the PP_3 complexes (Figure 2). The semiempirical parameter Q is an approximation to the paramagnetic contribution (second term) in Ramsey's shielding equation.[28] It is assumed that the first ionization potential of the variable substituent, I, should be roughly proportional to the mean excitation energy ΔE, which is not known. The use of a correction factor P/r^3, where P is the polarizability of the bonded atom and r is the interatomic distance, results in the relationship $Q = P/Ir^3$.[27,28]

Acknowledgment. We are grateful to Mississippi State University for a Sabbatical Leave to E.G. and to the Procter and Gamble Co.'s University Exploratory Research Program for partial support of this study.

Registry No. $[NiCl(Ptas)]AsF_6$, 101348-53-2; $[NiBr(Ptas)]AsF_6$, 101348-55-4; $[NiI(Ptas)]AsF_6$, 101348-57-6; $[Ni(CN)(Ptas)]AsF_6$, 101374-88-3; $[Ni\{P(OMe)_3\}(Ptas)](AsF_6)_2$, 101375-11-5; $[Ni(NO_3)(Ptas)]AsF_6$, 101375-13-7; $[Ni(PPh_3)(Ptas)](AsF_6)_2$, 101348-59-8; $[Ni(PEt_3)(Ptas)](AsF_6)_2$, 101348-61-2; $[Ni(NCS)(Ptas)]AsF_6$, 101348-63-4; $[Ni(SCN)(Ptas)]AsF_6$, 101348-65-6; Ptas, 101348-66-7; PCl_3, 7719-12-2; P, 7723-14-0; (*o*-bromophenyl)dimethylarsine, 4457-88-9.

Supplementary Material Available: A listing of analytical data for $[NiX(Ptas)][AsF_6]_{1,2}$ complexes (1 page). Ordering information is given on any current masthead page.

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[28] Ramsey, N. F. *Phys. Rev.* **1950**, *78*, 699.

[29] The periodic group notation in parentheses is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

Contribution from the Departments of Chemistry, McMaster University, Hamilton, Ontario L8S 4M1, Canada,
and University of Toronto, Toronto, Ontario M5S 1A1, Canada

Selenium-77 NMR and Raman Study of $S_xSe_{4-x}^{2+}$ Cations and Crystal Structure of $(S_{3.0}Se_{1.0})_2(Sb_4F_{17})(SbF_6)_3$ Containing a Disordered Mixture of $S_xSe_{4-x}^{2+}$ Cations[1]

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Received April 25, 1985

The series of "square-planar" cations $S_xSe_{4-x}^{2+}$ (x = 0–3) has been characterized by Raman and ^{77}Se NMR spectroscopy. Chemical shifts range from 587 to 729 ppm with respect to saturated aqueous H_2SeO_3, and the ^{77}Se–^{77}Se coupling constant in SSe_3^{2+} is 336 Hz. The mean ^{77}Se T_1 value is 0.38 s. The structure of $(S_{3.0}Se_{1.0})_2(Sb_4F_{17})(SbF_6)_3$ has been determined by X-ray crystallography (monoclinic, space group $B2_1/c$, a = 15.267 (3) Å, b = 13.440 (4) Å, c = 16.437 (6) Å, β = 91.59 (2)°, Z = 4, and R = 0.078 for 3670 observed reflections). Occupational disorder, anion–cation interactions, and the geometry of the $Sb_4F_{17}^-$ anion in this compound are discussed.

Introduction

The species S_4^{2+}, Se_4^{2+}, and Te_4^{2+} were among the first of the polyatomic cations of the chalcogens to be characterized by conductometric and cryoscopic measurements nearly 20 years ago.[3] The square-planar geometry of these cations has since been established by X-ray crystallography.[4–6] Similarly, the mixed cations $Te_xSe_{4-x}^{2+}$ (x = 0–4) have been characterized by ^{77}Se and ^{125}Te NMR studies,[7,8] and the X-ray crystal structures of $(Te_2Se_2)(Sb_3F_{14})(SbF_6)$ and $(Te_{3.0}Se_{1.0})(Sb_3F_{14})(SbF_6)$ have recently been determined.[9] In this investigation we have prepared for the first time the analogous cations $S_xSe_{4-x}^{2+}$. The Se-containing members of this series (x = 0–3) have been characterized in SO_2 solution by ^{77}Se NMR spectroscopy (^{77}Se: spin $^1/_2$, 7.50% natural abundance, 5.26×10^{-4} relative receptivity to ^1H), and the X-ray crystal structure of $(S_{3.0}Se_{1.0})_2(Sb_4F_{17})(SbF_6)_3$ has shown this compound to contain a mixture of square-planar $S_xSe_{4-x}^{2+}$ cations along with the novel $Sb_4F_{17}^-$ anion. Although several mixed Te/Se cations and two Te/S cations have been reported,[10–12] this is the

Table I. Crystal Data and Details of X-ray Intensity Measurements and Structure Refinement for $(S_{3.0}Se_{1.0})_2(Sb_4F_{17})(SbF_6)_3$

syst	monoclinic
$a \times b \times c$, Å	15.267 (3) × 13.440 (4) × 16.437 (6)
β, deg	91.59 (2)
V, Å^3	3371 (2)
space group	$B2_1/c$
Z/D_c, g cm^{-3}/temp, °C	4/3.68/22
μ, cm^{-1}	84.8
no. of reflns used in cell detn (2θ range, deg)	15 (19–30)
radiation	Mo K$\bar{\alpha}$ (λ = 0.71069 Å), graphite monochromated
max 2θ, deg/scan type	55/θ–2θ
scan range	Kα_1 − 1.0° to Kα_2 + 1.0°
scan rates, deg min^{-1}	6.0–29.3 (dependent on prescan)
std reflns (no./interval)	2/48
quadrants collcd	$h,k,\pm l$
no. of data collcd (incl stds and B-centered reflcns)	8803
abs cor (ABSORB)	A^*: 2.51–3.88
cryst dimens, cm	{0,1,0}: 0.0065 (1,0,1): 0.0135 (0,0,−1): 0.0085 (1,0,0): 0.0085
no. of nonzero data	3670
no. of data with $F > 6\sigma(F)$	2912
R factors	
6σ: R_1 (R_2)	0.0631 (0.0690)
all: R_1 (R_2)	0.0776 (0.0893)
max shift/error (las cycle), %	12
weighting scheme: $w^{-1} = \sigma(F)^2 + GF^2$	G = 0.0088

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[1] Presented in part at the 28th Congress of the International Union of Pure and Applied Chemistry, Vancouver, Canada, 1981, and the 10th International Symposium on Fluorine Chemistry, Vancouver, Canada, 1982.

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Table II. Final Atomic Positional Parameters (×10^4) with Estimated Standard Deviations in Parentheses for $(S_{3.0}Se_{1.0})_2(Sb_4F_{17})(SbF_6)_3$

atom	*x*	*y*	*z*
Se(1)[a]	6551 (1)	344 (2)	2356 (1)
Se(2)[a]	7473 (2)	314 (2)	3380 (2)
Se(3)[a]	3202 (2)	784 (2)	2432 (1)
Se(4)[a]	2712 (2)	−113 (2)	3382 (2)
Sb(1)	147.1 (6)	2002.0 (7)	2345.7 (5)
Sb(2)	33.6 (5)	3556.1 (6)	4498.6 (4)
Sb(3)	2597.3 (6)	2387.8 (7)	5199.3 (5)
Sb(4)	5000.0 (0)	0.0 (0)	0.0 (0)
F(11)	227 (8)	1650 (8)	1254 (6)
F(12)	63 (8)	2360 (7)	3473 (5)
F(13)	45 (7)	3333 (7)	2095 (6)
F(14)	1356 (6)	2154 (8)	2454 (7)
F(15)	−1089 (6)	1874 (8)	2312 (7)
F(16)	251 (7)	673 (6)	2627 (6)
F(21)	825 (6)	4163 (8)	3768 (5)
F(22)	−921 (5)	4048 (6)	3811 (5)
F(222)	0 (0)	5000 (0)	5000 (0)
F(31)	1913 (8)	1760 (9)	5949 (8)
F(32)	3321 (8)	3012 (10)	4451 (7)
F(33)	3491 (8)	1418 (9)	5368 (7)
F(34)	1768 (9)	3396 (10)	5056 (7)
F(35)	2099 (8)	1650 (12)	4351 (8)
F(36)	3060 (8)	3155 (8)	6049 (6)
F(41)	5839 (7)	−79 (7)	877 (6)
F(42)	5094 (6)	1386 (6)	23 (6)
F(43)	4082 (6)	90 (8)	729 (6)

[a] Cation sites partially occupied by both sulfur and selenium. See Table III.

Table III. Occupation of the Cation Sites in $(S_{3.0}Se_{1.0})_2(Sb_4F_{17})(SbF_6)_3$

site	population param	no. of electrons	S fraction	Se fraction
Se(1)	0.684 (6)	23.2 (3)	0.60 (2)	0.40 (2)
Se(2)	0.552 (7)	18.8 (4)	0.85 (2)	0.15 (2)
Se(3)	0.641 (7)	21.8 (4)	0.68 (2)	0.32 (2)
Se(4)	0.539 (7)	18.3 (4)	0.87 (2)	0.13 (2)
		total	3.00 (4)	1.00 (4)

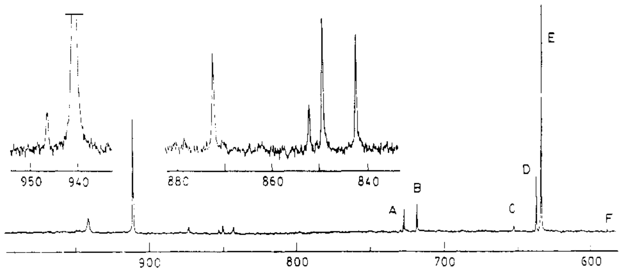

Figure 1. ^{77}Se NMR spectrum of the solution resulting from the reaction of 2S + 2Se + $3AsF_5$ in SO_2 (0.0914 g of S; 0.2213 g of Se; 0.715 g of AsF_5; 3 mL of SO_2; 76.41 MHz; 7100 scans; 6.1 Hz/pt). Peaks A–F are of $S_xSe_{4-x}{}^{2+}$ cations. Unlabeled resonances result from mixed S/Se cations of unknown stoichiometry. Expanded spectra: 150 000 scans.

first report of mixed S/Se polyatomic cations.

Experimental Section

Materials. Sulfur (BDH) and selenium (Koch-Light Laboratories Ltd.) were dried under vacuum at 22 °C overnight. Sulfur dioxide (Canadian Liquid Air) was stored over P_4O_{10} for at least 24 h before use. Arsenic pentafluoride and AsF_3 were prepared from the elements and stored in nickel cylinders; SbF_5 (Ozark-Mahoning) was distilled under vacuum and stored in an FEP bottle in a drybox.

NMR Spectroscopy. Samples were prepared in 10 mm o.d. precision glass, round-bottom NMR tubes (Wilmad) joined to $^1/_4$ in. o.d. standard-wall tubing. The appropriate solvent was vacuum-distilled onto the solute before flame-sealing. Samples of reaction mixtures were obtained by attaching NMR tubes to side arms of the reaction vessels before adding the reagents.

Spectra were recorded unlocked with a Bruker WM-400 spectrometer. A pulse width of 40 μs corresponded to a nuclide tip angle of approximately 90°. Spectra were generally recorded in 16K of memory with a spectral width of 50 kHz. Line-broadening parameters used in exponential smoothing of the free induction decays were less than or equal to the data point resolutions. The inversion–recovery pulse sequence, $(180°-\tau-90°-T)_n$, was used to obtain the relaxation times (T_1), and the value of T_1 was extracted from the experimental data by using a nonlinear least-squares routine.

Raman Spectroscopy. Spectra were recorded on the instrument described elsewhere.[13] Solid samples were sealed in glass capillaries; solutions were observed in the same sample tubes used for the NMR analysis.

X-ray Crystallography. Pale yellow crystals of $(S_{3.0}Se_{1.0})_2(Sb_4F_{17})(SbF_6)_3$ were sealed in Lindemann capillaries in a drybox. Preliminary precession photographs were used to check crystal quality and to obtain cell and space group information. Further work was on a Syntex $P2_1$ diffractometer. Crystal data and the conditions used for the data collection are given in Table I. For each reflection, stationary-background counts were recorded at each end of the scan, each for one-fourth of the scan time. No systematic trends in the intensities of two standards collected every 48 reflections were observed. Lorentz and polarization corrections were applied to all data. Absorption corrections were applied after the composition of the crystal had been established.

The structure was solved by the use of a combination of direct methods and the Patterson function to locate several heavy-atom positions. Subsequent cycles of least-squares and Fourier calculations revealed all missing atoms. Since there were significant differences in the thermal parameters and bond lengths for the atoms (assumed Se) in the two cations about two of the centers of symmetry in the unit cell, the occupancy factors were allowed to refine. This significantly improved the residuals and allowed the composition of the compound to be established as $(S_{3.0}Se_{1.0})_2(Sb_4F_{17})(SbF_6)_3$. Least-squares refinement of this model (minimizing $\sum w(\Delta F)^2$) then converged to the residuals in Table I.

Neutral-atom scattering factors were taken from ref 14. Calculations were performed on CDC 6400 and SEL 75 computers using programs in the XRAY[15] and SHELX[16] systems. The final atomic positional parameters and occupational factors are given in Tables II and III, respectively.

Preparation of $(S_{3.0}Se_{1.0})_2(Sb_4F_{17})(SbF_6)_3$. A trace of Br_2 (0.02 g, 0.1 mmol) was distilled onto a frozen mixture of SbF_5 (6.11 g, 28.2 mmol) and SO_2 (40 mL) in one bulb of a double-bulb glass vessel equipped with a magnetic stir bar and a glass frit separating the two bulbs. Upon melting, the cold solution was poured onto a mixture of selenium (0.5564 g, 7.047 mmol) and sulfur (0.6799 g, 21.20 mmol) powders. The pale orange solution color of Br_2 was immediately replaced by a deep green and then a deep blue-green color after about 0.25 h. After being stirred for 12 h, the solution was filtered and allowed to stand for 48 h when a few canary yellow crystals were observed under the deep blue solution. After 30 days the solution was poured off, leaving a large quantity of pale yellow crystals as well as the few canary yellow crystals. Precession photographs revealed that the latter crystals were $(Se_4)(Sb_2F_4)(Sb_2F_5)(SbF_6)_5$,[17] and an X-ray crystal structure determination revealed the composition of the pale yellow compound to be $(S_{3.0}Se_{1.0})_2(Sb_4F_{17})(SbF_6)_3$.

Preparation of $(S_{3.0}Se_{1.0})(AsF_6)_2$. A pale yellow powder of nominal composition $(S_{3.0}Se_{1.0})(AsF_6)_2$ was obtained by combining sulfur (0.4355 g, 13.58 mmol) and selenium (0.3576 g, 4.529 mmol) with AsF_5 (3.08 g, 18.1 mmol) and a trace of Br_2 (0.02 g, 0.1 mmol) in 20 mL of SO_2 in one bulb of a double-bulb vessel as described above, stirring for 1 week, and removing all volatiles by cooling the other bulb in liquid N_2.

Results and Discussion

NMR Spectroscopy. Several resonances were observed in the ^{77}Se NMR spectrum of an SO_2 solution obtained by reacting a

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(10) Boldrini, P.; Brown, I. D.; Gillespie, R. J.; Ireland, P. R.; Luk, W.-C.; Slim, D. R.; Vekris, J. E. *Inorg. Chem.* **1976**, *15*, 765.

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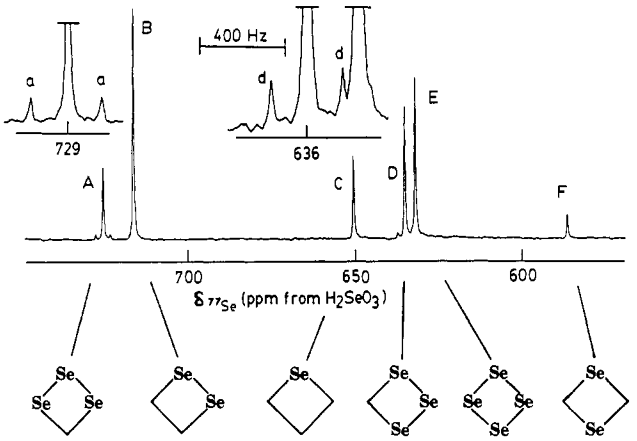

Figure 2. ^{77}Se NMR spectrum of the solution resulting from the reaction of $2S + 2Se + 4AsF_5 + Br_2$ (trace) in SO_2 (0.0542 g of S; 0.1325 g of Se; 0.57 g of AsF_5; 3 mL of SO_2; 0.02 g of Br_2; 76.41 MHz; 5000 scans; 6.1 Hz/pt). Expanded spectra show satellite doublets a and d resulting from ^{77}Se–^{77}Se coupling in SSe_3^{2+}. T_1 results (s): (A) 0.34; (B) 0.39; (C) 0.36; (D) 0.43; (E) 0.39.

Table IV. Intensity (Relative Values) in ^{77}Se NMR Spectra of $S_xSe_{4-x}^{2+}$ as a Function of Reactant Ratio

	chemical shift,[b] ppm					
x:y ratio[a]	729[c]	720	651	636[c]	633[d]	587
1:3	9	22	9	19	40	2
2:2	10	32	12	19	24	3
3:1	5	34	41	6	10	3
3.7:0.3		11	82		7	

[a] All reactions are $xS + ySe + 4AsF_5 + Br_2$ (trace) in SO_2. Equilibrium was reached within 24 h at room temperature. [b] With respect to saturated aqueous H_2SeO_3 at 24 °C. $\delta(Me_2Se) = \delta(H_2SeO_3) + 1302.6$ ppm. [c] SSe_3^{2+}. [d] Se_4^{2+}.

1:1 mixture of sulfur and selenium powders with AsF_5 (Figure 1). One of these resonances, at 633 ppm with respect to saturated aqueous H_2SeO_3 (1936 ppm with respect to Me_2Se), was also observed when $Se_4(AsF_6)_2$ was dissolved in SO_2. Chemical shifts observed for Se_4^{2+} in oleum range from 636 to 646 ppm.[8] Several other resonances in Figure 1 were close to the Se_4^{2+} resonance, suggesting that they resulted from mixed S/Se cations isostructural with Se_4^{2+}, that is, $S_xSe_{4-x}^{2+}$. The remaining resonances, ranging from 840 to 950 ppm, do not correspond to any of the known selenium homopolyatomic cations[18] and probably result from mixed-S/Se cations of unknown structure.

Passmore and co-workers[6] have determined that the formation of S_4^{2+} or Se_4^{2+} using AsF_5 as an oxidant is greatly facilitated by a trace of Br_2 or I_2. When the 1:1 S/Se mixture was allowed to react with AsF_5 in the presence of Br_2, the higher frequency resonances in the ^{77}Se spectrum of the resulting solution disappeared and the $S_xSe_{4-x}^{2+}$ resonances became more intense (Figure 2). Two resonances, A and D, are observed in a ratio of 2:1 with satellite doublets about each of them. The only $S_xSe_{4-x}^{2+}$ cation expected to display coupling is SSe_3^{2+}, which would also be expected to give two resonances in a ratio of 2:1, as observed. The satellite doublets are of 8.8 and 17.5% relative intensity for the large and the small resonances, respectively. The expected relative intensities for coupling to one and two equivalent, natural-abundance selenium nuclei, as in SSe_3^{2+}, are 8.2 and 16.3%, respectively. The ^{77}Se–^{77}Se coupling (336 Hz) is considerably larger than that observed for $TeSe_3^{2+}$ in 30% oleum (188 Hz).[8] Resonance C grows the most dramatically upon increasing the S:Se ratio of the reactants (Table IV) and is presumably due to the sulfur-rich S_3Se^{2+} cation. The relative intensity of the remaining two resonances is fairly constant for all of the mixtures, as would be expected for the two $S_2Se_2^{2+}$ cations. In the case of $Te_2Se_2^{2+}$ the cis cation is usually observed in higher concentration than the trans cation (see for example ref 7, Figure 1). For this reason the more intense resonance, B, can be tentatively assigned to *cis*-$S_2Se_2^{2+}$ and resonance F to *trans*-$S_2Se_2^{2+}$. On the basis of these assignments the three highest frequency resonances (A, B, and C) have sulfur trans to the selenium nucleus being observed, while for the three lower frequency resonances (D, E, and F) the trans atom is selenium. In both of these groups of three resonances, one of the three is of substantially lower frequency than the remaining two, and the selenium environment corresponding to this resonance is cis to two sulfur atoms. The remaining two resonances in each group have approximately equal chemical shifts. In each case, one of these selenium environments is cis to one selenium and to one sulfur atom, while the other selenium environment is cis to two selenium atoms. These consistencies in the selenium environments lend some support to the above chemical shift assignments. It is anticipated that ^{33}S NMR spectra could be recorded to corroborate the above assignments. Ambiguity in the assignments of the *cis*-and *trans*-$S_2Se_2^{2+}$ cations would be eliminated in the (unlikely) event that ^{33}S–^{77}Se couplings were resolved.

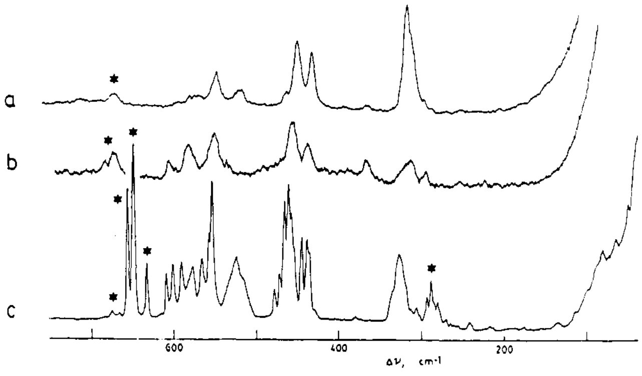

Figure 3. Raman spectra (5145 Å) of (a) the $(S_{2.0}Se_{2.0})(AsF_6)_2$ solution of Figure 2, (b) solid $(S_{3.0}Se_{1.0})(AsF_6)_2$, spinning sample, at 77 K, and (c) powdered crystals of $(S_{3.0}Se_{1.0})_2(Sb_4F_{17})(SbF_6)_3$ at 77 K. The peaks marked with an asterisk are anion bands.

It has been reported that Te_4^{2+} and Se_4^{2+} do not scramble to give mixed square-planar species in solution.[8,12] When $Se_4(AsF_6)_2$ and $S_4(AsF_6)_2$ were mixed in equal proportions in SO_2 solution, the ^{77}Se NMR spectrum revealed only Se_4^{2+} after 2 h at room temperature. After 2 weeks, however, the complete range of $S_xSe_{4-x}^{2+}$ cations was observed, with approximately the same product distribution as in Figure 2. The different behavior of these pairs of cations is probably related to the electropositive nature of tellurium. The Se_4^{2+} cation can readily oxidize Te_4^{2+} to Te_6^{4+}, and oxidation–reduction occurs rather than scrambling. Although S_4^{2+} is similarly a stronger oxidant than Se_4^{2+}, no polyatomic cation of selenium is known with a higher oxidation state than in Se_4^{2+}, and oxidation–reduction is therefore unlikely in this mixture. It is expected that a Te_4^{2+}/S_4^{2+} mixture would result in oxidation–reduction products rather than the as yet unknown $Te_xS_{4-x}^{2+}$ cations.

The mixed S/Se compound $(S_{3.0}Se_{1.0})_2(Sb_4F_{17})(SbF_6)_3$ reacts with 100% H_2SO_4, is almost completely insoluble in SO_2, and is only sparingly soluble in AsF_3. The spectrum in AsF_3 after 250000 scans consisted of five resonances in the same region as described above for $S_xSe_{4-x}^{2+}$ cations in SO_2 (635.7, 646.4, 671.3, 726.4, and 728.2 ppm with relative intensities 1:2:1:4:1, respectively). Apparently, several of the possible $S_xSe_{4-x}^{2+}$ species are present in the structure. A similar situation exists for $(Te_{3.0}Se_{1.0})(Sb_3F_{14})(SbF_6)$, where it has been shown by ^{77}Se and ^{125}Te NMR that the structure contains several different $Te_xSe_{4-x}^{2+}$ cations rather than simply a disordered Te_3Se^{2+} cation.[9]

Spin–lattice relaxation time (T_1) measurements were carried out for the five most intense lines in Figure 2, and the results are presented with the figure. The average T_1 value is 0.38 s with the unique selenium atom of SSe_3^{2+} having the lowest observed value, 0.34 s, and the other selenium environment of this cation

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(18) Burns, R. C.; Collins, M. J.; Gillespie, R. J.; Schrobilgen, G. J. *Inorg. Chem.*, in press.

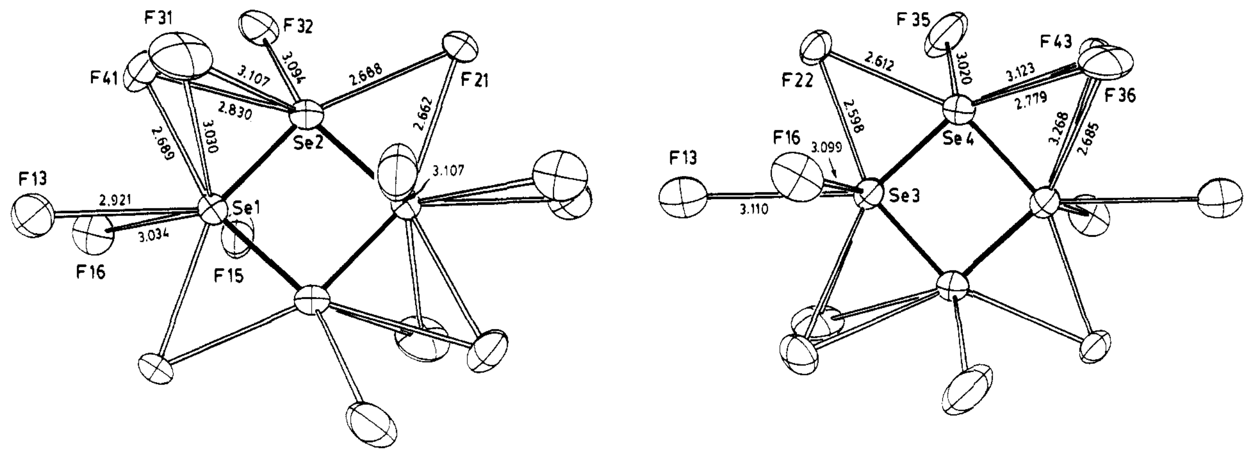

Figure 4. Anion–cation interactions of $(S_{3.0}Se_{1.0})_2(Sb_4F_{17})(SbF_6)_3$. Bond lengths (Å): Se(1)–Se(2) = 2.165 (3); Se(1)–Se(2′) = 2.137 (3); Se(3)–Se(4) = 2.125 (4); Se(3)–Se(4′) = 2.109 (4). Bond angles (deg): Se(2)–Se(1)–Se(2′) = 89.1 (2); Se(1)–Se(2)–Se(1′) = 90.9 (2); Se(4)–Se(3)–Se(4′) = 89.0 (2); Se(3)–Se(4)–Se(3′) = 91.0 (2).

having the highest value, 0.43 s. T_1 values of 5–10 s for aqueous solutions of Na_2SeO_3 and Na_2SeO_4 and 0.3–1.4 s for aqueous solutions of $NaHSeO_3$ and H_2SeO_3 and values ranging from 0.7 s for H_2Se to 31 s for $(C_6H_5CH_2Se)_2$ have been reported along with discussions of the likely relaxation mechanisms.[19,20]

Raman Spectra. The Raman spectra of the solution used to produce the ^{77}Se NMR spectrum given in Figure 2 and for a compound of nominal composition $(S_{3.0}Se_{1.0})(AsF_6)_2$ are given in Figure 3. The signal-to-noise ratio is better for the solution spectrum as the solid decomposed markedly in the laser beam even at 77 K. Three regions in the spectra can be distinguished: (1) S–S stretches at 610–500 cm^{-1}, (2) S–Se stretches at 490–400 cm^{-1}, and (3) Se–Se stretches at 350–300 cm^{-1}. As expected, the intensities of the bands in the Se–Se region increase relative to those in the S–S region as the Se:S ratio increases from 1:3 (Figure 3b) to 1:1 (Figure 3a). Three similar regions are observed in the Raman spectra of disordered S_xSe_{8-x} rings, although the peaks are all shifted to lower frequency for S_xSe_{8-x}, reflecting the lower bond order.[21] The Raman spectrum of $(S_{3.0}Se_{1.0})_2(Sb_4F_{17})(SbF_6)_3$ is very complex since the $Sb_4F_{17}^-$ anion probably has numerous bands in the same region as those of $S_xSe_{4-x}^{2+}$ (Figure 3c).

X-ray Crystallography. Both sulfur and selenium react with SbF_5 in SO_2 solution to give $(M_4)(Sb_2F_4)(Sb_2F_5)(SbF_6)_5$ (M = S or Se), crystallizing in space group $P2_1/c$.[17,22] The compound isolated from a mixture of sulfur and selenium powders, however, crystallizes in space group $B2_1/c$ and has been shown by X-ray crystallography to have the composition $(S_{3.0}Se_{1.0})_2(Sb_4F_{17})(SbF_6)_3$, containing the hitherto unknown $Sb_4F_{17}^-$ anion.

The two crystallographically independent $S_{3.0}Se_{1.0}^{2+}$ cations in the present structure about the centers of symmetry at ($^1/_4$, 0, $^1/_4$) and ($^3/_4$, 0, $^1/_4$) are disordered, and each atomic site is partially occupied by both sulfur and selenium (Table III). Since the S:Se stoichiometry in the reaction was 3:1, it is not surprising that the composition of the resulting cations is $S_{3.0}Se_{1.0}^{2+}$. On the basis of the crystallographic evidence alone one cannot distinguish between a disordered S_3Se^{2+} cation and a disordered mixture of $S_xSe_{4-x}^{2+}$ cations with average composition $S_{3.0}Se_{1.0}^{2+}$. However, the NMR and Raman evidence described above indicates that the solid compound contains a mixture of $S_xSe_{4-x}^{2+}$ cations.

The bond lengths in the present cations (Figure 4) are significantly different, and the mean values for the two cations (2.151 and 2.117 Å) are somewhat long for bonds containing respectively 0.55 and 0.45 selenium at the two bonded sites. For comparison the mean S–S and Se–Se bond lengths in $(S_4)(Sb_2F_4)(Sb_2F_5)(SbF_6)_5$ and $(Se_4)(Sb_2F_4)(Sb_2F_5)(SbF_6)_5$ are 1.988 and 2.256 Å, respectively.[17,22]

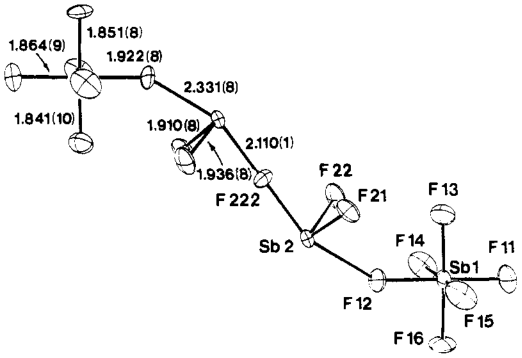

Figure 5. $Sb_4F_{17}^-$ anion in $(S_{3.0}Se_{1.0})_2(Sb_4F_{17})(SbF_6)_3$. Selected bond angles (deg): F(12)–Sb(2)–F(21) = 79.3 (4); F(12)–Sb(2)–F(22) = 80.9 (4); F(12)–Sb(2)–F(222) = 156.7 (2); F(21)–Sb(2)–F(22) = 88.1 (4); F(21)–Sb(2)–F(222) = 82.8 (3); F(22)–Sb(2)–F(222) = 83.6 (3); Sb(1)–F(12)–Sb(2) = 150.8 (5); Sb(2)–F(222)–Sb(2′) = 180.

As described elsewhere,[17] the slight deviations of the square-planar cations from perfect squares and the variations in bond lengths for a given cation from one structure to another may be attributed in part to charge-transfer interactions of the cations with the accompanying anions. In all known cases of M_4^{2+} cations (M = S, Se, and/or Te), each edge of the square is bridged by at least one anion atom and there are usually several additional short anion–cation contacts along the extensions of the diagonals. These positions may be correlated with the symmetries of the available lowest unoccupied molecular orbitals of the M_4^{2+} cation.[17] Contacts to the $S_{3.0}Se_{1.0}^{2+}$ cations of $(S_{3.0}Se_{1.0})_2(Sb_4F_{17})(SbF_6)_3$ (Figure 4) exhibit similar arrangements. For both of the independent cations the four shortest contacts (ranging from 2.598 to 2.830 Å) bridge the edges of the cation. The largest number of contacts are at sites relatively rich in selenium. There are six contacts to X(1) and five contacts to X(3), which are 40.2 and 32.1% selenium, respectively, while X(2) and X(4), with 15.3 and 12.8% selenium, have only four contacts.

The two crystallographically independent SbF_6^- anions in the structure have normal bond lengths and angles except that the fluorine atoms involved in the shorter contacts to the cation and to the $Sb_4F_{17}^-$ anion have somewhat longer Sb–F bonds. The $Sb_4F_{17}^-$ anion (Figure 5) contains two Sb(III) and two Sb(V) atoms and can be broken into an $Sb_2F_5^+$ cation and two SbF_6^- anions. The Sb–F bonds vary in length from 1.85 Å (mean) for the terminal Sb(V)–F bonds to 2.33 Å for the bonds linking the SbF_6^- and $Sb_2F_5^+$ units. The central fluorine atom of $Sb_2F_5^+$ lies on a center of symmetry so that the Sb(III)–F–Sb(III) bond angle

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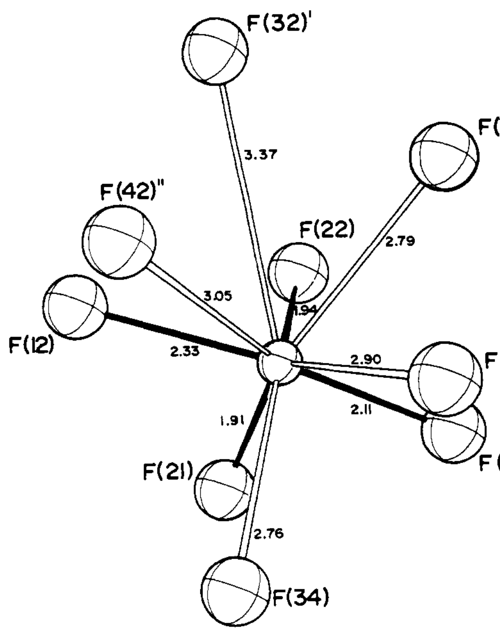

Figure 6. View of the Sb(III) atom of the $Sb_4F_{17}^-$ anion directed toward the assumed direction of the lone pair of electrons of Sb(III). Interionic contacts are indicated by unfilled bonds.

is 180° and the lone pairs on the two Sb(III) atoms are staggered. The Sb(III)–F–Sb(III) bond angles in previously observed $Sb_2F_5^+$ units range from 149.8° in $(SbF_3)_3SbF_5$[23] to 180° in $(SbF_3)_6(SbF_5)_5$.[24] The analogous angle in the isoelectronic $Sn_2F_5^-$ anion[25] is 134°. The primary geometry of the Sb(III) atom in the $Sb_4F_{17}^-$ anion can be described as trigonal-bipyramidal AX_4E, where the lone pair of electrons and the two terminal fluorine atoms occupy the equatorial plane and the bridging fluorine atoms are axial (see Sb(2), Figure 5). In the present structure there are five additional Sb(III)···F contacts shorter than the sum of the van der Waals radii of Sb and F, and overall the environment may be described as $AX_4YY'_4E$[26] (Figure 6). This is a distorted version of an $AX_3Y_3Y'_3E$ arrangement based on a tricapped trigonal prism with (F(222), F(21), F(22)), (F(12), F(34), F(33)′), and (F(32)′, F(11)‴, F(42)″) as the X, Y, and Y′ atoms.[26] A bond valence calculation[27] using all interactions around Sb(III) gives a sum of 3.12. The crystal packing consists of layers of $Sb_4F_{17}^-$ and SbF_6^- anions approximately perpendicular to *b* linked by the Sb(III)···F interactions involving the remaining SbF_6^- anions. The cations are situated in stacks between these anions.

Conclusions

The first examples of mixed S/Se polyatomic cations, $S_xSe_{4-x}^{2+}$, have been prepared by direct oxidation of the elements with AsF_5 and by scrambling of S_4^{2+} and Se_4^{2+} cations in SO_2 solution. The square-planar geometry of the $S_xSe_{4-x}^{2+}$ cations and the existence of the $Sb_4F_{17}^-$ anion have been established by the crystal structure of the new compound $(S_{3.0}Se_{1.0})_2(Sb_4F_{17})(SbF_6)_3$. Evidence for a second series of S/Se cations has been obtained by ^{77}Se NMR spectroscopy. The chemical shifts of these species indicate that they are not isostructural with the presently known polyatomic cations of selenium.

Acknowledgment. We thank Dr. R. E. Lenkinski and J. B. Macdonald of the South Western Ontario NMR Center (Guelph) for assistance in obtaining many of the NMR spectra, Dr. R. C. Burns for helpful discussions regarding the chemical shift assignments, and the Natural Sciences and Engineering Research Council of Canada for supporting this work.

Registry No. $(S_{3.0}Se_{1.0})_2(Sb_4F_{17})(SbF_6)_3$, 101248-77-5; $(Se_4)(Sb_2F_4)(Sb_2F_5)(SbF_6)_5$, 82434-40-0; $(S_{3.0}Se_{1.0})(AsF_6)_2$, 101248-72-0; Se_4, 12310-32-6; Se_3S, 101248-73-1; *cis*-Se_2S_2, 101248-74-2; *trans*-Se_2S_2, 101248-75-3; SeS_3, 101248-71-9; Se, 7782-49-2; S, 7704-34-9; ^{77}Se, 14681-72-2.

Supplementary Material Available: Supplementary Tables I–III, containing complete bond lengths and bond angles, anisotropic thermal parameters, and final structure factor amplitudes for $(S_{3.0}Se_{1.0})_2(Sb_4F_{17})(SbF_6)_3$, respectively (21 pages). Ordering information is given on any current masthead page.

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Preparation and Structure of $[W_2(CO)_{10}Se_4][AsF_6]_2$ and Related Compounds

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Received October 9, 1985

The reactions of $Se_4(AsF_6)_2$, $Se_8(AsF_6)_2$, and $Se_{10}(SbF_6)_2$ with $Mo(CO)_6$ and $W(CO)_6$ in liquid SO_2 give the diamagnetic products $[M_2(CO)_{10}Se_4][EF_6]_2$ (M = Mo, W; E = As, Sb) in high yields. The structure of $[W_2(CO)_{10}Se_4][AsF_6]_2$ (Ia) has been established by X-ray crystallography. Crystals of Ia are monoclinic, space group $P2_1/c$, with $a = 8.688$ (1) Å, $b = 7.036$ (1) Å, $c = 21.767$ (1) Å, $\beta = 95.30$ (1)°, $U = 1324.9$ (4) Å^3, and $D_{calcd} = 3.36$ g cm^{-3} for $Z = 2$. The structure consists of two centrosymmetrically related pentagonal-bipyramidal $W(CO)_5(\eta^2\text{-}Se_2)^+$ groups linked by weak Se–Se bonds of length 3.015 (2) Å between the diselenide groups. The Se–Se distance in the η^2-Se_2 moiety (2.213 (2) Å) is the shortest solid-state Se–Se bond reported to date. The interactions between the diselenide groups are analogous to those observed in the $Se_4S_2N_4^{2+}$ cation, and the bonding is discussed with use of this cation as a model.

Introduction

The chalcogen cations such as Se_4^{2+}, Te_6^{4+}, S_8^{2+}, and S_{19}^{2+} are now well-known, and a considerable amount of structural and spectroscopic information has been obtained in recent years,[1,2] but their chemistry has not been extensively investigated. Reactions of these cations with elemental sulfur, selenium, and tellurium yield a variety of heteroatomic clusters.[3] The cations react with perfluorocarbons, giving various perfluorinated tellurides, selenides, and sulfides.[4] Reaction with hydrocarbons results

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