Supplemental Information

to

The Highest Bond Order Between Heavier Main-Group Elements in an Isolated Compound? Energetics and Vibrational Spectroscopy of $S_2I_4(MF_6)_2$ (M = As, Sb).

by

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1. Cation-Anion Contacts in the Structure of $S_2I_4(AsF_6)_2$.

Fig. 1 S...F contacts in $S_2I_4(AsF_6)_2$ (S...F contacts: S5...F1 3.041(7), S5...F2 3.094(7), S5...F5' 3.174(8), S5...F8'' 2.95(2) Å).

Fig. 2. a) Bond valence map of the ordered As_2F_6 unit showing F...S and F...I contacts below their van de Waals distance of 3.20 and 3.45 Å, respectively (bond distance in Å and valence units (v.u.)). The calculated atomic valences: As2 4.79, F1 0.94, F2 0.92, F3 0.97; the formal charge on $As_2F_6^-$: -0.78. b) van der Waals contacts between $As_2F_6^-$ and $S_2I_4^{2+}$. Symmetric operations: a (-x,y,0.5-z), b (-x,-y,-z), c (x,-y,0.5+z).

a) (F' atoms with 74% occupancies) **b) (F'' atoms with 26% occupancies)**

Fig 3. a,b) Bond valence maps of the disordered As1F_6 unit showing $\text{F} \cdots \text{S}$ and $\text{F} \cdots \text{I}$ contacts below their van de Waals distance of 3.20 and 3.45 Å, respectively (bond distance in Å; the bond valences (v.u.) in parenthesis and in bold have taken into account of the occupancies of the fluorine atoms). The total calculated atomic valences: As1 4.82, F4' 0.73, F5' 0.72, F6' 0.66, F7'' 0.24, F8'' 0.28, F9'' 0.26; the formal charge on As1F_6^- : -0.97. **c)** van der Waals contacts between the disordered As1F_6^- and $\text{S}_2\text{I}_4^{2+}$ units.

2. Why As1F_6^- is disordered?

The disordered As1F_6^- anion comes in two packages F4, F5 and F6 and F7, F8 and F9 of a disordered anion which occur in the ratio of 3:1. The disordered As1F_6^- is surrounded by six $\text{S}_2\text{I}_4^{2+}$ units, whereas the As2F_6^- anion is only surrounded by four cations. The anion As2F_6^- with the fluorines F1, F2 and F3 has contacts only to I1 (and S); the disordered As1F_6^- splits its attention between I1 and I2 (overall more or less equally) and to S to much the same extent as for the As2F_6^- anion. This is shown in the Fig. 2 and 3. From Figure 3 one can count up the contacts to each package of the disordered As2F_6^- anions and note immediately that the higher populated anion with the fluorines F4, F5 and F6 has the greater number of contacts and the shortest. Therefore the disorder can be explained by the number of contacts between anion and cation.

3. Packing in the Structure of $\text{S}_2\text{I}_4(\text{AsF}_6)_2$.

Fig 4. The packing of AsF_6^- octahedrons and $\text{S}_2\text{I}_4^{2+}$ units in a quadruple cell ($2 \times 2 \times 1$). The coordination number of $\text{S}_2\text{I}_4^{2+}$ is ten, that of the ordered As2F_6^- is four, and that of the disordered As1F_6^- six. Thus the average coordination number of the anion is five.

4. Determination of Solution FT-Raman Spectra

Three sets of experiments were carried out in SO_2 , AsF_3 and HSO_3F , using reaction vessels as shown in Figure 5b. This vessel design incorporates a third PTFE (polytetrafluoroethylene) piston (J. Young) and a 5 mm NMR tube (Wilmad) into a standard reaction vessel (Figure 5a). The 5 mm tube was long enough to be inserted into both the room- and low temperature sample compartments of the Bruker FRA-106 Raman attachment, allowing in situ preparation and adjustments to the solution concentration of samples by pouring an aliquot of reaction mixture into the 5 mm tube. FT-Raman spectra of frozen solutions were obtained by dipping the NMR tube, containing an aliquot of reaction mixture, into a dewar of liquid nitrogen to rapidly freeze the solution before insertion into the precooled low temperature sample compartment.

For each solvent, two reaction vessels of the type shown in Figure 5b were used: one for the in situ preparation of $\text{S}_2\text{I}_4(\text{AsF}_6)_2$ and subsequent addition of ca. 100% excess AsF_5 ; and a second vessel for the in situ reaction of $\text{S}_2\text{I}_4(\text{AsF}_6)_2 + 2.08 \text{I}_2$. For the first reaction, $\text{S}_2\text{I}_4(\text{AsF}_6)_2$ was prepared in situ in bulb **B** of the reaction vessel, to obtain the ‘base’ solution FT-Raman spectra. The reaction was allowed to stir for ca. one hour, resulting in a dark red-brown solution. A small aliquot of solution was poured from bulb **B** into the 5 mm tube, then into bulb **A**, to rinse the 5 mm tube. To obtain a spectrum that was not dominated by solvent peaks (e.g. SO_2 : 1351, 1147, 517 cm^{-1}), it was necessary to first concentrate the reaction solution by condensing a portion of the solvent (SO_2 or AsF_3) into the bulb **A** until the solution was thick but saturated. Concentration of the samples in HSO_3F was found to not be necessary, which was advantageous since the high viscosity and low vapour pressure of HSO_3F makes it difficult to work with this material through a sintered glass frit. An aliquot of the saturated solution was poured into the 5 mm tube, and an FT-Raman spectrum was acquired.

For the addition of excess (ca. 100%) AsF_5 in SO_2 and AsF_3 , the aliquot of solution in the NMR tube was washed back into the reaction bulb **B**, and the solvent in bulb **A** was condensed back to bulb **B**. In this way, the error in weight from the small amount of material in bulb **A** was minimised. The solvent was not condensed back to bulb **A** in the case of HSO_3F . The excess AsF_5 was then condensed onto the reaction mixture at $-196\text{ }^\circ\text{C}$. After warming to r.t. and stirring for one hour, a subsequent FT-Raman solution spectrum was recorded using the aforementioned procedure. In a second vessel, a molar ratio of 1 $\text{S}_2\text{I}_4(\text{AsF}_6)_2$ to 2.08 I_2 (matching the previously found experimental stoichiometry)³ was prepared *in situ*, and solution spectra were recorded in a similar manner. For both SO_2 and AsF_3 , FT-Raman spectra of the recovered solids were also obtained after pumping off all volatile materials. Experimental data is given in Table 1.

Fig 5. Schematic figure of the vessels used for the reaction (a) and the *in situ* Raman solution studies (b).

Table 1. Experimental data for preparation of solid and solution FT-Raman spectra samples.

Reaction	Reagent (g / mmol)			Solvent (g)			Figure
	S ₈	I ₂	AsF ₅ (SbF ₅)	SO ₂	AsF ₃	HSO ₃	
solid							
S ₂ I ₄ (AsF ₆) ₂	0.252 / 0.983	2.005 / 7.901	2.056 / 12.098	8.659			Manuscript
S ₂ I ₄ (SbF ₆) ₂	0.368 / 1.439	2.874 / 11.323	(4.066 / 18.758)				Manuscript
in SO₂							
S ₂ I ₄ (AsF ₆) ₂	0.112 / 0.437	0.893 / 3.518	0.913 / 5.372	7.377			8
plus excess AsF ₅ ^a			1.809 / 10.645				
S ₂ I ₄ (AsF ₆) ₂ with excess I ₂	0.166 / 0.648	2.724 / 10.731	1.586 / 9.333	11.841			
in AsF₃							
S ₂ I ₄ (AsF ₆) ₂	0.202 / 0.787	1.583 / 6.234	1.639 / 9.647		12.849		
plus excess AsF ₅ ^a			3.354 / 19.738				
S ₂ I ₄ (AsF ₆) ₂ with excess I ₂	0.150 / 0.585	2.483 / 9.781	1.224 / 7.204		17.095		
in HSO₃F							
S ₂ I ₄ (AsF ₆) ₂	0.281 / 1.095	2.273 / 8.955	2.311 / 13.602			7.63	
plus excess AsF ₅ ^a			4.488 / 26.411				7
S ₂ I ₄ (AsF ₆) ₂ with excess I ₂	0.084 / 0.328	1.385 / 5.458	0.667 / 3.926			4.986	

^a indicates total amount of AsF₅ present

4. IR and Raman Spectra of $S_2I_4^{2+}$.

Fig. 6. Calculated vibrational (MPW1PW91/3-21G*) modes of $S_2I_4^{2+}$.

Fig 7. Raman spectrum of $S_2I_4(AsF_6)_2$ in HSO_3F with an excess of AsF_5 .

Fig 8. Raman spectrum of $\text{S}_2\text{I}_4(\text{AsF}_6)_2$ in SO_2 .

5. Calculation of the Geometry of $\text{S}_2\text{I}_4^{2+}$

The structure of $\text{S}_2\text{I}_4^{2+}$ was calculated with different methods and basis sets using Gaussian 98 and Gaussian 03. A summary is given in Table 2. We note that a calculation using the recent release of the Gaussian program (Gaussian 03) is giving a different minimum structure (C_2 instead of C_{2v}), whereas the C_{2v} geometry is a saddle point, demonstrating the problems calculating the correct geometry.

The calculated dihedral angle (I1-S-S-I1) usually is greater than the experimental one. It is also noticeable, that the calculated dihedral angles with different methods and basis sets varies over a certain range. This is explained by the very shallow potential energy surface (see Fig. 9).

Table 2. Observed and calculated geometries for $S_2I_4^{2+}$, as well as the observed and calculated frequencies (cm^{-1}).

	RHF	RHF	RHF	MP2	B3PW91	B3LYP	B3LYP	MPW1	MPW1	MPW1	MPW1	MPW1
Basis Set (I)	3-21G*	3-21G*	3-21G*	3-21G*	3-21G*	3-21G*	SV(P)	3-21G*	3-21G*	6-311G*	3131-d/E	4s4p+3df/E
Basis Set (S)	3-21G*	6-31G*	6-31G* [†]	3-21G*	3-21G*	3-21G*	SV(P)	3-21G*	6-311+G*	6-311G*	6-31G*	6-311+G(3df)
Geometries												
S-S [Å]	1.796	1.802	1.802	1.909	1.861	1.869	1.874	1.854	1.862	1.855	1.858	1.844
S-I [Å]	3.155	3.155	3.153	3.114	3.128	3.186	3.194	3.103	3.095 3.080	3.124	3.154 3.155	2.907 3.279
I-I [Å]	2.631	2.631	2.631	2.665	2.628	2.655	2.670	2.622	2.622	2.637	2.628	2.606
D(I-I-S-S) [°]	0	0	0	0	0	0	0	0	0.22	0	0	2.82
D(I-S-S-I) [°]	104.21	103.81	104.4	100.99	116.48	117.32	112.19	110.43	107.3	110.58	110.82	107.53
Frequencies												
Nimag	1	1	1	1	0	0	0	0	0	1	0	0
ω_{12}	-107	-124	-124		27		26	23	21	-13	24	20
ω_{11}	28	22	23		36		30	32	32	25	25	26
ω_{10}	29	31	30		41		35	37	35	32	32	35
ω_9	34	33	33		43		38	41	43	36	35	36
ω_8	84	74	74		101		95	106	103	96	96	93
ω_7	152	145	145		126		123	142	144	132	127	142
ω_6	172	158	159		164		146	170	164	153	150	164
ω_5	184	173	173		198		185	201	192	183	187	196
ω_4	228	221	221		210		199	220	220	206	206	219
ω_3	257	256	256		250		228	253	253	244	240	244
ω_2	258	258	257		250		228	254	253	245	241	244
ω_1	882	868	864		762		749	774	754	762	772	773

Note: MPW1 refers to the MPW1PW91 method; DZ+P/E basis set for I is (5s5p1d)/[3s3p1d] with a quasi-relativistic pseudopotential (ECP46MWB); 3131-d/E refers to (3s,3p)/[1111,1111,1], augmented by a d polarization function with ECP46MWB; 4s4p+3df/E to (4s,4p)/[11111,11111,111,1] with ECP46MWB; D is the dihedral angle between two S_2I_2 planes in $S_2I_4^{2+}$.

Fig. 9. Calculated (MPW1PW91/3-21G*) relative Energies of $S_2I_4^{2+}$ (C_{2v}) on varying the dihedral (I-I-S-S-I) angle.

6. Estimation of S-S and I-I Bond Orders

The S-S and I-I bond orders in $S_2I_4^{2+}$ were estimated by correlation of the experimental data with known compounds (taken from Table 1 of the manuscript). The bond orders of these compounds were set by definition. We are aware that this only can be a rough correlation, because we compare very different molecules and data established by different methods and temperature. Further we simplify the situation by assuming a linear correlation in each case. However the qualitative results are all in good agreement.

The above estimated S-S bond order of 2.4 is in agreement with the bond order based on a modified Pauling equation (see manuscript and Ref. 3).

It is well known that the force constants for a single, double, and triple bond are for second row elements (e.g. carbon) are as 1 : 2 : 3. A bond is the stronger the resistant force $F = f \cdot r$ is stronger. Therefore the bond order is proportional to the force constant.

The situation becomes much more complicated for the stretching frequency, because the force constant is proportional to the square of the stretching frequency, there is no linear correlation of stretching frequency and force constant. However, a linear plot of the stretching frequencies and bond distances versus the bond order allows a rough graphical estimation of the S-S bond order in $S_2I_4^{2+}$.

7. Estimate of the Enthalpy of the Reaction $\text{S}_2\text{I}_4(\text{AsF}_6)_2 (\text{s}) + \text{I}_2 (\text{s}) \rightarrow 2 \text{SI}_3(\text{AsF}_6) (\text{s})$

The enthalpy of the reaction in Equation (1) can be estimated according to the following method.

The sublimation enthalpy of $\text{I}_2 (\text{s})$ was taken from the literature: $\Delta_f H^0(\text{I}_2, \text{g}, 298 \text{ K}) = 62.4 \text{ kJ mol}^{-1}$,¹ and the reaction enthalpy (ΔH_r) of Equation (2) was calculated as $\Delta H_r = -204.1 \text{ kJ mol}^{-1}$ at the MPW1PW91/3-21G* level (*c.f.* $\Delta H = -63 \text{ kJ mol}^{-1}$ in ref. 3). The lattice enthalpies (ΔH_L) of the salts were estimated according to the new lattice enthalpy equation (Equation (3)) by Jenkins et al.,² where α ($\text{kJ mol}^{-1} \text{ nm}$) and β (kJ mol^{-1}) are coefficients of best fit, z_+ and z_- are the respective charges on the cations and anions, ν is the number of ions per molecule and is equal to $(p+q)$ for a salt M_pX_q , and V (nm^3) is the molecular (formula unit) volume of the salt.

$$U_{\text{POT}} = |z_+||z_-|\nu \left(\frac{\alpha}{\sqrt[3]{V}} + \beta \right) \quad (3)$$

The molecular volumes (Table 3) were estimated as described below. Using $\alpha = 133.5 \text{ kJ mol}^{-1} \text{ nm}$ and $\beta = 60.9 \text{ kJ mol}^{-1}$ (1:2 salt) in Equation (3), the lattice potential energy was estimated as $U_{\text{POT}}(\text{S}_2\text{I}_4(\text{AsF}_6)_2) = 1432 \text{ kJ mol}^{-1}$ [$\text{S}_2\text{I}_4(\text{SbF}_6)_2 = 1415 \text{ kJ mol}^{-1}$] (*c.f.* $U_{\text{POT}}(\text{S}_2\text{I}_4(\text{AsF}_6)_2) = 1393 \text{ kJ mol}^{-1}$ in ref. 3).

Applying $\alpha = 117.3 \text{ kJ mol}^{-1} \text{ nm}$ and $\beta = 51.9 \text{ kJ mol}^{-1}$ (1:1 salt) in Equations (3), the lattice potential energy for $\text{SI}_3(\text{AsF}_6)$ [$\text{SI}_3(\text{SbF}_6)$] was estimated as $U_{\text{POT}} = 462 \pm 16 \text{ kJ mol}^{-1}$ [423 ± 64

kJ mol^{-1}]. Thus the enthalpy of Equation (1) was estimated as $\Delta H = 366 \pm 32 \text{ kJ mol}^{-1}$ for the AsF_6^- case [c.f $\Delta H = 356 \text{ kJ mol}^{-1}$ in ref. 3] and $456 \pm 128 \text{ kJ mol}^{-1}$ for the SbF_6^- case. The reaction enthalpies of various possible reactions in the $\text{S}_2\text{I}_4^{2+}$ system were deduced using similar methods.

8. Estimation of molecular (ion) volumes

The molecular volume of $\text{S}_2\text{I}_4(\text{AsF}_6)_2$ was taken from the X-ray crystal structure:³ $V(\text{S}_2\text{I}_4(\text{AsF}_6)_2) = 1.694/4 = 0.424 \text{ nm}^3$ [$V(\text{S}_2\text{I}_4(\text{SbF}_6)_2) = 1.774/4 = 0.444 \text{ nm}^3$].

The ion volume of SI_3^+ was estimated as follows: Upon studying the ion volumes of the series of SeX_3^+ and TeX_3^+ ($X = \text{I, Br, Cl}$), the differences of the ion volumes between MI_3^+ and MBr_3^+ ($M = \text{Se, Te}$) are almost the same, 0.051 ± 0.013 and $0.051 \pm 0.022 \text{ nm}^3$ for Se and Te, respectively. Applying their average value of $0.051 \pm 0.016 \text{ nm}^3$ to the $\text{SI}_3^+/\text{SBr}_3^+$ series, the ion volume of SI_3^+ was estimated as $0.174 \pm 0.030 \text{ nm}^3$. This value is reasonable when compared to the difference in the ion volumes of the series MI_3^+ , MBr_3^+ and MCl_3^+ ($M = \text{S, Se, Te}$). Combining the estimated ion volume of SI_3^+ with that for AsF_6^- (28), $V(\text{AsF}_6^-) = 0.110 \pm 0.007 \text{ nm}^3$ [$V(\text{SbF}_6^-) = 0.121 \pm 0.112 \text{ nm}^3$], we can estimate $V(\text{SI}_3(\text{AsF}_6)) = 0.284 \pm 0.037 \text{ nm}^3$ [$\text{SI}_3(\text{SbF}_6) 0.295 \pm 0.142 \text{ nm}^3$].

Table 3. The Estimated Ion Volumes (nm³) and Lattice Energies (kJ/mol).

	S ₄ ²⁺	S ₂ ⁺	S ₂ I ⁺	S ₂ I ₂ ⁺	SI ₂ ⁺	SI ₃ ⁺	S ₂ I ₄ ²⁺	I ₂ ⁺	I ₃ ⁺	I ₄ ²⁺	I ₅ ⁺
cation charge	2	1	1	1	1	1	2	1	1	2	1
anion charge	1	1	1	1	1	1	1	1	1	1	1
α^2	133.5	117.3	117.3	117.3	117.3	117.3	133.5	117.3	117.3	133.5	117.3
β^2	60.9	51.9	51.9	51.9	51.9	51.9	60.9	51.9	51.9	60.9	51.9
Ion Volume (nm³)	0.084	0.045	0.096	0.108	0.107	0.174	0.204	0.072	0.131	0.132	0.210
<i>V</i> (AsF₆⁻ salt) (nm³)	0.304	0.115	0.206	0.218	0.217	0.284	0.424	0.182	0.241	0.352	0.320
<i>U</i>_{POT} (kJ/mol)	1557	586	501	494	494	461	1432	518	481	1500	447
<i>Lattice Energies (kJ/mol)</i>²	1557	541±36							481±25		447±25
<i>V</i> (Sb₂F₁₁⁻ salt) (nm³)	0.538	0.272	0.323	0.335	0.334	0.401	0.658	0.299	0.358	0.586	0.437
Lattice Enthalpy (kJ/mol)	1350	466	446	442	442	422	1286	455	434	1323	413
<i>U</i>_{POT} (kJ/mol)	1343	462	441	437	437	417	1279	451	429	1315	408

Note: (1) Anion volumes: *V*(AsF₆⁻) = 0.110 ± 0.007 nm³, *V*(SbF₆⁻) = 0.121 ± 0.012, *V*(Sb₂F₁₁⁻) = 0.227 ± 0.020 nm³ taken from Ref. 2.

(2) The estimated cation volume for S₄²⁺, S₂⁺, I₂⁺, I₃⁺, I₄²⁺ and I₅⁺ taken from Ref. 1, S₂I₄²⁺ from X-ray structure; SI₃⁺ was estimated above; others as follows:

(3) S₂N⁺ (0.060 ± 0.009 nm³) < S₂I⁺ < I₃⁺ (0.131 ± 0.007 nm³); S₄²⁺ (0.084 nm³) < S₂I₂⁺ < I₄²⁺ (0.132 ± 0.013 nm³); SI₂⁺ ~ 1/2 (S₂I₄²⁺) (0.104 nm³)

9. Calculated Geometries of Sulfur, Iodine and Sulfur-Iodine Species

Methods and basis sets used: A = MPW1PW91/3-21G*, B = C = MPW1PW91/6-311+G(d),
D = CCSD/SDB-cc-pVTZ.

Table 4. Calculated Geometries (Å and °) of Possible Sulfur Species in $S_2I_4^{2+}$ Solution.

	S_4^{2+}			S_2^+		
	A	B/C	D	A	B/C	D
S-S	1.818	2.044	2.032	1.817	1.825	1.831
S-S-S	90.0	90.0	90.0	-	-	-
NIMAG	0	0	-	0	0	-

NIMAG = number of imaginary frequencies

Table 5. Calculated Geometries (Å and °) of Possible Iodine Species in $S_2I_4^{2+}$ Solution.

	I_2			I_2^+			I_4^+			I_3^+			I_5^+		
	A	B/C	D	A	B/C	D	A	B/C	D	A	B/C	D	A	B/C	D
I-I	2.684	2.700	2.690	2.607	2.620	2.598	2.611	2.624	2.608	2.678	2.697	2.688	2.676	2.692	2.687
							3.340	3.373	3.349				2.932	2.964	2.941
I-I-I	-	-	-	-	-	-	90.0	90.0	90.0	107.3	107.0	109.5	104.5	104.5	104.9
													180.0	180.0	176.2
NIMAG	0	0	-	0	0	-	0	0	-	0	0	-	1	1	-

Table 6. Calculated Geometries (Å and °) of Possible Sulfur-Iodine Species in $\text{S}_2\text{I}_4^{2+}$ Solution.

	S_2I^+			SI_2^+			SI_3^+			S_2I_2^+		
	A	B/C	D	A	B/C	D	A	B/C	D	A	B/C	D
S-S	1.862	1.870	1.877	-	-	-	-	-	-	2.048	2.056	2.021
S-I	2.392	2.407	2.373	2.348	2.357	2.335	2.423	2.435		2.350	2.364	2.371
							2.423	2.437	2.409			
							2.423	2.437				
I-S-I	-	-	-	111.6	111.3	109.62	107.2	107.1		-	-	-
							107.4	107.4	105.87			
S-S-I	116.5	116.5	114.13	-	-	-	107.4	107.4		112.0	112.3	101.36
							-	-	-			
NIMAG	0	0	-	0	0	-	0	0	-	0	0	-

10. Visualization of Sulfur, Iodine and Sulfur-Iodine Species Calculated on MPW1PW91/6-311+G* Level

$C_2 S_2 I_4^{2+}$

$C_{2v} S_2 I_4^{2+}$

S_4^{2+}

I_4^{2+}

I_3^+

I_5^+

$S_2 I^+$

SI_2^+

SI_3^+

$S_2 I_2^+$

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