analogous reaction leading to $S_2I_4(AsF_6)_2(s)$ according to eq 7 (in Scheme III) has an enthalpy of ca. −92 kcal·mol⁻¹, significantly larger than any reasonable $T\Delta S$ value at room temperature and the sum of the errors in the estimated thermodynamic values. If $SI_3AsF_6(s)$ is formed at all, then it must simultaneously disproportionate and dissociate into $S_2I_4(AsF_6)_2(s)$ and $I_2(s)$ (eq 8), with an enthalpy of ca. −85 kcal·mol⁻¹ (Scheme IV). The major driving force for the dissociation is the higher crystal lattice energy of $S_2I_4(AsF_6)_2(s)$ (−333 kcal·mol⁻¹) relative to that of $2SI_3AsF_6(s)$ (−2 × 124 = −248 kcal·mol⁻¹). In the gas phase the thermodynamic stability of $2SI_3^+(g)$ is very similar to that of $S_2I_4^{2+}(g)$ and $I_2(g)$. (The enthalpy of eq 9 is ca. +15 kcal·mol⁻¹, Scheme V).

$$2SI_3AsF_6(s) = S_2I_4(AsF_6)_2(s) + I_2(s) \quad (8)$$

$$2SI_3^+(g) = S_2I_4(AsF_6)_2(g) + I_2(g) \quad (9)$$

The corresponding enthalpies of the analogous reactions to that of eq 9, but with other halogens, are more endothermic as the $S^+–X$ (X = F, Cl, Br) bonds have higher dissociation energies than $S^+–I$, and the ionization energies of the halogens are greater than that of I_2. This leads to a higher stability of $2SX_3(AsF_6)(s)$ relative to $S_2X_4(AsF_6)_2(s)$ and $X_2(s)$. So far no $S_2X_4(AsF_6)_2(s)$ has been reported.

The reverse of eq 8 is the iodination of $S_2I_4(AsF_6)_2(s)$ leading to $2SI_3AsF_6$, which is substantially endothermic (ca. +85 kcal·mol⁻¹). Therefore, not only are the π bonds in $S_2I_4^{2+}$ thermodynamically stable, they are also stable with respect to addition of I_2.

The disproportionation of $2SI_3AsF_6(s)$ into $S_2I_4(AsF_6)_2(s)$ and $I_2(s)$ is reminiscent of the disproportionation of group 2 1:1 salts into the metal and the corresponding divalent salt, e.g., eq 10. The

$$2CaF(s) = CaF_2(s) + Ca(s) \quad (10)$$

driving force in both cases is a gain in crystal lattice energy; i.e., the crystal energy of the 2:1 salt is greater than twice that of the 1:1 salt.

Acknowledgment. We thank the National Sciences and Engineering Research Council of Canada for financial support, Mr. S. Parsons for carrying out some of the STO-3G calculations, and Mr. S. Parsons and Dr. C.-M. Wong for help with obtaining crystallographic information.

Registry No. S_8, 10544-50-0; I_2, 7553-56-2; AsF_5, 7784-36-3; SbF_5, 7783-70-2; $S_2I_4(AsF_6)_2$, 74775-08-9; $S_2I_4(SbF_6)_2$, 137059-02-0; $S_4(AsF_6)_2$, 74775-27-2; Cl_2, 7782-50-5; Br_2, 7726-95-6; SCl_3AsF_6, 27075-96-3; SBr_3AsF_6, 30313-36-1; $(SbF_3)_5(SbF_5)_3$, 137058-97-0; $S_4(Sb_2F_{11})_2$, 65107-03-1; S_4^{2+}, 12597-09-0; I_2^+, 28712-14-3; I_4^{2+}, 12596-35-9; Cl_4^{2+}, 137058-98-1; $O_2Cl_4^{2+}$, 137058-99-2; $S_2I_4^{2+}$, 74775-07-8; SI_3AsF_6, 137059-01-9; SI_3^+, 137059-00-8.

Supplementary Material Available: Stereoviews of the packing in the unit cells of $S_2I_4(AsF_6)_2$ and $S_2I_4(SbF_6)_2$ and tables of magnetic susceptibility data for $S_2I_4(MF_6)_2$ (M = As, Sb), data for various reactions that led to solid $S_2I_4(AsF_6)_2$ as the major product, data for various attempted preparations of SI_3AsF_6 in SO_2 solution, data for various attempted preparations of halogen derivatives of SI_3AsF_6 and $S_2I_4(AsF_6)_2$, crystallographic data for $S_2I_4(MF_6)_2$ (M = As, Sb), and anisotropic temperature factors for $S_2I_4(MF_6)_2$ (15 pages); tables of observed and calculated structure factors for $S_2I_4(AsF_6)_2$ and $S_2I_4(SbF_6)_2$ (14 pages). Ordering information is given on any current masthead page.

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(76) The model tends to give a low estimate of this and related enthalpies. See footnote *d* of Table VII.

(77) Mallouk, T. E.; Rosenthal, G. L.; Muller, G.; Brusasco, R.; Bartlett, N. *Inorg. Chem.* **1984**, *23*, 3167.

(78) Sanderson, R. T. *Chemical bonds and bond energy*; Academic Press: New York, 1971.

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