Preparation, X-ray Crystal Structure Determination, Lattice Potential Energy, and Energetics of Formation of the Salt $S_4(AsF_6)_2 \cdot AsF_3$ Containing the Lattice-Stabilized Tetrasulfur [2+] Cation. Implications for the Understanding of the Stability of M_4^{2+} and M_2^{+} (M = S, Se, and Te) Crystalline Salts

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$S_4(AsF_6)_2 \cdot AsF_3$ was prepared by the reaction of sulfur with arsenic pentafluoride in liquid AsF_3 (quantitatively) and in anhydrous HF in the presence of trace amounts of bromine. A single-crystal X-ray structure of the compound has been determined: monoclinic, space group $P2_1/c$, $Z = 4$, $a = 7.886(1)$ Å, $b = 9.261(2)$ Å, $c = 19.191(3)$ Å, $\beta = 92.82(1)°$, $V = 1399.9(4)$ Å^3, $T = 293$ K, $R_1 = 0.052$ for 1563 reflections ($I > 2\sigma(I)$ 1580 total and 235 parameters). We report a term-by-term calculation of the lattice potential energy of this salt and also use our generalized equation, which estimates lattice energies to assist in probing the homopolyatomic cation thermochemistry in the solid and the gaseous states. We find $S_4(AsF_6)_2 \cdot AsF_3$ to be more stable ($\Delta_f H°[S_4(AsF_6)_2 \cdot AsF_3,c] \approx -4050 \pm 105$ kJ/mol) than either the unsolvated $S_4(AsF_6)_2$ ($\Delta_f H°[S_4(AsF_6)_2,c] \approx -3104 \pm 117$ kJ/mol) by 144 kJ/mol or two moles of S_2AsF_6 (c) and AsF_3 (l) by 362 kJ/mol. The greater stability of the S_4^{2+} salt arises because of the greater lattice potential energy of the 1:2 solvated salt (1734 kJ/mol) relative to twice that of the 1:1 salt (2 × 541 = 1082 kJ/mol). The relative lattice stabilization enthalpies of M_4^{2+} ions relative to two M_2^+ ions (i.e., in $M_4(AsF_6)_2$ (c) with respect to two M_2AsF_6 (c) (M = S, Se, and Te)) are found to be 218, 289, and 365 kJ/mol, respectively. Evaluation of the thermodynamic data implies that appropriate presently available anions are unlikely to stabilize M_2^+ in the solid phase. A revised value for $\Delta_f H°[Se_4(AsF_6)_2,c] = -3182 \pm 106$ kJ/mol is proposed based on estimates of the lattice energy of $Se_4(AsF_6)_2$ (c) and a previously calculated gas-phase dimerization energy of $2Se_2^+$ to Se_4^{2+}.

Introduction

Considerable progress[1−5] has been made in the characterization and rationalization of the homopolyatomic cations of group 16. Nevertheless, numerous puzzling observations remain. These include the fact that while S_n^{2+} (n = 4, 8, 19) cations have been prepared, the sulfur analogues of Se_{10}^{2+},[6,7] Se_{17}^{2+},[3] and Te_6^{4+} [8] and several other recently prepared tellurium homopolyatomic cations[3] have not. An attempt to make a thermochemical analysis of this area of chemistry is hampered because of the lack of gas-phase thermodynamic data, and any attempts to extrapolate the known (or related) data are fraught with uncertainty. Although the sulfur cations are found in stable salts of weakly basic anions such as AsF_6^-, $Sb_2F_{11}^-$, and SO_3F^-, the corresponding salts of $AlCl_4^-$ and $Al_2Cl_7^-$ have not been isolated.[9] The intense blue color given on oxidation of sulfur, and associated with S_8^{2+}, has been ascribed to the radical cation S_5^+,[10,11] although exactly how S_8^{2+} and S_5^+ are related has not yet been completely elucidated and analogous Se_5^+ has not been detected. Another radical has been identified in solutions by electron spin resonance (ESR) spectroscopy and has been assigned as both S_7^+ [11,12] and S_8^+.[13] S_4^+, S_8^+, and possibly S_{12}^{2+}, S_2^+, and S_4^{2+} were proposed as products of the anodic oxidation of sulfur in NaCl−$AlCl_3$ melts at 423 K.[14]

Clearly, many of these observations could possibly be accounted for once a fuller understanding of the energetics of the group 16 homopolyatomic cations, in all phases including

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solution, is established. This aim is probably best achieved by means of a concerted approach, such as the one we are adopting. This involves the use of a combination of preparative/synthetic investigations coupled with associated calorimetric studies and crystallographic determinations leading to computational studies at the appropriate *ab initio* level to obtain any relevant and experimentally unavailable ancillary gas-phase data.[15−17] It has proved possible to mount an extensive and systematic study[16,17] of the effect of inclusion of electron correlation and of the modification of the basis set size, on the results of computation of the dimerization enthalpy of $2M_2^+$ (g) → M_4^{2+} (g) (M = S, Se). Such studies now place us in a good position to understand the requirements for making reliable *ab initio* calculations of gas-phase data for other systems. In addition, lattice enthalpies can now be estimated more readily by our generalized equation,[18−20] which was derived as an extension of Bartlett's equation[21] that was only applicable to 1:1 salts.

In this paper we report the preparation, X-ray crystal structure determination, and energetics of the salt $S_4(AsF_6)_2 \cdot AsF_3$. This leads us to an estimate of the energetics associated with the AsF_3 "solvation" of the parent $S_4(AsF_6)_2$ salt. Unfortunately, the $S_4(AsF_6)_2 \cdot AsF_3$ salt of interest, like the related salt $S_4(AsF_6)_2 \cdot 0.6SO_2$, is an unsuitable candidate for fluorine bomb calorimetry because of the instability with respect to loss of solvent molecules on handling and because of the resulting uncertainty in the exact formulation of the sample. Therefore, direct experimental determination of the enthalpies of formation of such systems is not possible. However, having determined the X-ray crystal structure of $S_4(AsF_6)_2 \cdot AsF_3$, we are able to make an estimate of the lattice enthalpy from the X-ray parameters by an extended term-by-term calculation reported below. In addition, we have recently calculated a converged average gas-phase dimerization enthalpy,[22] $\Delta H(1)$, of −257 kJ/mol for the dissociation of S_4^{2+} (g) to $2S_2^+$ (g):

$$S_4^{2+}\ (g) \rightarrow 2S_2^+\ (g) \qquad \Delta H(1) \tag{2}$$

The corresponding values of $\Delta H(1)$ for Se[17] is −199 kJ/mol and for Te[23] is −137 kJ/mol. It is, however, S_4^{2+}, and not S_2^+, that is found in the solid state, as for example in $S_4(AsF_6)_2 \cdot 0.6SO_2$,[24] $(S_7X)_4S_4(AsF_6)_6$ (X = Br[25] and I[24,26]), $S_4(Sb_2F_4)(Sb_2F_5)(SbF_6)_5$,[27] and now reported in $S_4(AsF_6)_2 \cdot AsF_3$ (this work). We show, in this study that the tetrasulfur [2+] cation is *lattice-stabilized* in $S_4(AsF_6)_2 \cdot AsF_3$ (c) and, therefore, by implication, likely to be so in other S_4^{2+}-containing salts.

In addition, on the basis of our previously determined standard enthalpy of formation of $Se_4(AsF_6)_2$ (c) and our earlier estimates of corresponding lattice energies, we showed that $Se_4(AsF_6)_2$ (c) was only marginally more stable than $2Se_2AsF_6$ (c) ($\Delta H(2)$ = 3 kJ/mol).[28]

$$Se_4(AsF_6)_2\ (c) \rightarrow 2Se_2(AsF_6)_2\ (c) \qquad \Delta H(2) \tag{3}$$

Similar studies[28] showed $Te_4(AsF_6)_2$ (c) to be stable relative to $2Te_2AsF_6$ (c) by 244 kJ/mol. Se_4^{2+}, not Se_2^+, and Te_4^{2+}, not Te_2^+, have been found in the solid state in a variety of salts.[2] However, Te_8^{4+} [29] and polymeric $(Te_4^{2+})_\infty$[3] are formed with the less basic $VOCl_4^{2-}$ and $Bi_2Cl_8^{2-}$ anions, respectively. On the other hand, is it possible to stabilize any M_2^+ salts (M = S, Se, Te) sufficiently [cf. $O_2^+AsF_6^-$ [30]] with a suitable large nonbasic anion? A rationalization of such observations and of the inconsistent trends estimated from the experimental enthalpies of formation for the $Se_4(AsF_6)_2$ and $Te_4(AsF_6)_2$ salts is therefore also the subject of this study.

Experimental Section

Caution! Anhydrous HF causes severe burns. All manipulations should be carried out in a fume hood. Protective clothing, safety glasses, and face shield should be worn when working with liquid HF or arsenic fluorides, which react with water to produce HF. If skin contact is suspected, the exposed area should be immediately irrigated with large amounts of flowing water and, after thorough washing (at least 15 min), massaged with calcium gluconate gel.[31] Seeking medical treatment is recommended. The immediate accessibility of an HF antidote gel is indispensable.

Materials and General Procedures. Arsenic pentafluoride (Ozark-Mahoning) and fluorine (Air Products) were used as received. Sulfur (Fisher Scientific, precipitated) was vacuum-dried before use. Bromine (Fisher Scientific) and arsenic trifluoride (Ozark-Mahoning) were vacuum-distilled and stored over P_4O_{10} and NaF, respectively. Hydrogen fluoride (Matheson, anhydrous, 99%) was doubly distilled and stored

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$$U_{POT}(M_pX_q) = |z_+z_-|\nu[\alpha V^{-1/3} + \beta] = 2I[\alpha V^{-1/3} + \beta] \tag{1}$$

where z_+ and z_- are the charges on the cation M^{q+} and anion X^{p-}, respectively, ν is the number of ions present in the lattice ($=p + q$), V is the volume of the formula unit M_pX_q in the crystalline lattice ($=V_{cell}/Z$, where V_{cell} is the volume of the unit cell and Z is the number of molecules (formula units) per cell), and in the alternative formulation, I is the ionic strength term defined as $(^1/_2)\sum n_k z_k^2$ where n_k is the number of ions of type k in the lattice bearing charge z_k and the summation over k is taken over all the ions in the lattice. α and β have been assigned[19] specific values depending on the stoichiometry of the salt M_pX_q. This equation then permits lattice energies to be assigned directly (and preferably) using the crystal structure molecular volume (V) data as determined experimentally from crystallographic determinations. Alternatively, if V_{cell} and Z are not available, V is determined from the estimated individual close-packing effective ion volumes V_+ and V_- (defined to be ion-additive such that $V = (pV_+ + qV_-)$. The values of V_+ and V_- (written in this paper as $V(M^{q+})$, $V(X^{p-})$) have recently been assigned.[19] Where values of V_+ and V_- are not listed in ref 19 it is possible to infer approximate volumes by considering size relationships between the ions that are listed. For example, from Table 6 in ref 19 we have $V(Br_2^+) = 0.057$ nm^3 and $V(SN^+) = 0.032$ nm^3, and since we can anticipate that $V(Br_2^+) > V(S_2^+) > V(SN^+)$, we can estimate that $V(S_2^+) \approx 0.045$ nm^3.

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over $K_2NiF_6{\cdot}KF$ (Ozark-Mahoning) in a prefluorinated FEP vessel (Fluorocarbon-Bunnel Plastics Division, Penntube products, Mickleton, NJ). This vessel was connected to a Teflon needle valve (SS 6393-11 Chemfluor & Elast-O-Fluor, Norton Co., purchased from Cole-Parmer Instrument Co.) with a Kel-F lid and aluminum compression fittings.

The reactions were carried out in prefluorinated FEP vessels (20 cm long, $^3/_4$ in. o.d. and 2 mm thick wall; tubes with thinner walls were found to collapse when subjected to dynamic vacuum) containing a Teflon coated magnetic stir bar. Any apparatus coming in contact with anhydrous HF was carefully dried and fluorinated before use. Sulfur and the product $S_4(AsF_6)_2{\cdot}AsF_3$ were manipulated in a Vacuum Atmospheres Dri-Lab equipped with a Dri-Train (HF-493) and an internal circulating drying unit containing 1 kg of 3 Å molecular sieves. Infrared, FT Raman spectra, and powder photographs were obtained as previously described.[32] The elemental analysis was carried out by Beller Mikroanalytisches Laboratorium, Göttingen, Germany. General techniques used are described in ref 33.

Preparation of $S_4(AsF_6)_2{\cdot}AsF_3$ in Anhydrous HF or Liquid AsF_3. We previously prepared $S_4(AsF_6)_2{\cdot}0.6SO_2$ quantitatively by the reaction of sulfur, AsF_5, and a trace amount of bromine in SO_2.[5,24] The salt $S_4(AsF_6)_2{\cdot}AsF_3$ was similarly synthesized in anhydrous HF. In a typical reaction, in a prefluorinated FEP vessel, anhydrous hydrogen fluoride (ca. 8 g) was condensed onto elemental sulfur (1.83 g, 7.13 mmol) followed by a large excess of AsF_5 (12.20 g, 71.80 mmol) relative to the amount indicated by eq 4, and a trace quantity of Br_2 (0.05 mmol).

$$^1/_2S_8\ (s) + 3AsF_5\ (g) \rightarrow S_4(AsF_6)_2{\cdot}AsF_3\ (c) \tag{4}$$

A dark-blue solution and solid were observed on warming the mixture to room temperature. The contents were stirred for 1 day, producing a light-blue solution over a white precipitate indicative of $S_4(AsF_6)_2$, which indicated that the oxidation reaction was complete. Thermal cycling of the mixture (4 cycles/day) between room temperature and 0 °C for 3 days gave a pale-blue crystalline solid containing some crystals. Great care was taken in removing the solvent (ca. 6 h, to constant weight) as to not destroy the crystals by expanding the last portion of volatile material into the line, isolating the reaction vessel, evacuating the line, etc. until the pressure above the crystals was zero. This gave a dark-blue crystalline solid and dark-blue powder, implying some decomposition to $S_8(AsF_6)_2$. An IR study of the volatile material showed peaks attributable to HF,[34,35] SiF_4 (trace),[36] AsF_5,[37] and AsF_3.[38] Close inspection of the material under a microscope showed most of the colorless crystals to be coated with an amorphous dark-blue material, which is likely $S_8(AsF_6)_2$. Several crystals were quickly mounted in rigorously dried glass capillaries under dry nitrogen and were identified as $S_4(AsF_6)_2{\cdot}AsF_3$ by X-ray crystallography. An amount of 7.23 g of product was recovered, giving an 80% yield based on the formation of $S_4(AsF_6)_2{\cdot}AsF_3$ or 101% yield based on $S_4(AsF_6)_2$. The bulk product gave a good X-ray powder diffraction pattern (Co Kα radiation) and was indexed against single-crystal data, consistent with the presence of both $S_4(AsF_6)_2{\cdot}AsF_3$ and $S_8(AsF_6)_2$. Powder photographic data have been deposited as Supporting Information. IR (cm^{-1}): 702(s), 665(w), 390(m) [$\nu_1(AsF_6^-)$][39] and 540(w) [$\nu_5(S_4^{2+})$].[5,40] FT-Raman (cm^{-1}) (deposited), relative intensities in parentheses:[41] 725 (0.5), 698 (0.4), 687 (2.0), 672 (1.4) [$\nu_1(AsF_6^-)$] and 552 (1.0), 546 (1.3) [$\nu_2(AsF_6^-)$];[39,42] 606 (1.4) [$\nu_3(S_4^{2+})$],[5,40] 590 (10) [$\nu_1(S_4^{2+})$], 373 (1.2) [$\nu_2(S_4^{2+})$, $\nu_5(AsF_6^-)$], and 119 (1.1) [lattice mode]. An almost identical FT Raman spectrum was obtained for $S_4(AsF_6)_2{\cdot}xSO_2$ ($x < 1$), both spectra deposited. The weak Raman spectrum of AsF_3 of solvation may be masked by the stronger AsF_6^- peaks. Anal. Calcd for $S_4(AsF_6)_2{\cdot}AsF_3$ (and $S_4(AsF_6)_2$): S, 20.10 (25.35); As, 35.23 (29.61); F, 44.67 (45.05). Found: S, 23.49; As, 34.92; F, 41.90.

Table 1. Crystallographic Data for $S_4(AsF_6)_2{\cdot}AsF_3$

chemical formula	$S_4(AsF_6)_2{\cdot}AsF_3$	cryst size, mm	0.14 × 0.23 × 0.31
fw	638.00	$F(000)$	1192
cryst syst	monoclinic	reflns for lattice parameters	25; θ 12−14°
space group	$P2_1/c$	abs correction	1.51−0.68
a, Å	7.886 (1)	2θ range	θ 3−23°
b, Å	9.261 (2)	scan type	$\omega-2\theta$
c, Å	19.191 (3)	hkl range	−8 to 8, 0 to 10, 0 to 20
β, deg	92.82 (1)	no. unique reflns	2022
V, Å^3	1399.9 (4)	no. obsd reflns [$I > 2\sigma(I)$]	1580
Z	4	no. parameters	235
temp, K	293 (2)	R_1[a]	0.052
D_{calcd}, g cm^{-3}	3.027	wR_2[b]	0.144
μ, cm^{-1}	75.419	GOF	1.796
λ, Å	0.70926		

[a] $R_1 = \sum||F_0| - |F_c||/\sum|F_0|$. [b] $w = 1/\{\sigma^2(F_0^2) + [(0.118)P]^2 + (6.5915)P\}$. $P = [2F_c^2 + \max(F_o^2,0)]/3$.

$S_4(AsF_6)_2{\cdot}AsF_3$ was prepared in 98% yield by means of the reaction of sulfur (0.93 g, 3.64 mmol) with a large excess AsF_5 (6.35 g, 37.40 mmol) in liquid AsF_3 (16.9 g) and a trace amount of bromine (0.04 mmol) in a two-bulbed glass vessel. A red solution over a crystalline white material was observed within 12 h at room temperature. Upon slow removal of the solvent, the white product (4.55 g, 4.65 g calculated) changed color and assumed a pale-blue color, interpreted as being indicative of the presence of a trace amount of $S_8(AsF_6)_2$. The FT Raman spectrum and powder photograph of $S_4(AsF_6)_2{\cdot}AsF_3$ made in AsF_3 were identical to that obtained from the salt made in HF.

Thermal Stability of Solid $S_4(AsF_6)_2{\cdot}AsF_3$. The $S_4(AsF_6)_2{\cdot}AsF_3$ salt prepared in AsF_3 can be stored over a period of at least 1 year, without any noticeable decomposition, in a sealed FEP tube under nitrogen, which in turn is sealed in a glass tube at −20 °C. Samples stored under the same conditions at room temperature and −10 °C started to exhibit signs of decomposition after only 2 weeks and 1 month, respectively. Decomposition was indicated by the formation of a yellow material, most likely to be elemental sulfur. Evacuation of a 3.8 g sample of $S_4(AsF_6)_2{\cdot}AsF_3$ for 1 h (80 h) through a liquid N_2 cooled tube led to loss of 0.01 g (0.19 g) AsF_3 or 1.3% (31%) of the AsF_3 of solvation (IR) but without noticeable change in crystallinity. Heating of $S_4(AsF_6)_2{\cdot}AsF_3$ at 45 °C for 4 h resulted in decomposition of the sample as indicated by the presence of sulfur. Crystals of $S_4(AsF_6)_2{\cdot}0.6SO_2$ collapsed to a pale-blue powder when subjected to a dynamic vacuum for less than 10 min at room temperature. Both salts become darker blue upon grinding, which indicates some disproportionation, decomposition, or else a reaction with moisture to give products containing $S_8(AsF_6)_2$.

X-ray Crystallography. The data for $S_4(AsF_6)_2{\cdot}AsF_3$ were collected at 293 K on a CAD4 four-circle diffractometer with an $\omega/2\theta$ scan mode with graphite-monochromated Mo Kα radiation. Crystallographic details are summarized in Table 1. The data were reduced to a standard scale[43] and corrected for Lorentz polarization and absorption (range 1.51−0.68) effects.[44] The structure was solved by direct methods using SHELXS.[45] The positions of all atoms were derived from an E-map, and the structure was refined with SHELX97,[46] $R_1 = 0.052$, w$R_2 = 0.144$ for 1563 reflections $I > 2\sigma(I)$ 1580 total and 235 parameters, with anisotropic thermal parameters on all atoms. One AsF_6^- group

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Table 2. Atomic Coordinates ($\times10^4$) and Equivalent Isotropic Displacement Parameters ($A^2 \times 10^3$) for $S_4(AsF_6)_2{\cdot}AsF_3$, with Estimated Standard Deviations in Parentheses[a]

atom	*x*	*y*	*z*	U_{eq}
As1	2327(2)	947(1)	4171(1)	27(1)
F11	2318(8)	627(8)	3282(3)	48(2)
*F12	3580(5)	2330(3)	4048(18)	80(9)
*F121	2540(6)	2710(3)	4070(2)	122(16)
F13	2295(12)	1268(9)	5059(3)	69(2)
*F14	1300(6)	−540(5)	4290(2)	110(2)
*F141	1820(6)	−720(4)	4313(14)	88(15)
*F15	4130(5)	60(4)	4307(16)	98(16)
*F151	4320(4)	700(7)	4200(2)	170(3)
*F16	170(6)	1130(6)	4120(3)	105(19)
*F161	590(6)	1810(5)	4050(3)	110(2)
As2	2648(1)	6604(1)	2723(1)	29(1)
F21	3772(10)	5294(10)	3132(5)	78(3)
F22	1382(10)	6813(10)	3406(4)	66(2)
F23	4085(10)	7774(10)	3053(6)	86(3)
F24	3865(11)	6340(11)	2025(4)	80(3)
F25	1523(10)	7856(8)	2291(4)	67(2)
F26	1227(8)	5371(7)	2395(4)	50(2)
S1	2481(3)	824(3)	1927(1)	29(1)
S2	2482(4)	1703(3)	976(1)	35(1)
S3	2146(4)	3572(3)	1412(1)	34(1)
S4	2185(3)	2682(3)	2354(1)	30(1)
As3	2723(2)	7297(1)	5316(1)	38(1)
F31	4145(11)	6647(11)	4782(4)	76(3)
F32	1042(11)	6508(11)	4913(4)	79(3)
F33	3042(13)	6003(9)	5937(4)	75(3)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor. Entries with an asterisk indicate that the disordered AsF_6^- is labeled as As1 and that each pair, F12 and F121, F14 and F141, F15 and F151, F16 and F161, has a 50:50% occupancy.

was disordered in two positions about an F−As−F axis. The structure was refined with different occupancies of the AsF_3 solvent molecule. The best, most reasonable fit was that for 100% occupancy. Atomic coordinates (Table 2) and selected interatomic distances (Table 3) are given here, while complete crystallographic details are included in the Supporting Information. Calculations were performed using the PC implementation of the NRCVAX program package.[47] Figure 1 gives details of the coordination found around the S_4^{2+} ion in the salt $S_4(AsF_6)_2{\cdot}AsF_3$, and Figure 2 provides details of the AsF_3 environment found in the salt.

Lattice Potential Energy and Associated Enthalpy Calculations

Estimate of the Enthalpy of Formation of $S_4(AsF_6)_2{\cdot}AsF_3$ and Its Relative Stability with Respect to $S_4(AsF_6)_2$. "Solvate" Stabilization. There is no crystal structure determination available for $S_4(AsF_6)_2$ because $S_4(AsF_6)_2$ crystallizes in the solvated form (e.g., with 1.0 AsF_3 (this work) or with 0.6 SO_2[24]). Accordingly, there is therefore no unit cell volume data from which to directly estimate the lattice energy of the parent salt. However, because we are able to obtain a value for the effective ion volume of S_4^{2+} (see later) and because we know the corresponding volume of the AsF_6^- ion,[19] we can use eq 1 (see ref 20) to obtain the lattice potential energy of $S_4(AsF_6)_2$ and hence compare it with the lattice potential energy of the solvated salt $S_4(AsF_6)_2{\cdot}AsF_3$. For the latter we have calculated the enthalpy change, $\Delta H(2)$, involved in the loss of 1.0 AsF_3 (as liquid) using the cycle in Figure 3. For this calculation we need to obtain the total lattice potential energy of the solvated salt. Using the crystal structure reported in this paper, we use the term-by-term approach to carry out an extended calculation.

In general, the total lattice potential energy, U_{POT}, of a salt M_aX_b is defined as

$$U_{POT} = U_{ELEC} - U_R + U_{dd} + U_{dq} - U_z \qquad (5)$$

where U_{ELEC} is the electrostatic energy of the lattice, U_R the closed-shell repulsion (or Born) term, U_{dd} the dipole-induced dipole dispersion energy (London energy term), U_{dq} the dipole-induced quadrupole energy, and U_z the zero-point energy. The corresponding lattice enthalpy, ΔH_L, for the salt is related to the above lattice potential energy $U_{POT}(M_aX_b)$ by the equation[48]

$$\Delta H_L = U_{POT}(M_aX_b) + [a((^1/_2)n_M{}^{b+} - 2) + b((^1/_2)n_X{}^{a-} - 2)]RT \qquad (6)$$

where $n_M{}^{b+}$ and $n_X{}^{a-}$ are both equal to 3 for monoatomic ions, 5 for linear polyatomic ions, and 6 for nonlinear polyatomic ions. In the case of $S_4(AsF_6)_2{\cdot}AsF_3$, ΔH_L is related to $U_{POT}[S_4(AsF_6)_2{\cdot}AsF_3]$ by the equation

$$\Delta H_L = U_{POT}[S_4(AsF_6)_2{\cdot}AsF_3] + 4RT \qquad (7)$$

Taking the crystal structure data found for $S_4(AsF_6)_2{\cdot}AsF_3$, we calculated the electrostatic energy of the crystal U_{ELEC} to be 1849 kJ/mol (using the method of Bertaut[49] and the modification by Templeton,[50] also discussed by Jenkins et al.[51−54]) using a program kindly supplied by Prof. Neil Bartlett to one of us (S.P.). The established procedure, described by Bartlett et al.[21] (and used by S.P. and J.P. for the calculation of lattice potential energy of $S_3N_2(AsF_6)_2$), was followed[55] for the remainder of this calculation. The repulsion energy U_R was calculated using the Born−Mayer[56] potential:

$$U_R = b\{\sum_{i\neq j}[(1 + q_i/n_i + q_j/n_j)\exp(r_i + r_j - r_{ij})/\rho]\} \qquad (8)$$

where *n* is the number of electrons in the outer shell of the ion (e.g., 7.327 for a fluorine atom with a charge of −0.327), r_i and r_j are the basic radii of the ions *i* and *j*, which were kept constant in these calculations, $b = 10^{-12}$ erg molecule^{-1}, and $\rho = 0.333$ Å. The basic radius of As in AsF_3 was calculated using the energy minimization criterion $(\partial U/\partial r) = 0$ to ensure that the lattice energy calculated corresponded to an energy minimum, following the procedures of Jenkins and Pratt,[52,57] such that

$$\begin{aligned} U_{ELEC} + 6U_{dd} + 8U_{qd} = {} & \{\exp(2r_S/\rho)\}\sum_{SS} + \\ & \{\exp((r_S + r_F)/\rho)\}\sum_{SF} + \{\exp((r_S + r_{As,cryst})/\rho)\}\sum_{SAs,cryst} + \\ & \{\exp((r_S + r_{F,cryst})/\rho)\}\sum_{SF,cryst} + \{\exp(2r_F/\rho)\}\sum_{FF} + \\ & \{\exp((2r_F)/\rho)\}\sum_{FF,cryst} + \{\exp((r_F + r_{As,cryst})/\rho)\}\sum_{FAs,cryst} + \\ & \{\exp((r_{F,cryst} + r_{As,cryst}\ \rho)\}\sum_{F,cryst\ As,cryst} + \\ & \{\exp(2r_{F,cryst}/\rho)\}\sum_{F,cryst\ F,cryst}\ ] \end{aligned} \qquad (9)$$

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Table 3. Selected Interatomic Distances (Å) and Angles (deg) in $S_4(AsF_6)_2 \cdot AsF_3$ (Estimated Standard Deviations in Parentheses)[a]

Bond Distances											
interionic S_4^{2+}				interionic AsF_6^-				interionic AsF_3			
S1−S2	1.999(4)	S2−S3	1.946(4)	As2−F21	1.675(8)	As2−F24	1.704(8)	As3−F31	1.667(8)	As3−F33	1.700(7)
	2.023(3)[b]		2.011(3)[b]	As2−F22	1.697(8)	As2−F25	1.657(7)	As3−F32	1.670(8)		
S1−S4	1.924(4)	S3−S4	1.986(4)	As2−F23	1.669(8)	As2−F26	1.700(6)				
	2.000(3)[b]		2.011(3)[b]								
Bond Angles											
interionic S_4^{2+}											
S2−S1−S4	91.7(2)	S2−S3−S4	91.5(2)								
	90.16[b]		90.15[b]								
S1−S2−S3	87.9(2)	S1−S4−S3	88.9(2)								
	89.51[b]		90.14[b]								
interionic AsF_6^-											
F21−As2−F22	92.2(4)	F22−As2−F26	87.7(4)	F21−As2−F26	90.6(4)	F24−As2−F25	90.9(5)				
F21−As2−F23	87.6(4)	F23−As2−F24	89.6(5)	F22−As2−F23	92.7(4)	F24−As2−F26	89.9(4)				
F21−As2−F24	87.7(5)	F23−As2−F25	94.2(5)	F22−As2−F24	177.6(4)	F25−As2−F26	87.6(4)				
F21−As2−F25	177.7(4)	F23−As2−F26	178.2(4)	F22−As2−F25	89.2(4)						
interionic AsF_3											
F31−As3−F32	95.8(4)	F32−As3−F33	95.9(5)								
F31−As3−F33	95.5(4)										
Bond Distances											
contacts[c]											
S1−F11	2.622(5)	S3−F26	2.678(10)	S2−F13	2.633(6)	S4−F23	3.099(15)	*S3−F14	3.118(24)	*As3−F141	2.775(23)
S1−F21	3.022(6)	S4−F11	2.662(5)	S2−F31	3.072(22)	S4−F25	3.039(13)	*S3−F16	3.189(18)	*As3−F151	3.132(21)
S1−F22	3.230(12)	*S4−F121	3.243(16)	S2−F32	3.218(27)	S4−F26	2.688(4)	S3−F23	3.183(17)	*As3−F16	2.960(20)
S1−F25	3.052(6)	S4−F21	3.137(12)	S2−F33	2.633(6)	*As3−F12	3.099(24)	S3−F24	3.159(11)	*As3−F161	3.032(24)
S1−F33	2.638(8)	S4−F22	3.211(23)	S3−F13	2.605(4)	*As3−F14	2.944(17)				
Bond Angles											
contacts[c]											
F11−S1−F33	133.4(2)	F31−S2−S1	117(7)	F33−S1−S4	157.3(2)	*F14−S3−S2	99.7(5)				
F11−S1−S2	159.1(2)	F31−S2−S3	110.1(3)	F13−S2−F31	73.7(5)	*F14−S3−S4	118.2(7)				
F11−S1−S4	69(2)	F32−S2−F33	93.9(2)	F13−S2−F32	70.7(5)	*F16−S3−F23	141.9(3)				
F21−S1−F22	164.2(2)	F32−S2−S1	67.6(2)	F13−S2−F33	135.8(2)	*F16−S3−F24	72.1(5)				
F21−S1−F25	95.7(3)	F33−S2−S3	158(1)	F13−S2−S1	156.4(2)	*F16−S3−F26	63.1(4)				
F21−S1−F33	69.8(7)	*F13−S3−F14	68.3(8)	F13−S2−S3	66.8(1)	*F16−S3−S2	130.6(4)				
F21−S1−S4	108.3(4)	*F13−S3−F16	72.0(6)	F31−S2−F32	119.7(2)	*F16−S3−S4	126.4(5)				
F22−S1−F25	95(2)	F13−S3−F24	105.9(4)	F31−S2−F33	79.6(2)	F23−S3−F24	72.9(4)				
F22−S1−F33	104.1(7)	F13−S3−F26	132.9(3)	F23−S3−F26	102.5(6)	F26−S3−S2	156.6(2)				
F22−S1−S2	74.6(8)	F13−S2−S2	68.3(2)	F23−S3−S2	76.8(4)	F26−S3−S4	68.3(2)				
F22−S1−S4	71.5(4)	F13−S3−S4	158.4(2)	F23−S3−S4	69.1(8)	S3−F11−S2	44.8(1)				
F25−S1−F33	65(4)	*F14−S3−F16	36.9(4)	F24−S3−F26	47.6(4)	S3−F23−S4	37.1(7)				
F25−S1−S2	127.6(3)	*F14−S3−F23	172.1(2)	F24−S3−S2	146.8(2)	S3−F26−S4	43.7(1)				
F25−S1−S4	135.6(3)	*F14−S3−F24	108.3(5)	F24−S3−S4	91.6(4)						
F33−S1−S2	67.4(2)	*F14−S3−F26	83.4(6)								

[a] Symmetry transformations used to generate equivalent atoms. The bond angles and distances for the disordered AsF_6^- are reported in Supporting Information. [b] These values were corrected for the libration motions with R =1.82, weighted R = 2.30, and root-mean-square discrepancy = 0.0005 for U values. [c] The contacts marked with an asterisk have a 50% occupancy.

in which the summation between atoms/ions X and Y is

$$\sum_{XY} = \sum_{X\neq Y}\{(1 + n_X/q_X + n_Y/q_Y)\exp((r_X + r_Y - r_{XY})/\rho)\} \quad (10)$$

Summations were truncated at a value r_{ij} = 8 Å; any self-interactions involving As were neglected and r_F, the basic radius of fluorine, was taken to be 1.066 Å. "As, cryst" and "F, cryst" in eq 9 represent the As and F atoms in the AsF_3 molecule of crystallization. Charges were calculated using the electronegativity equalization procedure of Jolly and Perry[58] and found to be the following. For the ion AsF_6^-, $q_{As} = +0.964$, $q_F = -0.327$ with $q_S = +0.5$. For the solvate molecule AsF_3, $q_{As} = +0.402$, $q_F = -0.134$. The basic radii were assigned as follows: r_S (=1.147 Å), r_F in AsF_6^- (=1.066 Å), $r_{F,cryst}$ in AsF_3 (=1.006 Å). Equation 9 can be solved for the unknown term exp($r_{As,cryst}$), leading to a value $r_{As,cryst}$ = 1.604 Å. Evaluating this unknown basic radii in this way compensates for inaccuracies that may exist in other parameters utilized.[52,57] U_R was calculated to be equal to 394.7 kJ/mol. The dipole−dipole dispersion energy U_{dd} was calculated using the London[59] equation:

$$U_{dd} = (^3/_2)\sum_{i\neq j}\left[\frac{\alpha_i\alpha_j\epsilon_i\epsilon_j r_{ij}^{-6}}{\epsilon_i + \epsilon_j}\right] \quad (11)$$

where α_i is the polarizability and ϵ_i is the characteristic energy of the atom or ion i, r_{ij} is the distance between i and j, and the summations were again truncated when r_{ij} reached the value of 8 Å. The polarizabilities of sulfur and arsenic were taken from

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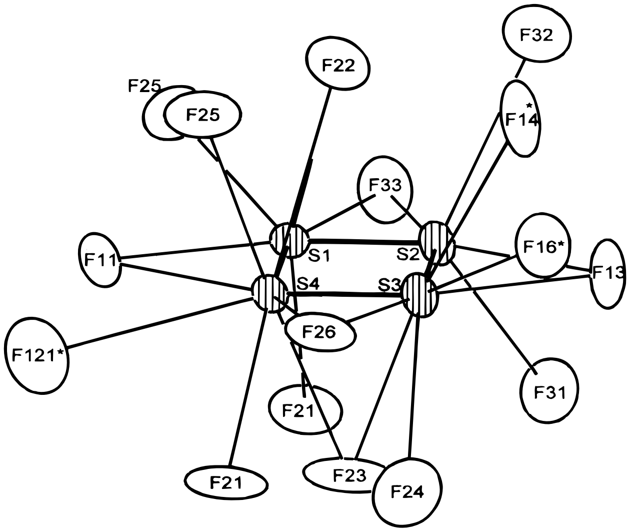

Figure 1. Coordination around the S_4^{2+} ion in the crystal of $S_4(AsF_6)_2{\cdot}AsF_3$. The fluorine atoms marked with an asterisk are disordered (i.e., correspond to 50% occupancy).

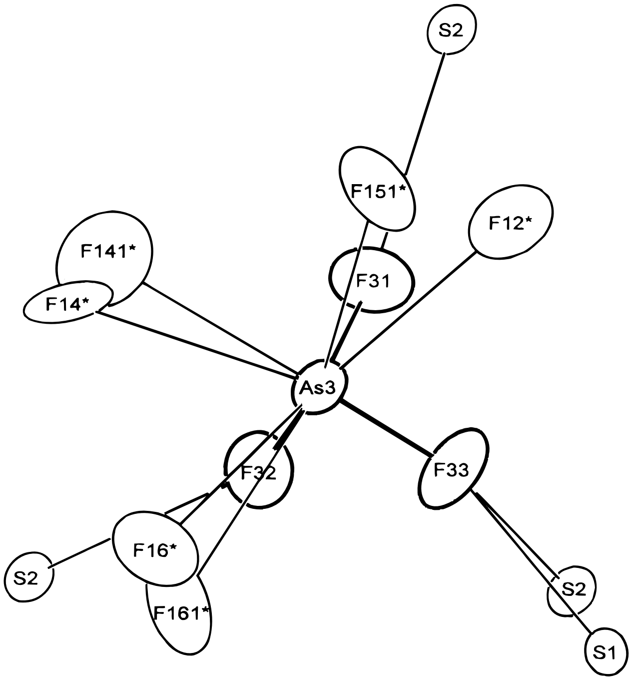

Figure 2. AsF_3 environment in the crystal of $S_4(AsF_6)_2{\cdot}AsF_3$. The fluorine atoms marked with an asterisk are disordered (i.e., correspond to 50% occupancy).

Bartlett's work[21] and took the values $\alpha_S = 1.20$ Å^3 for sulfur and $\alpha_{As} = 0.65$ Å^3 and $\alpha_F = 0.80$ Å^3 for both AsF_6^- and AsF_3, respectively. The corresponding characteristic energies were taken as $\epsilon_S = 21.06$ eV for sulfur and $\epsilon_{As} = 16.77$ eV and $\epsilon_F = 49.57$ eV for both AsF_6^- and AsF_3 (for cationic centers these correspond to 0.9 of the second ionization potential of the free atom). The dipole−quadrupole dispersion term U_{qd} was approximated to be $0.12U_{dd}$, leading to values for U_{dd} of 250.3 kJ/mol and for U_{qd} of 30.1 kJ/mol. The zero-point energy term U_z is small for systems containing these relatively massive ions and is approximated here to be 0.8 kJ /mol. The total lattice potential of the salt $S_4(AsF_6)_3{\cdot}AsF_3$ is therefore calculated (eq 5) to be 1734 kJ/mol, and the lattice enthalpy (eq 7) is hence 1744 kJ/mol.

In the thermochemical cycle of Figure 3, $\Delta H(1)$ has the value, −257 ± 8 kJ/mol. The lattice potential energies of $S_4(AsF_6)_2{\cdot}AsF_3$ (calculated above to be 1734 kJ/mol) and S_2AsF_6 (541 ± 16 kJ/mol[60]) along with[61] $\Delta_f H°[AsF_3,l] = -821$ kJ/mol and $\Delta_f H°[AsF_3,g] = -785.5$ kJ/mol (and hence $\Delta_{vap}H°[AsF_3,l] = 35.5$ kJ/mol) when used in the upper, inner cycle give $\Delta H(2) = 362$ kJ/mol. The standard enthalpy of formation of our solvated salt, $\Delta_f H°[S_4(AsF_6)_2{\cdot}AsF_3,c]$ can be estimated (using the left-hand cycle of Figure 3) to be −4050 ± 105 kJ/mol, using the calculated lattice potential energy of the salt, together with $\Delta_f H°[S_4^{2+},g] = 2318 \pm 8$ kJ/mol,[16,17] $\Delta_f H°[AsF_6^-,g] = -1919$ kJ/mol,[23] and $\Delta_f H°[AsF_3,g] = -785.5$ kJ/mol.[61] Employing this standard enthalpy of formation, $\Delta_f H°[S_4(AsF_6)_2{\cdot}AsF_3,c]$, in the outermost cycle of Figure 3 with $\Delta_f H°[S_2AsF_6,c] = -1433$ kJ/mol[15] and $\Delta_f H°[AsF_3,l] = -821$ kJ/mol also leads to a consistent value of $\Delta H(2)$ (see Figure 3) = 363 kJ/mol. Accordingly we conclude that the enthalpy required to remove the "lattice solvate" (1.0 AsF_3) from the salt and form two molecules of S_2AsF_6 is 362 kJ/mol.

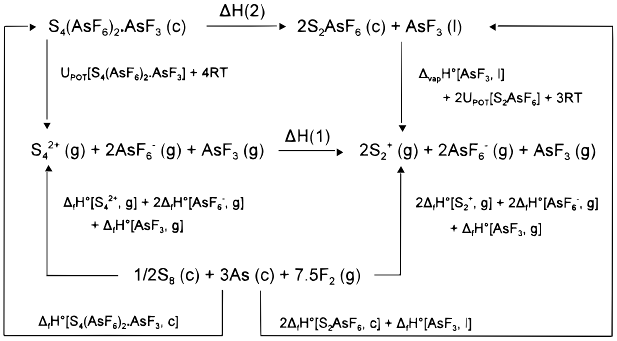

Figure 3. Thermochemical cycle for $S_4(AsF_6)_2{\cdot}AsF_3$ losing "AsF_3 solvate" molecules and forming the monocation salt.

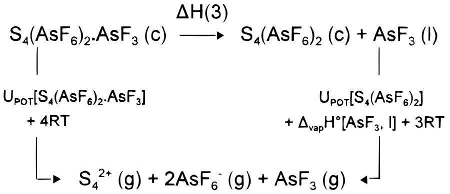

Figure 4. Thermochemical cycle for $S_4(AsF_6)_2{\cdot}AsF_3$ losing "AsF_3 solvate" molecules and forming the parent salt.

In the thermochemical cycle of Figure 4, $\Delta H(3)$ represents the removal of "lattice solvate" while retaining the (notional) parent salt $S_4(AsF_6)_2$. From the cycle,

$$\Delta H(3) = U_{POT}[S_4(AsF_6)_2{\cdot}AsF_3] - U_{POT}[S_4(AsF_6)_2] - \Delta_{vap}H°[AsF_3,l] + RT \quad (12)$$

The enthalpy change $\Delta H(3)$ of the reaction

$$S_4(AsF_6)_2{\cdot}AsF_3\ (c) \rightarrow S_4(AsF_6)_2\ (c) + AsF_3\ (l) \quad (13)$$

would, in the absence of our generalized equation, have been difficult to estimate. Crystals of $S_4(AsF_6)_2$ have not been obtained, and hence, no extended calculation (similar to the one we have described for $S_4(AsF_6)_2{\cdot}AsF_3$) can be made. On the other hand, on the basis of the X-ray crystal data for $S_4(AsF_6)_2{\cdot}AsF_3$, an extended calculation for $S_4(AsF_6)_2$ missing the solvation molecule (i.e., holes replacing AsF_3) gives a value of

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(60) The estimated value for $U_{POT}[S_2AsF_6]$ is 541 ± 16 kJ/mol (using appropriate values of α and β for MX_2 and for MX salts listed in ref 19 and assuming that $V[S_2^+] = 0.045 \pm 0.025$ nm^3; see ref 20).

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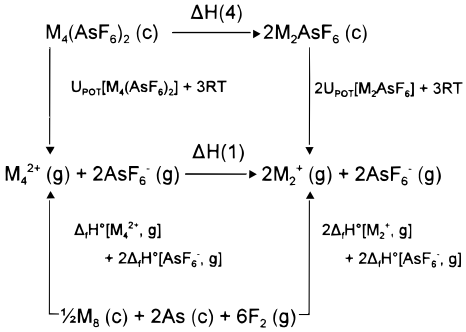

Figure 5. Thermochemical cycle for $M_4(AsF_6)_2/M_2AsF_6$ system. The standard state represented in the cycle is for M = S. In the case of M = Se and Te, 4M (c) should replace $^1/_2M_8$ (c).

1598 kJ/mol[62] for the potential energy of $S_4(AsF_6)_2$. There is also no cell volume data, and so eq 1 [see ref 20] cannot be used directly. Fortunately, it is possible to estimate the effective ion volume of S_4^{2+}.[19,63] Combining this with $2V(AsF_6^-)$[19] enables us to estimate that $U_{POT}[S_4(AsF_6)_2] = 1557$ kJ/mol (and, assuming a similar procedure for Se_4^{2+} and Te_4^{2+}, also that $U_{POT}[Se_4(AsF_6)_2] = 1544$ kJ/mol and $U_{POT}[Te_4(AsF_6)_2] = 1518$ kJ/mol[63]). Using the lattice energy of the solvated $S_4(AsF_6)_2 \cdot AsF_3$ we have calculated above and using our estimate for $\Delta_{vap}H°[AsF_3,l]$ (see Figure 3), we find $\Delta H(3) = 144$ kJ/mol (see Figure 4).

Lattice Stabilization of the Dimerized Crystalline Salt $M_4(AsF_6)_2$ with Respect to $2M_2AsF_6$ (M = S, Se, Te). We now consider the reaction

$$M_4(AsF_6)_2\ (c) \rightarrow 2M_2AsF_6\ (c) \qquad \Delta H(4), \Delta S(4), \Delta G(4) \tag{14}$$

In another publication[15] we have shown that $2S_4^+$ ions are more stable than the dimerized ion S_8^{2+} in the gas phase by some 207 kJ/mol,[15] and yet $S_8(AsF_6)_2$ (and hence the S_8^{2+}) is more stable in the crystalline lattice than $2S_4AsF_6$[15] by some 208 kJ/mol. Similarly, we have found that $2S_2^+$ ions are 257 kJ/mol more stable in the gas phase than an S_4^{2+} ion (discussed earlier). Since it is S_4^{2+} and not S_2^+ that appears to be stabilized in the solid state, we can use the cycle of Figure 5 to consider whether the S_4^{2+} will be lattice-stabilized (as in eq 14 when $\Delta H(4) > 0$). A further question of interest concerns the trends exhibited for lattice stabilization as we descend down the chalcogenide group.

We need, therefore, to evaluate $\Delta H(4)$ in the cycle for M = S, Se, and Te. First, $\Delta H(4)$ can be estimated from the upper, inner cycle of Figure 5 using the lattice energies of the two salts involved and the previously estimated $\Delta H(1)$. The lattice potential energy $U_{POT}[M_2AsF_6]$ of M_2AsF_6 is also, in the absence of crystal structure data, estimated using eq 1 and close-packing effective ion volume data.[19,63] $\Delta H(1)$ for (M = S) takes the value[17] -257 ± 8 kJ/ mol. The corresponding values for $\Delta H(1)$ for the other tetrachalcogen dications are -199 kJ/mol (M = Se)[17] and -137 kJ/mol (M = Te).[23] A value for $\Delta H(4)$ of 218 kJ/mol (M = S) is found that agrees with the value found for $[\Delta H(2) - \Delta H(3)]$ above. For M = Se, $\Delta H(4)$ was found to be 289 kJ/mol and for M = Te, $\Delta H(4) = 365$ kJ/mol, with standard deviations of approximately 34 kJ/mol. Similar magnitudes ($\Delta H(4) = 219 \pm 35$ kJ/mol (M = S), 289 ± 35 kJ/mol (M = Se), and 365 ± 35 kJ /mol) are calculated using the outer cycle of Figure 5 and utilizing the standard enthalpies of formation.[64] Standard molar entropies $S°[M_4(AsF_6)_2]$ (=588 J/K mol (M = S); =640 J/K mol (M = Se); =668 J/K mol (M = Te)) and $S°[M_2AsF_6]$ (=294 J/K mol (M = S); =320 J/K mol (M = Se); =334 J/K mol (M = Te)) can be estimated using Latimer's rules[65−67] but are clearly of no use for estimating $\Delta S(4)$ for the dimerization processes. What can be said, however, is that the absolute standard entropies are undoubtedly very similar, and therefore, $\Delta S(4) \approx 0$ and $\Delta G(4) \approx \Delta H(4)$. Such considerations as these indicate that because $\Delta H(4)$ and hence $\Delta G(4)$ are positive, the M_4^{2+} ions (like S_8^{2+}) are indeed *lattice-stabilized* in the solid state.

Relative Stabilities of the Lattice-Stabilized $M_4(AsF_6)_2$ Salts. Our value, estimated in a previous paper[16] for $\Delta_fH°[S_4(AsF_6)_2,c]$ of -3104 ± 117 kJ/mol, when compared with the experimental[28] standard enthalpies of formation $\Delta_fH°[Se_4(AsF_6)_2,c] = -3093$ kJ/mol and $\Delta_fH°[Te_4(AsF_6)_2,c] = -3354$ kJ/mol, does not exhibit anticipated monotonic variation with increasing atomic number of the cation as we descend the chalcogen group from sulfur to tellurium (see, for example, the trends observed in the hexahalometalates[68,69]). In our work with O'Hare[28] concerning the actual calorimetric measurement of $\Delta_fH°[Se_4(AsF_6)_2,c]$, there were a number of difficulties experienced when handling this particular salt. These are mentioned in the paper and were not mirrored in the work involving the compound $Te_4(AsF_6)_2$,[28] whose value of $\Delta_fH°[Te_4(AsF_6)_2,c]$ is therefore more reliable than that measured for the selenium analogue. The massic energy of combustion of $Se_4(AsF_6)_2$ in fluorine has been redetermined,[70] and the standard enthalpy of formation was derived, -3057.8 ± 3.8 kJ/mol, consistent with our previous value.[71] We estimated[64] a value of -3182 ± 106 kJ/mol for $\Delta_fH°[Se_4(AsF_6)_2,c]$.

Results and Discussion

X-ray Crystal Structure of $S_4(AsF_6)_2 \cdot AsF_3$. The crystal structure of $S_4(AsF_6)_2 \cdot AsF_3$ consists of discrete square planar

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(62) The lattice enthalpy of the salt without holes is then expected to be greater than 1598 ± 10 kJ/mol. This is approximately equal to the value of 1557 ± 20 kJ/mol of the lattice potential enthalpy derived from the volumes. We note that the sum of the errors is less than the difference. Further investigation will be needed to resolve this issue.

(63) $U_{POT}[S_4(AsF_6)_2] = 1557 \pm 20$ kJ/mol ($V[S_4^{2+}] = 0.084$ nm^3 from extrapolation of known ion volumes[19] of Se_4^{2+} and Te_4^{2+} analogues against the respective atomic covalent radii); $U_{POT}[Se_4(AsF_6)_2] = 1544 \pm 13$ kJ/mol ($V[Se_4^{2+}] = 0.094$ nm^3) and $U_{POT}[Te_4(AsF_6)_2] = 1518 \pm 17$ kJ/mol ($V[Te_4^{2+}] = 0.115$ nm^3); $U_{POT}[S_2AsF_6] = 541 \pm 16$ kJ/mol, as discussed earlier;[60] $U_{POT}[Se_2AsF_6] = 528 \pm 20$ kJ/mol (assuming $V[I_2^+] > V[Se_2^+] > V[S_2^+]$; $V[Se_2^+] = 0.059$ nm^3) and $U_{POT}[(Te_2AsF_6] = 508 \pm 15$ kJ/mol [$V[TeCl_3^+] > V[Te_2^+] > V[I_2^+]$; $V[Te_2^+] = 0.086$ nm^3.

(64) $\Delta_fH°[S_4^{2+},g] = 2318$ kJ/mol, $\Delta_fH°[Se_4^{2+},g] = 2207$ kJ/mol, $\Delta_fH°[Te_4^{2+},g] = 2009$ kJ/mol, $\Delta_fH°[S_2^+,g] = 1031$ kJ/mol, $\Delta_fH°[Se_2^+,g] = 1004$ kJ/mol,[15] and $\Delta_fH°[Te_2^+,g] = 936$ kJ/mol.[61] $\Delta_fH°[AsF_6^-,g] = -1919$ kJ/mol.[15,23] By use of these values of $\Delta_fH°[Se_4^{2+},g]$, $\Delta_fH°[AsF_6^-,g]$, and the lattice potential of $Se_4(AsF_6)_2$ (c) given in ref 62 and in Figure 5, $\Delta_fH°[Se_4(AsF_6)_2,c]$ of -3182 ± 106 kJ/mol is obtained.

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(67) $S°[S] = 36$ J/K mol; $S°[Se] = 49$ J/K mol; $S°[Te] = 56$ J/K mol; $S°[As] = 48$ J/K mol; $S°[F] = 29$ J/K mol.

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(71) The difference between our suggested (see text) result and the former[28] result is possibly due to the presence of ∼0.1 AsF_3 molecule in the lattice. Anal. Calcd for $Se_4(AsF_6)_2$ (and $Se_4(AsF_6)_2 \cdot 0.06AsF_3$): Se, 45.53 (45.02); As, 21.60 (22.00); F, 32.87 (32.98). Found:[28] Se, 44.91; As, 21.70; F, 33.10. The lower experimental value for $\Delta_fH°[Se_4(AsF_6)_2,c]$ recently obtained indicates the presence of even more AsF_3 in the sample. Incorporation of SO_2 in the lattice was ruled out because the gaseous products of reaction 15 yielded only SeF_6 and AsF_5 (IR); no SO_2F_2 was detected.

$$Se_4(AsF_6)_2\ (c) + 11F_2\ (g) = 4SeF_6\ (g) + 2AsF_5\ (g) \tag{15}$$

Table 4. Bond Distances and Angles in AsF_3 and Other Molecules Containing AsF_3 of Solvation

molecule	ave S−S distance (Å)	ave angle (deg)
AsF_3 (g)[77]	1.706(2)	96.2(2)
$S_4(AsF_6)_2 \cdot AsF_3$ (c)	1.679(8)	95.7(4)
$Te_6(AsF_6)_2 \cdot 2AsF_3$ (c)[8]	1.69(2)	92(1)
$[(S_7I)_2I][SbF_6]_3 \cdot 2AsF_3$ (c)[26]	1.70(3)	93.1(1)

S_4^{2+} cations, octahedral AsF_6^- anions, and AsF_3 molecules weakly linked by cation−fluorine interactions shown in Figures 1 and 2, with bond distances and angles reported in Table 3. The average sulfur−sulfur bond distance and angle in $S_4(AsF_6)_2 \cdot AsF_3$ [1.964(4) Å, 90(2)°] are not significantly different from those observed in $S_4(AsF_6)_2 \cdot 0.6SO_2$ [2.014(4) Å, 90(1)°],[24] $(S_7I)_4S_4(AsF_6)_6$ [1.98(1) Å, 90.0(5)°],[26] $(S_7Br)_4S_4(AsF_6)_6$ [1.95(2) Å, 89.9(8)°],[25] and $S_4(Sb_2F_4)(Sb_2F_5)(SbF_6)_5$ [1.988(5) Å, 90.0(2)°].[27] The sulfur−sulfur bond distances in $S_4(AsF_6)_2 \cdot AsF_3$ were corrected for the librational motions, resulting in the most reliable value so far determined [$S{-}S_{av} = 2.011(3)$ Å], in agreement with a calculated[16] D_{4h} structure [B3PW91/6-311G(2df), S−S = 2.027 Å] and consistent with the presence of a delocalized $3p\pi{-}3p\pi$ bond and bond order of 1.25 (cf. S−S distance in S_8, 2.051 Å;[72] corrected for librational motions, 2.060 Å). The pattern of sulfur−fluorine contacts is similar to those found in other M_4^{2+} (M = S, Se, Te) salts.[8] The strongest contacts are those in the M_4^{2+} plane [F33, F11, F26 and F13; Figure 1] bridging the chalcogen atoms, which is in agreement with the Laplacian model of total charge density.[73] A positive charge of approximately $+^1/_2$ is estimated from the number and strength of the cation−anion contact for each of the sulfur atoms.[74] The average As−F distances and F−As−F angles are 1.684(8) Å and 90.0(4)° for the ordered anion and are not significantly different from the corresponding values in $KAsF_6$ [1.719(3) Å and 90.0(2)°].[76]

The AsF_3 molecule has the expected AX_3E geometry with an average bond distance and angle [1.679(8) Å, 95.7(4)°] similar to that of AsF_3 (g) [1.706(2) Å, 96.2(2)°][77] and that of AsF_3 of solvation in related molecules (Table 4). The overall coordination around the arsenic atom of the AsF_3 molecule (Figure 2) is completed by six contacts from the disordered fluorine atoms of an AsF_6^- anion. Taking into account the 50% occupancy of the six fluorine sites, there are four contacts grouped around the lone pair electrons (in terms of the VSEPR model),[78,79] leading to an $AX_3Y_2Y_2'E$ environment similar to that in $Te_6(AsF_6)_4 \cdot 2AsF_3$.[8] The F12 and F14 (or F141) can be considered to cap the faces (Y) and F151 and F16 (or F161) to bridge the edges (Y′) of the trigonal pyramid. In addition, the fluorine atoms of AsF_3 donate to the S_4^{2+} by forming four contacts. Overall, AsF_3 acts as both a donor to the S_4^{2+} [sum of bond valency units = 0.71 vu] and as an acceptor from the AsF_6^- [sum of bond valency units = 0.17 vu] and therefore is a better donor than acceptor.[74] In solid AsF_3,[80] the donor and acceptor abilities of AsF_3 are equal [sum of bond valency units estimated to be 0.18 vu (acceptor) and 0.19 vu (donor)].

Factors Governing the Formation and Stability of $S_4(AsF_6)_2 \cdot AsF_3$. Previous results in this laboratory have shown that the preparation of $S_4(AsF_6)_2 \cdot 0.6SO_2$, by the oxidation of sulfur with AsF_5 in liquid SO_2, is only possible in the presence of a trace amount of chlorine, bromine, iodine, or $AsCl_4AsF_6$.[24] In the absence of a trace quantity of halogen, only $S_8(AsF_6)_2$ is produced.[5] Therefore, the halogen-facilitated oxidation method provides a convenient route to salts of the S_4^{2+} cation, the trace of halogen enhancing the oxidizing power of AsF_5. We now show that $S_4(AsF_6)_2 \cdot AsF_3$ can similarly be prepared in AsF_3 or in anhydrous HF by the oxidation of elemental sulfur with AsF_5 in the presence of traces of bromine.

Crystals of $S_4(AsF_6)_2 \cdot AsF_3$ were initially obtained from anhydrous HF as products of reaction 4. However, disproportionation of S_4^{2+} to products including S_8^{2+} was observed upon removal of the solvent, or if the salt were left in HF for more than 1 day, as indicated by color changes of the solid product (i.e., from white to blue). This is consistent with the work done by O'Donnell concerned with the importance of the acidity level on the stabilization of cationic species in acidic media.[81] For example, I_2^+ is stable in solution of highest acidity but disproportionates in turn to I_3^+, I_5^+, I_2, and IF_5 as the availability of the base of the solvent system is increased.[65,82] Highly oxidized cationic species can therefore only exist in very acidic media. In this work, an excess of AsF_5 (ca. 7 mol % AsF_5 present in HF) relative to the amount indicated by eq 4 was used. The acidity level [Hammett acidity function $H_0 = -19.49$ for 5 mol % AsF_5 in HF][83] of the solvent system appeared to be negative enough for the initial production of $S_4(AsF_6)_2 \cdot AsF_3$ but not sufficiently negative to avoid slow disproportionation to $S_8(AsF_6)_2$, perhaps by reactions of the type shown in

$$S_4(AsF_6)_2 + HF_2^- \rightarrow S_4FAsF_6 + AsF_6^- + HF \quad (16)$$

$$3S_4FAsF_6 \rightarrow SF_3AsF_6 + S_{11}(AsF_6)_2 \quad (17)$$

$$4S_{11}(AsF_6)_2 + 3S_4(AsF_6)_2 \rightarrow 7S_8(AsF_6)_2 \quad (18)$$

Attempts to make S_7F^+, the fluorocation analogue of S_7I^+ [84] and S_7Br^+,[25] in anhydrous HF lead in all cases[85] to disproportionation to products that included SF_3AsF_6; therefore, the disproportionation shown in eq 17 is possible.[86] The slow decrease in acidity level of the solvent system could be due to (i) the increase in fluoride anions that are leached from the FEP vessel, rendering the solvent more basic and accounting for the originally white product becoming pale-blue after 4 days [$H_0 = -15.1$ for pure HF, $H_0 \approx -11$ for HF stored in Kel-F],[87] as

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(74) In a cation, the positive charge on an atom is related to the strength of the contacts and is assessed by the sum of the bond valences (*S*) in valency units (vu). The bond valence in vu is calculated by the Brown relation:[75] $S = (R/R_0)^{-N}$, where *R* is the observed distance (Å), $R_0 = 1.550$ and $N = 3.8$ for S(IV)···F (note that the valency of S in S_4^{2+} is not IV and that $R_0 = 1.605$ and $N = 4.69$ for As(III)−(V)···F. In S_4^{2+}, the sums of the S−F contact valencies on the sulfur atoms (S1 0.49, S2 0.40, S3 0.53, and S4 0.59 vu) imply a charge of ca. $+^1/_2$ per atom.

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(86) However, we did not detect SF_3AsF_6 in the FT Raman spectrum or X-ray powder photograph of $S_4(AsF_6)_2 \cdot AsF_3$ and its decomposition products. We cannot rule out another sulfur fluorocation [e.g., S_7F^+ (refer to text)] in the disproportionation products.

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shown in

$$F^- + HF \rightarrow HF_2^- \qquad (19)$$

and (ii) the removal of the solvent, which removes the excess AsF_5, thus lowering the acidity level (higher concentration of HF_2^-) and causing further disproportionation to products including $S_8(AsF_6)_2$. The weight of the product, corresponding to an 80% yield based on the formation of $S_4(AsF_6)_2{\cdot}AsF_3$ or to a 101% yield based on $S_4(AsF_6)_2$, implies a significant loss of AsF_3 on pumping and extensive disproportionation to $S_8(AsF_6)_2$, which was identified by its blue color and from the X-ray powder photograph. However, we prepared crystalline $S_4(AsF_6)_2{\cdot}AsF_3$ in liquid AsF_3 essentially quantitatively (98% yield). Thus, liquid AsF_3 (and SO_2)[5] are as effective in stabilizing S_4^{2+} as HF/AsF_5 and HF/SbF_5 mixtures and considerably easier to manipulate.

$S_4(AsF_6)_2{\cdot}AsF_3$ was shown to lose AsF_3 less easily than SO_2 from $S_4(AsF_6)_2{\cdot}0.6SO_2$ under similar conditions.[85] The strengths of the contacts that AsF_3 and SO_2 make to their surroundings in $S_4(AsF_6)_2{\cdot}AsF_3$ and $S_4(AsF_6)_2{\cdot}0.6SO_2$ were assessed, by the relative magnitude for the bond valences,[74] as 0.88 and 0.16 vu, respectively (i.e., AsF_3 is a stronger base than SO_2). This implies that AsF_3 is more strongly held in the lattice than SO_2, which is consistent with the observations. The AsF_3 is also less easily lost relative to SO_2 in other salts (e.g., $Te_6(AsF_6)_4{\cdot}2AsF_3$ in comparison with $Te_6(AsF_6)_4{\cdot}2SO_2$).[8] The lattice enthalpy of $S_4(AsF_6)_2{\cdot}AsF_3$ (1744 kJ/mol) is significantly higher than that in which AsF_3 is removed (i.e., in which there are "holes" replacing the AsF_3 with the rest of the lattice intact and a value of 1557 ± 20 kJ/mol for $S_4(AsF_6)_2$ derived from our generalized equation). This implies that the solvation enthalpy in the lattice for AsF_3 is 187 kJ/mol [lattice enthalpy of $S_4(AsF_6)_2{\cdot}AsF_3$ minus lattice enthalpy of $S_4(AsF_6)_2$], which is significantly greater than its sublimation enthalpy ($\Delta_{sub}H$ of AsF_3 (s) is 46 kJ/mol, estimated from $\Delta_{fus}H = 10.41$ kJ/mol[61] and $\Delta_{vap}H = 35.5$ kJ/mol).

Estimates of the Standard Gibbs Free Energy for the Reaction $4M\ (s) + 3AsF_5\ (g) = M_4(AsF_6)_2\ (c) + AsF_3\ (l)$ (M = S, Se, Te). By use of our estimates of the standard enthalpies of formation of $S_4(AsF_6)_2{\cdot}AsF_3$ (c) (−4050 kJ/mol) and of $M_4(AsF_6)_2$ (c) (−3104 kJ/mol for M = S, −3182 kJ/mol for M = Se,[64] −3354 kJ/mol for M = Te[28]) and their standard molar entropies[65−67] (723, 588, 640, and 668 J/K mol, respectively), the standard Gibbs free energies ($\Delta_rG° = \Delta_rH° - T\Delta_rS°$; T = 298 K) for the formation of $S_4(AsF_6)_2{\cdot}AsF_3$ (c) (eq 20), $S_4(AsF_6)_2$ (c), $Se_4(AsF_6)_2$ (c), and $Te_4(AsF_6)_2$ (c) (eq 21) were estimated to be −225, −109, −187, and −359 kJ/mol, respectively.

$$4S\ (s) + 3AsF_5\ (g) \rightarrow S_4(AsF_6)_2{\cdot}AsF_3\ (c) \qquad (20)$$

$$4M\ (s) + 3AsF_5\ (g) \rightarrow M_4(AsF_6)_2\ (s) + AsF_3\ (l) \quad [M = S, Se, Te] \qquad (21)$$

This indicates that the reactions are exothermic ($\Delta_rH° < 0$) and thermodynamically allowed ($\Delta_rG° < 0$) and occur readily at room temperature. However, this route to $S_4(AsF_6)_2{\cdot}AsF_3$ (c) is kinetically unfavorable and will not proceed in the absence of a trace quantity of bromine,[5] even when AsF_5 is in excess. In contrast, the reaction of tellurium and AsF_5 leading to $Te_4(AsF_6)_2$ occurs readily at room temperature, and in the presence of excess AsF_5, the initially formed $Te_4(AsF_6)_2$, is further oxidized to $Te_6(AsF_6)_4$,[8] which in the presence of bromine undergoes further oxidation to TeF_4 or TeF_3AsF_6.[88] $Se_8(AsF_6)_2$ reacts with excess AsF_5 on prolonged heating at 60 °C, but $Se_4(AsF_6)_2$ is not further oxidized in the presence of bromine or excess AsF_5. Consistently, the formation of MF_4 (M = S, Se, Te) according to eq 22 is estimated[89] to be thermodynamically more favorable for tellurium, where $\Delta H(5)$ is 69 kJ/mol (M = S), −25 kJ/mol (M = Se), and −180 kJ/mol (M = Te).

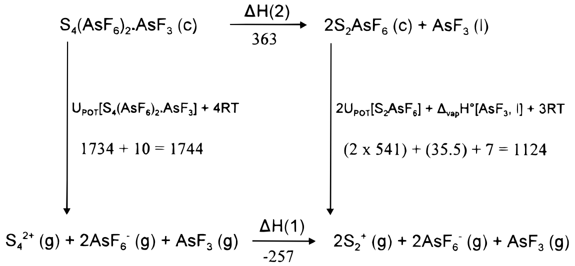

Figure 6. Thermochemical cycle for $S_4(AsF_6)_2{\cdot}AsF_3$ forming the S_2AsF_6 salt (values in kJ/mol).

$$M\ (s) + 2AsF_5\ (g) \rightarrow MF_4\ (\text{standard state}) + 2AsF_3\ (l) \quad \Delta H(5) \qquad (22)$$

Therefore, the formation of $M_4(AsF_6)_2$ is kinetically controlled with a high activation energy for the reaction leading to $S_4(AsF_6)_2$. These observations may be attributed in part to thermodynamic factors, i.e., the decrease in the ionization energy (IP(S), 999.6 kJ/mol; IP(Se), 942 kJ/mol; IP(Te), 869.3 kJ/mol)[92] and the higher M−F (M = S, Se, Te) bond energies in TeF_4 compared with those in SeF_4 and SF_4 (bond energies of TeF (g), SeF (g), and SF (g) are 378, 357, and 360 kJ/mol, respectively[90]).

Lattice Stabilization of S_4^{2+} in $S_4(AsF_6)_2{\cdot}AsF_3$ (c). We have established by theoretical calculations (B3PW91)[22] that the S_4^{2+} ion in the gas phase is unstable to dissociation to two S_2^+ (g). However, it is observed in the solid state in various salts including $S_4(AsF_6)_2{\cdot}AsF_3$ (c) for which we have determined the X-ray crystal structure. This allows us to obtain a good-quality estimation of the lattice potential by an extended calculation. The lattice energy of the hypothetical S_2AsF_6 (c) has been estimated using our empirical approach with reasonable confidence. We therefore establish a value of $\Delta H(2) = 363$ kJ/mol as illustrated in Figure 6. Thus, although S_4^{2+} is unstable in the gas phase to two S_2^+, this is compensated for by the greater crystal lattice potential of the 1:2 salt relative to twice that of the 1:1 salt. The standard Gibbs free energy, $\Delta G(2)$ (=$\Delta H(2) - T\Delta S(2)$), is also positive; thus, S_4^{2+} is *lattice-stabilized* in $S_4(AsF_6)_2{\cdot}AsF_3$ (c).

Lattice Stabilization of M_4^{2+} (M = S, Se, and Te) in $M_4(AsF_6)_2$ (c). It was not possible to obtain a pure sample of $S_4(AsF_6)_2$ (c) free of solvent, and although we thought we had obtained a sample of pure $Se_4(AsF_6)_2$ (c) on the basis of elemental analyses and vibrational spectroscopy, we suggest that it contained a small amount of arsenic trifluoride of crystallization. We obtained $Te_4(AsF_6)_2$ (c)[28] but not crystals. Therefore, extended calculations using atomic coordinates as input

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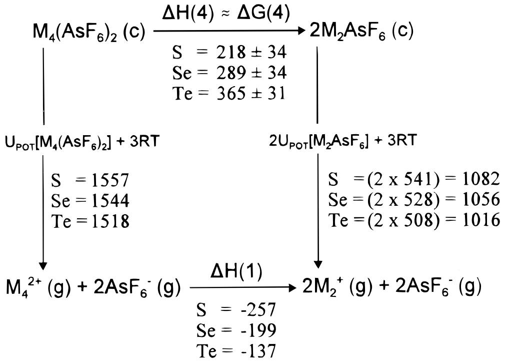

Figure 7. Thermochemical cycle for $M_4(AsF_6)_2$ (M = S, Se, and Te) forming the M_2AsF_6 salts (values in kJ/mol).

are not possible for $M_4(AsF_6)_2$ (c). However, lattice potential energies of $M_4(AsF_6)_2$ (c) and M_2AsF_6 (c) were estimated from the sum of the ionic volumes (see above). Our calculations show[16,17,23] that all M_4^{2+} (g) are unstable to dissociation to two M_2^+ (g). However, $\Delta H(4)$ is positive in all cases as shown in Figure 7. The Gibbs free energy, $\Delta G(4)$, of reaction 4 is also positive, and all M_4^{2+} are *lattice-stabilized* in $M_4(AsF_6)_2$ (c) and by implication in all the observed M_4^{2+}-containing salts in the solid state.

Resolution of the Inconsistent Value of the Experimentally Determined Heat of Formation of $Se_4(AsF_6)_2$ (c).[28] We previously showed that from the experimentally determined standard heat of formation of $Te_4(AsF_6)_2$ (c) that it was stable relative to two moles of Te_2AsF_6 (c). However, the related standard heat of formation of $Se_4(AsF_6)_2$ (c) implied that it was only 3 kJ/mol more stable than two moles of Se_2AsF_6 (c). In this paper we derive a standard heat of formation for $Se_4(AsF_6)_2$ of -3182 ± 106 kJ/mol that is consistent with both $S_4(AsF_6)_2$ (c) and $Te_4(AsF_6)_2$ (c) and implies that the former experimental value was likely in error because of the presence of some arsenic trifluoride of solvation. The derived value of $\Delta H(4)$ of 289 ± 34 kJ/mol is consistent with the values for sulfur and tellurium and the observed presence of Se_4^{2+} in $Se_4(AsF_6)_2$ and the salts.[2,4] This is another illustration of the usefulness of determining the thermodynamics of a series of salts by as many methods as possible.

Guide to the Synthesis of a M_2^+-Containing Salt. To be able to stabilize M_2^+ in the solid state, we would require minimizing the difference between the lattice energies (of $M_2^+A^-$ and $M_4^{2+}(A^-)_2$, A^- = anion). The formation of the homopolyatomic monocations will then be favored. This can be best accomplished with large anions because the lattice energies are inversely proportional to the ionic radii. Increasing the size of the anion reduces the magnitude of the lattice potential energies, and the magnitude for the $M_4(AsF_6)_2$ salt would be expected to diminish to a greater extent than that for the M_2AsF_6 salt. It is for this reason, for example, that $S_3N_2^{2+}$ is lattice-stabilized in $S_3N_2(AsF_6)_2$ but $S_3N_2(Sb_2F_{11})_2$, containing the larger anion, dissociates to $SNS(Sb_2F_{11})$ and $SN(Sb_2F_{11})$.[55] Similarly, I_4^{2+} is lattice-stabilized in $I_4(AsF_6)_2$ but not as the $Sb_2F_{11}^-$ salt.[4,93,94] Computation of anion volumes using our eq 1 shows that in order to make $\Delta H(4) < 0$, the S_2^+ cation would have to be combined with an anion having a volume of 5 nm^3 (5000 Å^3). In the case of Se_2^+ the volume increases to 13 nm^3 (13 000 Å^3). For Te_2^+, the anion would have to have a volume of 70 nm^3 (70 000 Å^3) (cf., $V[Sb(OTeF_5)_6^-]$ = 0.71 nm^3 (710 Å^3),[95] $V[CB_{11}H_{12}-] \approx 0.5$ nm^3 (500 Å^3)[96]—an obvious indication that stabilization of a dichalcogen monocation in a crystalline lattice appears to be extremely unlikely to be realizable for any chalcogenide M_2^+ ion when paired with conventional type anions! Our prediction therefore is that such salts cannot be formed in preference to the dimerized salts.

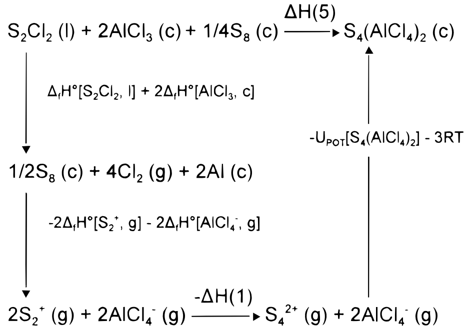

Figure 8. Thermochemical cycle for a possible preparative route to $S_4(AlCl_4)_2$.

Failure to Prepare $S_4(AlCl_4)_2$. $AlCl_4^-$ (tetrachloroaluminate anion) is capable of lattice-stabilizing a wide variety of cations, including the homopolychalcogen dications Te_4^{2+},[97] Te_6^{2+},[97] and Se_8^{2+},[97−99] in the solid state, but no evidence has yet been found of $S_4(AlCl_4)_2$ despite attempts to prepare this compound. The thermochemical cycle of Figure 8 can be employed to study this chemistry. S_2Cl_2, $AlCl_3$, and elemental sulfur suggest themselves as potential starting materials for the preparation of $S_4(AlCl_4)_2$.

$$S_2Cl_2\ (l) + 2AlCl_3\ (c) + (^1/_4)S_8\ (c) \rightarrow S_4(AlCl_4)_2\ (c) \qquad \Delta H(6) \quad (23)$$

The calculated enthalpy change of the preparation route (eq 23), $\Delta H(6)$, is 97 ± 117 kJ/mol. This result possibly explains the failure to secure a preparation method for this material. Further, more detailed analysis shows that it arises (i) from the smaller magnitude of the halide ion affinity of $AlCl_3$ compared with that for AsF_5, for the salt which can be made, and (ii) as a result of the relatively large size of the tetrachloroaluminate anion, $AlCl_4^-$ ($V[AlCl_4^-]$ = 0.156 nm^3)[19] when compared to that of the hexafluoroarsenate anion, AsF_6^- ($V[AsF_6^-]$ = 0.110 nm^3).[19] We employ the ancillary data $\Delta_f H°[S_2Cl_2, l] = -59.4$ kJ/mol,[23] $\Delta_f H°[AlCl_3,c] = -704$ kJ/mol, $\Delta_f H°[S_2^+,g] = 1031$ kJ/mol (above), $\Delta_f H°[AlCl_4^-,g] = -1196$ kJ/mol, and $-\Delta H(1) = 257$ kJ/mol (see Figure 8) and the lattice potential energy estimates of $U_{POT}[S_4(AlCl_4)_2]$ from eq 1 (=1456 ± 115 kJ/mol) for these calculations.

Conclusion

Although S_4^{2+}, Se_4^{2+}, and Te_4^{2+} are observed as stable salts and in solution, in the gas phase the dications are kinetically stable but thermodynamically unstable to dissociation to the monocations. Thus, the dications are *lattice-stabilized* and the cycloaddition are *lattice-enforced*. Grein has shown that the cycloaddition is a symmetry-forbidden cycloaddition with a

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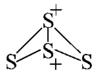

Figure 9. S_4^{2+} (g) σ-bonded dimer.

transition state of ca. 209 kJ/mol for S_4^{2+} at the RHF/6-31G* level of calculation.[100] The dimerization of two M_2AsF_6 (c) to $M_4(AsF_6)_2$ (c) (M = S, Se, Te) results in an increase in the charge of the cation (from +1 to +2) and in the number of ions in the formula unit (from 2 to 3), leading to an increase in the lattice energy by a factor of 3, as approximated by the Kapustinskii equation.[101] For small cations such as M_2^+, the crystal lattice energy will always favor the 2:1 salt. Ironically, O_2^+ salts, which contain the smallest X_2^+ cations of all, have never been observed as O_4^{2+}. Here, the high π-bond energy (351 kJ/mol) relative to the low σ-bond energy (142 kJ/mol) and the unfavorable electrostatic energy required for dimerization are all reflected in a dimerization energy for $2O_2^+$ to O_4^{2+} of 1035 kJ/mol [B3PW91/6-311+G(3d2f)].[2]

The formation of small π-bonded species in preference to larger σ-bonded frameworks is a feature of the chemistry of second period elements, and the higher stability of S_2^+ (g) relative to S_4^{2+} (g) is reminiscent of the greater stability of O_2 compared to O_4. This is further illustrated by the results[17] of *ab initio* calculations [B3PW91/6-311+G(3d2f)] of a rectangular (D_{2h} S_4^{2+} (g)) $\pi^*-\pi^*$ dimer only slightly higher in energy (76 kJ/mol) relative to that of the square planar S_4^{2+} (g), both lower in energy than the σ-bonded dimer (Figure 9) (155 kJ/mol). The tendency of positively charged sulfur to form stable pπ−pπ bonds is reflected in the structures of many related cations (e.g., $S_2I_4^{2+}$,[102] which contains the shortest S−S bond of any isolated compound, corresponding to a bond order of 2.33).

Many multicharged polyatomic anions and cations are thermodynamically unstable in the gas phase with respect to smaller, less charged fragments.[103] In some cases the calculations show that the multicharged ions do not lie in a minimum of a potential energy surface (i.e., do not exist as such in the gas phase). This led one author to entitle his paper "Are the 'Textbook Anions' O^{2-},[104] $[CO_3]^{2-}$, and $[SO_4]^{2-}$ Fictitious?"[105] We propose that these related gas-phase unstable multicharged polyatomic ions are also lattice-stabilized in the solid state.

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Supporting Information Available: Tables S1−S5 listing complete crystallographic details, bond distances and angles, atomic coordinates, and anisotropic temperature factors for $S_4(AsF_6)_2 \cdot AsF_3$, Table S6 listing observed and calculated powder photography data for $S_4(AsF_6)_2 \cdot AsF_3$, compared with observed powder data for $S_8(AsF_6)_2$, and Figure S1 showing the FT-Raman spectrum obtained for $S_4(AsF_6)_2 \cdot AsF_3$ made in anhydrous HF, compared with that for $S_4(AsF_6)_2 \cdot xSO_2$ ($x < 1$). This material is available free of charge via the Internet at http://pubs.acs.org.

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