of R_1 (ca. 5 and 9.5 G, respectively; see also ref 35), the hyperfine splitting would not be resolved, assuming similar resolution. Furthermore, the signal of R_2 splits into three lines on freezing at 77 K, implying less than axial symmetry, as observed for the static conformations of either of the S_7 rings in the S_{19}^{2+} cation. However, other radicals such as S_8^+ might also be expected to fit these criteria. It must be concluded that the progressive oxidation of sulfur to give singly charged cation radicals and doubly charged cations, several of which may be in equilibrium at any one time, is by no means well understood at present.

Note Added in Proof: Very recently, X-ray crystallographic studies of the compounds $S_4(AsF_6)_2 \cdot 0.6(SO_2)$ and $S_4(S_7I)_4$-$(AsF_6)_2$ have confirmed that the S_4^{2+} cation does have a square-planar structure in the $(S_{16}^{2+})(AsF_6)_2$ solid state.[41]

(41) Passmore, J.; Sutherland, G.; White, P. S., unpublished results.

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Preparation and Characterization of $Se_{10}(AsF_6)_2$, $Se_{10}(SbF_6)_2$, and $Se_{10}(AlCl_4)_2$ and Crystal Structure of $Se_{10}(SbF_6)_2$

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Preparative routes for the title compounds are described along with a single-crystal X-ray structural study of the $Se_{10}(SbF_6)_2$ salt. Crystals of $Se_{10}(SbF_6)_2$ form deep red plates which crystallize in the monoclinic space group $P2_1/c$ with $a = 19.869$ (5) Å, $b = 16.200$ (4) Å, $c = 13.282$ (3) Å, $\beta = 109.24$ (2)°, and $d_{calcd} = 4.15$ g cm^{-3} for $Z = 8$. The structure has been determined by direct methods and refined by least squares to final agreement indices $R_1 = 0.096$ and $R_2 = 0.128$ for 2832 observed reflections ($I/\sigma(I) > 3.0$). The Se_{10}^{2+} cation can be described as a six-membered boat-shaped ring linked across the middle by a chain of four selenium atoms, that is, a bicyclo[4.2.2]decane type structure, and is isostructural with the known $Te_2Se_8^{2+}$ cation. The selenium–selenium bonds in the cation vary greatly in length from 2.24 to 2.44 Å. These variations in the bond lengths and the relationship of the cage structure of Se_{10}^{2+} to the cuneane and pentagonal-prism structures are discussed. The electronic absorption and diffuse reflectance spectra of the Se_{10}^{2+} cation are also reported and compared with that of the Se_8^{2+} cation.

Introduction

Two homopolyatomic cations of selenium, Se_4^{2+} and Se_8^{2+}, are well-known, and a number of salts of both cations have been prepared.[1-5] X-ray crystallographic determinations of the structures of $Se_4(HS_2O_7)_2$[5] and $Se_8(AlCl_4)_2$[4] have established that Se_4^{2+} is square planar and that Se_8^{2+} is an eight-membered ring with an exo–endo conformation and a long cross-ring bond. The analogous cations of sulfur, S_4^{2+}[7,9] and S_8^{2+},[8-10] have similar shapes. In addition a third cation, which

was previously reported as S_{16}^{2+},[8,9] has recently been shown by an X-ray crystallographic study of the hexafluoroarsenate salt to be the cation S_{19}^{2+}.[11] This species consists of two seven-membered rings joined by a five-atom chain. No evidence has been obtained for an analogous selenium species, although the results of a recent potentiometric and spectrophotometric study of cationic species of selenium in NaCl–AlCl₃ melts have been interpreted as indicating the presence of the Se_{12}^{2+} and Se_{16}^{2+} cations.[12] Recently, the heteropolyatomic cation $Te_2Se_8^{2+}$ has been prepared by the reaction of tellurium with Se_8^{2+}, and an X-ray crystallographic study indicated that it has a bicyclic structure with an eight-membered ring fused to a six-membered ring.[13] The object of the present work was to attempt the preparation of the analogous homopolyatomic cation Se_{10}^{2+} and/or other homopolyatomic cations of selenium containing the element in a lower formal oxidation state than that found in the Se_8^{2+} species. This paper reports the preparation and characterization of the compounds $Se_{10}(AsF_6)_2$, $Se_{10}(SbF_6)_2$, and $Se_{10}(AlCl_4)_2$, and an X-ray

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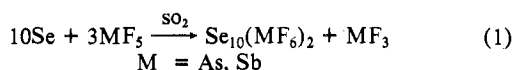
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Se₁₀(AsF₆)₂, Se₁₀(SbF₆)₂, and Se₁₀(AlCl₄)₂ — Se$_{10}$(AsF$_6$)$_2$, Se$_{10}$(SbF$_6$)$_2$, and Se$_{10}$(AlCl$_4$)$_2$

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crystallographic study of Se$_{10}$(SbF$_6$)$_2$.

Experimental Section

Materials. Elemental selenium ("Baker Analyzed", J. T. Baker Chemical Co.) was used as supplied. Arsenic pentafluoride (Ozark Mahoning Co.) was used directly from the cylinder. Antimony pentafluoride (Ozark Mahoning Co.) was doubly distilled in a Pyrex glass still in an atmosphere of dry nitrogen. Anhydrous sulfur dioxide (Matheson of Canada) was stored over P$_4$O$_{10}$ and was distilled directly before use. Commercial aluminum trichloride was purified by vacuum sublimation, after a prior sublimation from aluminum powder to remove the iron impurity. Selenium monochloride (Galland-Schlesinger Chemical Co., Ltd.) was distilled in a dry atmosphere before use. All other materials were of reagent grade quality and were used directly as supplied.

Preparation of Se$_{10}$(AsF$_6$)$_2$ and Se$_{10}$(SbF$_6$)$_2$. The hexafluoroarsenate and hexafluoroantimonate salts of Se$_{10}$$^{2+}$ were prepared in SO$_2$ by oxidation of selenium metal with AsF$_5$ and SbF$_5$, respectively, in the presence of excess metal.

$$10\text{Se} + 3\text{MF}_5 \xrightarrow{\text{SO}_2} \text{Se}_{10}(\text{MF}_6)_2 + \text{MF}_3 \qquad (1)$$
$$\text{M} = \text{As, Sb}$$

These reactions are conveniently carried out in double-arm ampules, as described previously.[14]

In a typical experiment AsF$_5$ (1.22 g, 0.0072 mol) was condensed onto selenium metal (2.00 g, 0.0253 mol) in about 30–40 cm^3 of SO$_2$ at −196 °C. Alternatively, when SbF$_5$ was used as the oxidant, it was added via a syringe to the second arm of the double-ampule apparatus inside a drybox and, after dissolution in the solvent, was poured over onto the metal at low temperatures. Oxidation of the metal occurred as the ampule was allowed to warm up to room temperature, giving a dark green solution, characteristic of the Se$_8$$^{2+}$ cation. Over a period of 2–3 days, or on heating to ca. 50 °C for a number of hours, the solution became brownish green, indicating further reaction. The solution was then filtered to remove the insoluble material. Several extractions were required in order to separate all of the product from the unreacted metal. The solid compound was then isolated by removal of the solvent. The yield was essentially quantitative on the basis of the amount of oxidant used.

Anal. Calcd for Se$_{10}$(AsF$_6$)$_2$: Se, 67.67; As, 12.84; F, 19.54. Found: Se, 67.04; As, 10.69; F, 21.30.

The hexafluoroarsenate salt was also prepared by the reaction of Se$_8$(AsF$_6$)$_2$[14] and elemental selenium. Presumably the hexafluoroantimonate salt could also be prepared in this manner.

Crystals of the hexafluoroantimonate salt suitable for X-ray study were obtained by the following procedure. Since this compound is more soluble in SO$_2$ at low temperatures than at room temperature, Se$_{10}$(SbF$_6$)$_2$ was first dissolved in SO$_2$ at ca. −70 °C by using an acetone–dry ice bath. The bath was subsequently allowed to warmup to room temperature over a period of 24 h, during which time crystals were deposited on the walls of the vessel. The solvent and soluble compound were then filtered to the other side of the reaction vessel and the crystals isolated, the final traces of SO$_2$ being removed under vacuum.

Preparation of Se$_{10}$(AlCl$_4$)$_2$. The tetrachloroaluminate salt was prepared from Se$_8$(AlCl$_4$)$_2$ by a disproportionation reaction in SO$_2$ solution, as described below. The Se$_8$(AlCl$_4$)$_2$ was initially prepared by the reaction of Se$_2$Cl$_2$ with AlCl$_3$ in SO$_2$. About 4 cm^3 (0.0484 mol) of Se$_2$Cl$_2$ was dissolved in ca. 80 mL of SO$_2$ at room temperature. This solution was then poured onto 11.12 g (0.0834 mol) of AlCl$_3$. Upon mixture, there was an immediate reaction to give a deep green solution. After the mixture was stirred for about 3 h at room temperature, a dark green solid had deposited, while the supernatant solution was dark green-brown. The solution was then filtered and the SO$_2$ distilled back so that the product could be washed. This was repeated three times. All the SO$_2$ solvent was then removed under vacuum. Anal. Calcd for Se$_8$(AlCl$_4$)$_2$: Se, 65.17; Al, 5.57; Cl, 29.26. Found: Se, 64.87; Al, 5.36; Cl, 29.12.

The salt Se$_8$(AlCl$_4$)$_2$ is only sparingly soluble in SO$_2$, giving a pale yellow solution, and prolonged washing and extraction of the soluble products resulted in disproportionation of the compound, to give Se$_{10}$(AlCl$_4$)$_2$ and other products. In a typical preparation Se$_8$(AlCl$_4$)$_2$

(9.35 g, 0.0096 mol) was stirred with ca. 80 cm^3 of SO$_2$ in a double-arm ampule at room temperature. After about 30 min the disproportionation reaction resulted in the formation of a brown solid and a reddish brown supernatant solution. The solution was filtered from the solid. The SO$_2$ was then distilled from the solution back onto the solid leaving a red-brown oil, presumably Se$_2$Cl$_2$, a white solid, presumably AlCl$_3$, and a trace of dark green Se$_8$(AlCl$_4$)$_2$, which is slightly soluble in SO$_2$. This process was repeated ten times, after which a homogeneous material was obtained. Anal. Calcd for Se$_{10}$(AlCl$_4$)$_2$: Se, 70.05; Al, 4.79; Cl, 25.16. Found: Se, 69.86; Al, 4.64; Cl, 24.79.

Spectra. Absorption spectra were obtained by using a Cary 14 spectrophotometer using 1-cm quartz cells, against a reference cell containing solvent. All solutions were handled in the drybox. Electronic diffuse reflectance spectra were recorded by using a Beckman DK-2A ratio recording spectrophotometer, equipped with a standard reflectance attachment. Samples were stored in airtight cells similar to those described by Reid, Scaife, and Wailes[15] and were recorded against MgO.

Analyses. Analyses were carried out by Alfred Bernhardt Microanalytisches Laboratorium, 5251 Elbach über Engelskirchen, West Germany.

X-ray Intensity Measurements. Crystals of Se$_{10}$(SbF$_6$)$_2$ occur as deep red-brown platelets with (100) developed. Several of these crystals were selected and mounted in ca. 0.2-mm diameter Pyrex capillaries under a nitrogen atmosphere in a specially designed drybox. Twinning was apparent in photographs of all but one of these crystals, and this crystal was used in all subsequent work.

Initial work on a Syntex P2$_1$ diffractometer gave a possible orthorhombic cell which was consistent with two zero layer precession photographs, both of which had apparent *mm* symmetry. However, closer examination of the data showed small but significant deviations in the *mm* symmetry of the zero layer photographs. Furthermore, when the crystal was returned to the diffractometer, axial photographs about two of the vectors of the possible orthorhombic cell failed to show mirror symmetry. Hence the true symmetry of the crystal is monoclinic $2/m$ which suggests that the crystal may be pseudomerohedrally twinned.[16,17] Among the possible monoclinic cells produced by the autoindexing program were two cells of approximately the same dimensions, which are related to each other by a 180° rotation about one of the axes ($c = 13.28$ Å). One of these cells was chosen, and examination of systematically absent reflections gave $P2_1/c$ as the space group. It was with this monoclinic cell that the structure was eventually solved.

Crystal Data. Se$_{10}$Sb$_2$F$_{12}$: fw = 1261.1; monoclinic; $a = 19.869$ (5), $b = 16.200$ (4), $c = 13.282$ (3) Å; $\beta = 109.24$ (2)°; $V = 4036$ (2) Å^3; and $d_{\text{calcd}} = 4.15$ g/cm^3 for $Z = 8$ (two independent molecules); Mo Kα radiation ($\lambda = 0.71069$ Å); μ(Mo Kα) = 221.9 cm^{-1}; $F(000)$ = 4400; systematic absences $h0l$, $l \neq 2n$, and $0k0$, $k \neq 2n$, indicate space group $P2_1/c$ (No. 14).

A preliminary study of crystals of the hexafluoroarsenate salt established that they were isomorphous with Se$_{10}$(SbF$_6$)$_2$. Crystals of Se$_{10}$(AsF$_6$)$_2$ are therefore monoclinic with cell dimensions $a = 19.464$ (31) Å, $b = 15.951$ (12) Å, $c = 13.104$ (23) Å, and $\beta = 109.3$ (9)°, but since X-ray diffraction from these crystals was poor, no further work on these crystals was attempted.

The crystal of Se$_{10}$(SbF$_6$)$_2$ used throughout was a thin plate of overall dimensions 0.025 × 0.19 × 0.29 mm in the a, b, c^* directions with the faces (±1, 0, 0), (0, ±1, 0), (1$\bar{1}$0), and (0$\bar{1}$1) developed. Accurate unit cell dimensions were obtained from this crystal by least-squares refinement of the diffracting positions of 15 high-angle (21.4° < 2θ < 28.0°) reflections by using graphite monochromatized Mo Kα radiation on a Syntex P2$_1$ diffractometer. Data were collected by using an orientation matrix based on this cell and θ–2θ scans over a scan range (Kα_1 − 0.8°) to (Kα_2 + 0.8°). A variable scan rate of 3.0–29.3°/min was used and depended on the intensity of a preliminary count. Stationary background counts were measured at each end of the scan, each for half of the scan time. The intensities of three standard reflections were collected after every 37 reflections to check

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Table I. Final Atomic Positional ($\times 10^4$) Parameters[a] with Standard Deviations in Parentheses for $Se_{10}(SbF_6)_2$

atom[b]	X/a	Y/b	Z/c	atom[b]	X/z	Y/b	Z/c
Sb(1)	8697 (2)	4249 (2)	−32 (3)	Se(19)	4547 (4)	7394 (4)	−1517 (5)
Sb(2)	1438 (2)	9025 (2)	434 (3)	Se(110)	3992 (4)	6182 (4)	−1544 (5)
Sb(3)	3666 (2)	4244 (2)	975 (3)	Se(21)	10210 (3)	7565 (4)	2244 (5)
Sb(4)	3629 (2)	975 (2)	1628 (3)	Se(22)	9675 (3)	8858 (3)	1429 (5)
Se(11)	5175 (3)	7596 (4)	397 (5)	Se(23)	9028 (3)	9267 (3)	2451 (5)
Se(12)	4660 (4)	8890 (4)	659 (5)	Se(24)	7875 (3)	8794 (4)	1481 (5)
Se(13)	4041 (4)	9305 (4)	−1020 (5)	Se(25)	7663 (3)	7797 (4)	2525 (5)
Se(14)	2873 (4)	8920 (4)	−1177 (5)	Se(26)	7984 (3)	6513 (4)	1829 (5)
Se(15)	2625 (3)	7871 (4)	−2373 (4)	Se(27)	9092 (3)	6149 (3)	3140 (5)
Se(16)	2885 (3)	6609 (4)	−1326 (5)	Se(28)	9618 (3)	7396 (4)	3562 (4)
Se(17)	3388 (3)	7185 (4)	448 (5)	Se(29)	9545 (3)	6573 (3)	961 (5)
Se(18)	4486 (3)	6620 (4)	1024 (5)	Se(210)	8436 (3)	7073 (4)	480 (4)
F(1)	8394 (21)	4875 (22)	9956 (28)	F(13)	3523 (36)	3411 (39)	123 (49)
F(2)[c]	9662 (–)	4330 (–)	812 (–)	F(14)	3202 (21)	4870 (24)	−190 (29)
F(3)[c]	8636 (–)	3222 (–)	589 (–)	F(15)	3805 (25)	5192 (28)	1800 (34)
F(4)	8751 (35)	5271 (41)	−646 (48)	F(16)	4186 (25)	3592 (27)	2191 (33)
F(5)	7748 (28)	4146 (32)	−913 (39)	F(17)	2832 (29)	4027 (33)	1307 (39)
F(6)	8958 (20)	3715 (21)	−1084 (26)	F(18)	4450 (28)	4400 (29)	565 (38)
F(7)	1380 (25)	8443 (27)	−851 (35)	F(19)	2797 (22)	1651 (24)	1140 (31)
F(8)	529 (19)	9501 (20)	−175 (25)	F(20)	4443 (27)	245 (29)	2207 (36)
F(9)	2347 (19)	8531 (21)	1068 (26)	F(21)	4017 (42)	1460 (46)	721 (58)
F(10)	1541 (23)	9516 (24)	1697 (31)	F(22)	3888 (34)	1721 (38)	2739 (48)
F(11)	1820 (16)	9939 (17)	−1 (22)	F(23)	3210 (36)	425 (41)	2470 (50)
F(12)	972 (19)	8095 (21)	843 (27)	F(24)	3275 (26)	255 (30)	525 (35)

[a] Thermal parameters for these atoms have been deposited as supplementary material. [b] The first digit in the numbering scheme for the selenium atoms refers to the two independent cations. [c] Positional parameters not refined in final cycle of least squares.

for instrument and crystal stability and showed no significant variation with time. A total of 7705 reflections in the octants h, k, $\pm l$ with $2\theta < 47.5°$ were collected, of which 3423 were considered observed ($I/\sigma(I) > 3.0$).

The observed intensities were corrected for Lorentz and polarization effects. In the latter stages of the refinement, corrections for absorption effects were calculated by the program ABSORB[18] using a Gaussian grid of 12 × 9 × 4. The A^* values were found to vary from 1.766 to 23.958. After averaging equivalent reflections a final data set of 2894 observed reflections was obtained and used in the final refinements.

Structure Solution and Refinement. The positions of all the heavy atoms in the structure were readily located by using the direct-methods program PHASE and SINGEN of the XRAY 71 system.[18] Subsequent Fourier maps enabled all of the fluorine atoms to be located. Several cycles of least-squares refinement with all the atoms of both Se_{10}-$(SbF_6)_2$ groups gave an R_1 value of 0.195 ($R_1 = \sum(|F_o| - |F_c|)/\sum|F_o|$) using isotropic temperature factors. After the application of an absorption correction to the data and the introduction of anisotropic temperature factors for the antimony and selenium atoms, several cycles of block-diagonal least squares eventually converged to $R_1 = 0.108$ and $R_2 = 0.130$, using unit weights ($R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w F_o^2]^{1/2}$).

This was considered to be a relatively poor agreement even after allowing for the large absorption corrections required by the large value to μ and the unfavorable shape of the crystal. An examination of the most intense reflections showed a slight tendency for F_c to be greater than F_o, but in each case the difference was comparable to the current residual so that no extinction corrections were considered necessary. An examination of the residuals for different parity groups again failed to reveal any systematic trends in the data, although it was noticed that among the weaker data there were 62 reflections with $F_o \gg F_c$ and for which the agreement in each case was relatively poor ($||F_o| - |F_c||/F_o > 0.6$). There appeared to be no systematic relationship between the indices of these reflections and, since these reflections were close to the observed/unobserved limit, they were eliminated from further refinement.

By use of the remaining 2832 reflections, refinement reduced R_1 to 0.097. Introduction of a weighting scheme and several further cycles of block-diagonal least squares eventually converged with $R_1 = 0.095$ and $R_2 = 0.127$. At this point it was noted that the geometry of one of the SbF_6^- anions was somewhat distorted from a regular octahedron, with some of the cis F–Sb–F angles as low as 65°. This distortion

involved the two fluorine atoms F(2) and F(3) with large temperature factors ($U \simeq 0.20$). Several attempts were made to refine these atoms into positions which would give a more regular octahedral geometry, but on each occasion the atoms refined back to their false minima with poor cis and trans angles. It was therefore decided to fix the positional parameters and only refine an isotropic temperature factor for these two fluorine atoms in the final cycles of refinement. Two further cycles of block-diagonal refinement then converged to give $R_1 = 0.096$ and $R_2 = 0.128$, where the weights used were given by the expression $w = 65/F^2$. In the final cycle of refinement the average parameter shift divided by its standard error was 0.035. The maximum shift/error for any parameter was 0.165 for the temperature factor of atom F(2). A final comparison of the average $w||F_o| - |F_c||^2$ as a function of F_o and sin θ revealed no systematic trends. A final difference Fourier contained several peaks and troughs of ± 2 e/Å³. The maximum peak and minimum trough were, however, +3.0 e/Å³ and −3.0 e/Å³ and were close to antimony atoms Sb(2) and Sb(4), respectively. These relatively large features in the difference Fourier are probably a result of small errors in the absorption correction.

The atomic scattering factors for neutral Sb, Se, and F in the analytical form were taken from ref 19. All calculations were performed on a CDC 6400 computer using a series of programs in the XRAY 71 system and some local programs.[18] The final atomic positional coordinates are given in Table I. Interatomic distances and angles and dihedral angles in the Se_{10}^{2+} cations are included in Table II, and some selected inter- and intramolecular contact distances are listed in Table III. A tabulation of the observed and calculated structure factors and thermal parameters is available.[20]

Discussion

The Preparation of $Se_{10}(AsF_6)_2$ and $Se_{10}(SbF_6)_2$. The hexafluoroarsenate salt was prepared by the reaction of excess selenium with AsF_5 in solution in SO_2 or by the reaction of an SO_2 solution of $Se_8(AsF_6)_2$ with elemental selenium at room temperature. The hexafluoroantimonate was prepared by the reaction of SbF_5 with excess selenium in solution in SO_2 but presumably can also be prepared by the alternative route. The reactions proceed according to the equations

$$10Se + 3MF_5 \rightarrow Se_{10}(MF_6)_2 + MF_3 \qquad (1)$$
$$M = As, Sb$$

$$2Se + Se_8(AsF_6)_2 \rightarrow Se_{10}(AsF_6)_2$$
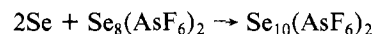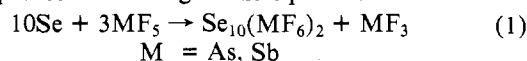
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(20) Supplementary material.

Table II. Bond Distances, Bond Angles, and Dihedral Angles with Standard Deviations in Parentheses for Se$_{10}$(SbF$_6$)$_2$

Bond Distances (Å)

	cation 1	cation 2		cation 1	cation 2
Se(1)-Se(2)	2.410 (9)	2.437 (8)	Se(5)-Se(6)	2.431 (8)	2.445 (9)
Se(1)-Se(8)	2.413 (9)	2.425 (10)	Se(6)-Se(7)	2.422 (8)	2.388 (8)
Se(1)-Se(9)	2.456 (8)	2.398 (8)	Se(6)-Se(10)	2.413 (10)	2.428 (10)
Se(2)-Se(3)	2.265 (8)	2.254 (10)	Se(7)-Se(8)	2.254 (9)	2.259 (8)
Se(3)-Se(4)	2.347 (10)	2.356 (8)	Se(9)-Se(10)	2.246 (9)	2.234 (9)
Se(4)-Se(5)	2.266 (8)	2.258 (9)			
Sb(1)-F(1)	1.91 (4)		Sb(3)-F(13)	1.72 (6)	
F(2)	1.88 (11)[a]		F(14)	1.83 (4)	
F(3)	1.88 (11)[a]		F(15)	1.85 (5)	
F(4)	1.86 (7)		F(16)	1.92 (4)	
F(5)	1.87 (5)		F(17)	1.88 (6)	
F(6)	1.86 (4)		F(18)	1.83 (6)	
Sb(2)-F(7)	1.93 (5)		Sb(4)-F(19)	1.91 (4)	
F(8)	1.88 (3)		F(20)	1.95 (5)	
F(9)	1.90 (3)		F(21)	1.81 (9)	
F(10)	1.81 (4)		F(22)	1.85 (6)	
F(11)	1.84 (3)		F(23)	1.83 (8)	
F(12)	1.94 (4)		F(24)	1.82 (5)	

Bond Angles (Deg)

	cation 1	cation 2		cation 1	cation 2
Se(2)-Se(1)-Se(8)	101.7 (4)	100.0 (3)	Se(5)-Se(6)-Se(7)	100.0 (3)	103.1 (3)
Se(2)-Se(1)-Se(9)	99.8 (3)	101.7 (3)	Se(5)-Se(6)-Se(10)	101.7 (3)	99.6 (3)
Se(8)-Se(1)-Se(9)	96.7 (3)	98.8 (3)	Se(7)-Se(6)-Se(10)	97.3 (3)	98.9 (3)
Se(1)-Se(2)-Se(3)	103.6 (3)	103.7 (3)	Se(6)-Se(7)-Se(8)	102.5 (3)	101.5 (3)
Se(2)-Se(3)-Se(4)	102.0 (4)	102.7 (3)	Se(7)-Se(8)-Se(1)	102.3 (3)	102.5 (3)
Se(3)-Se(4)-Se(5)	104.0 (4)	104.0 (3)	Se(1)-Se(9)-Se(10)	102.3 (3)	102.8 (3)
Se(4)-Se(5)-Se(6)	105.9 (3)	104.5 (4)	Se(9)-Se(10)-Se(6)	102.1 (3)	102.9 (3)
F(1)-Sb(1)-F(2)	93.(4)[a]		F(13)-Sb(3)-F(14)	87 (2)	
F(3)	95 (4)[a]		F(15)	176 (3)	
F(4)	85 (3)		F(16)	93 (2)	
F(5)	90 (2)		F(17)	92 (3)	
F(6)	175 (1)		F(18)	83 (3)	
F(2)-Sb(1)-F(3)	90 (5)[a]		F(14)-Sb(3)-F(15)	89 (2)	
F(4)	90 (4)[a]		F(16)	178 (2)	
F(5)	178 (4)[a]		F(17)	94 (2)	
F(6)	90 (4)[a]		F(18)	85 (2)	
F(3)-Sb(1)-F(4)	180 (4)[a]		F(15)-Sb(3)-F(16)	91 (2)	
F(5)	90 (3)[a]		F(17)	89 (2)	
F(6)	90 (4)[a]		F(18)	95 (2)	
F(4)-Sb(1)-F(5)	90 (2)		F(16)-Sb(3)-F(17)	88 (2)	
F(6)	91 (3)		F(18)	93 (2)	
F(5)-Sb(1)-F(6)	88 (2)		F(17)-Sb(3)-F(18)	176 (2)	
F(7)-Sb(2)-F(8)	93 (2)		F(19)-Sb(4)-F(20)	175 (2)	
F(9)	88 (2)		F(21)	92 (3)	
F(10)	176 (2)		F(22)	83 (2)	
F(11)	91 (2)		F(23)	88 (3)	
F(12)	89 (2)		F(24)	92 (2)	
F(8)-Sb(2)-F(9)	179 (2)		F(20)-Sb(4)-F(21)	93 (3)	
F(10)	91 (2)		F(22)	96 (2)	
F(11)	88 (1)		F(23)	87 (3)	
F(12)	88 (2)		F(24)	89 (2)	
F(9)-Sb(2)-F(10)	89 (2)		F(21)-Sb(4)-F(22)	100 (3)	
F(11)	93 (1)		F(23)	176 (3)	
F(12)	91 (2)		F(24)	83 (3)	
F(10)-Sb(2)-F(11)	90 (2)		F(22)-Sb(4)-F(23)	84 (3)	
F(12)	90 (2)		F(24)	174 (3)	
F(11)-Sb(2)-F(12)	176 (1)		F(23)-Sb(4)-F(24)	93 (3)	

Dihedral Angles (Deg)

	cation 1	cation 2		cation 1	cation 2
Se(8)-Se(1)-Se(2)-Se(3)	−108.5	+6.3	Se(6)-Se(7)-Se(8)-Se(1)	+91.8	−92.8
Se(9)-Se(1)-Se(2)-Se(3)	−9.4	+107.5	Se(7)-Se(8)-Se(1)-Se(2)	+37.6	+123.0
Se(1)-Se(2)-Se(3)-Se(4)	+99.8	−96.9	Se(7)-Se(8)-Se(1)-Se(9)	−63.8	+19.4
Se(2)-Se(3)-Se(4)-Se(5)	−110.8	+112.7	Se(2)-Se(1)-Se(9)-Se(10)	−121.1	−40.3
Se(3)-Se(4)-Se(5)-Se(6)	+95.5	−95.8	Se(8)-Se(1)-Se(9)-Se(10)	−17.9	+61.9
Se(4)-Se(5)-Se(6)-Se(7)	−5.5	+105.6	Se(1)-Se(9)-Se(10)-Se(6)	+92.0	−94.4
Se(4)-Se(5)-Se(6)-Se(10)	−105.2	+4.1	Se(9)-Se(10)-Se(6)-Se(5)	+37.7	+122.7
Se(5)-Se(6)-Se(7)-Se(8)	−121.2	−38.8	Se(9)-Se(10)-Se(6)-Se(7)	−64.2	+17.6
Se(10)-Se(6)-Se(7)-Se(8)	−17.8	+63.3			

[a] Positional parameters of these atoms not refined during last cycle of least squares; standard deviations in parentheses are estimated from the errors associated with the previous cycle.

Table III. Contact Distances (Å) in $Se_{10}(SbF_6)_2$

	cation 1	cation 2		cation 1	cation 2
		Intramolecular			
Se(1)···Se(3)	3.674 (8)	3.690 (9)	Se(4)···Se(7)	3.485 (9)	
Se(1)···Se(7)	3.636 (9)	3.653 (10)	Se(4)···Se(10)		3.428 (9)
Se(1)···Se(10)	3.664 (8)	3.620 (8)	Se(5)···Se(7)	3.718 (8)	3.786 (9)
Se(2)···Se(4)	3.584 (8)	3.600 (10)	Se(5)···Se(8)		3.726 (8)
Se(2)···Se(7)	3.692 (9)		Se(5)···Se(9)	3.690 (9)	
Se(2)···Se(8)	3.741 (9)	3.723 (9)	Se(5)···Se(10)	3.757 (9)	3.723 (10)
Se(2)···Se(9)	3.722 (9)	3.749 (8)	Se(6)···Se(8)	3.649 (7)	3.600 (8)
Se(2)···Se(10)		3.737 (8)	Se(6)···Se(9)	3.625 (10)	3.648 (11)
Se(3)···Se(5)	3.635 (8)	3.636 (9)	Se(7)···Se(9)		3.372 (10)
Se(3)···Se(8)		3.405 (8)	Se(7)···Se(10)	3.629 (10)	3.659 (8)
Se(3)···Se(9)	3.386 (9)		Se(8)···Se(9)	3.639 (9)	3.661 (9)
Se(4)···Se(6)	3.749 (9)	3.721 (9)	Se(8)···Se(10)	3.301 (9)	
		Interionic^a			
Se(12)···Se(13)^I	3.823 (9)		Se(18)···Se(19)^{III}	3.602 (9)	
Se(14)···Se(24)^I	3.961 (9)		Se(25)···Se(210)^{III}	3.719 (8)	
Se(15)···Se(17)^{II}	3.686 (10)		Se(28)···Se(29)^{III}	3.642 (9)	
Se(17)···Se(19)^{III}	3.988 (8)				
Se(14)···F(7)	3.22 (5)		Se(26)···F(1)	3.11 (4)	
Se(16)···F(14)	3.16 (4)		Se(29)···F(4)	3.05 (6)	
Se(18)···F(15)	3.03 (5)				
Se(11)···F(21)^{IV}	2.95 (9)		Se(21)···F(7)^{IX}	3.25 (4)	
Se(11)···F(22)^{V}	2.93 (6)		Se(21)···F(2)^{X}	3.21 (9)	
Se(12)···F(16)^{V}	3.06 (4)		Se(21)···F(12)^{XI}	2.89 (4)	
Se(12)···F(20)^{VI}	3.13 (5)		Se(22)···F(12)^{XI}	3.18 (4)	
Se(13)···F(15)^{II}	2.89 (5)		Se(22)···F(8)^{XII}	3.09 (3)	
Se(14)···F(24)^{VI}	3.04 (5)		Se(23)···F(4)^{III}	2.86 (7)	
Se(15)···F(9)^{II}	3.00 (3)		Se(23)···F(2)^{X}	2.86 (10)	
Se(15)···F(5)^{VII}	2.98 (5)		Se(24)···F(11)^{XII}	3.04 (3)	
Se(18)···F(22)^{V}	3.11 (6)		Se(25)···F(17)^{V}	2.89 (6)	
Se(110)···F(18)^{IV}	3.08 (5)		Se(25)···F(19)^{V}	2.91 (5)	
Se(110)···F(20)^{VIII}	3.14 (5)		Se(27)···F(8)^{IX}	3.17 (3)	
Se(110)···F(23)^{VIII}	3.09 (6)		Se(27)···F(10)^{XIII}	2.97 (4)	
			Se(29)···F(6)^{XIV}	2.96 (4)	

^{a} Roman numerals as superscripts refer to atoms related to the position x, y, z by the transformations: (I) $1-x$, $2-y$, $-z$; (II) x, $^3/_2-y$, $-^1/_2+z$; (III) x, $^3/_2-y$, $^1/_2+z$; (IV) $1-x$, $1-y$, $-z$; (V) $1-x$, $^1/_2+y$, $^1/_2-z$; (VI) x, $1+y$, z; (VII) $1-x$, $^1/_2+y$, $-^1/_2-z$; (VIII) x, $^1/_2-y$, $-^1/_2+z$; (IX) $1+x$, $^3/_2-y$, $^1/_2+z$; (X) $2-x$, $^1/_2+y$, $^1/_2-z$; (XI) $1+x$, y, z; (XII) $1-x$, $2-y$, $-z$; (XIII) $1-x$, $-^1/_2+y$, $^1/_2-z$; (XIV) $2-x$, $1-y$, $-z$.

Even if a large excess of selenium was used in these reactions, there was no evidence for the formation of any cations of higher molecular weight such as Se_{12}^{2+} and Se_{16}^{2+} that have been previously claimed or an Se_{19}^{2+} cation analogous to the known S_{19}^{2+} species.[11] Finely powdered samples of both solid salts are brown and are considerably more soluble in SO_2 at low temperatures than at room temperature, to give green-brown solutions. Similar stable green-brown solutions may be obtained in 95.5% H_2SO_4, but dissolution of Se_{10}^{2+} in 100% H_2SO_4 results in fairly rapid oxidation to the green Se_8^{2+} species (see below).

The Preparation of $Se_{10}(AlCl_4)_2$. This salt was prepared from $Se_8(AlCl_4)_2$ by a reaction of a type that has not previously been encountered in studies of the chalcogen cations. The starting compound $Se_8(AlCl_4)_2$ was also prepared by a novel method. Previously this salt has been prepared by fusing an appropriate mixture of selenium, selenium tetrachloride, and aluminum trichloride.[4] We attempted to carry out the same reaction in SO_2 as solvent but the product always contained unreacted selenium. Accordingly, other preparative routes were sought and it was found, somewhat surprisingly, that Se_2Cl_2 reacted with $AlCl_3$ without the addition of elemental selenium to give dark green crystalline $Se_8(AlCl_4)_2$, which is only very sparingly soluble in SO_2. It appears that the Se_2Cl_2 disproportionates according to the equation

$$5Se_2Cl_2 + 4AlCl_3 \rightarrow Se_8(AlCl_4)_2 + 2SeCl_3(AlCl_4)$$
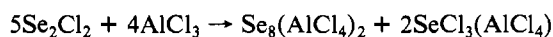
On washing $Se_8(AlCl_4)_2$ with relatively large quantities of SO_2 it undergoes a disproportionation reaction to give a brown insoluble compound which was identified as $Se_{10}(AlCl_4)_2$ and

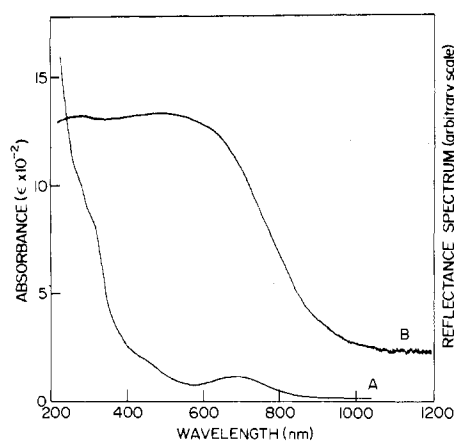**Figure 1.** Electronic absorption spectrum of $Se_{10}(AsF_6)_2$ in 95.5% H_2SO_4 (A) and diffuse reflectance spectrum of $Se_{10}(SbF_6)_2$ (B).

a yellow solution which appeared to contain Se_2Cl_2. The exact nature of this disproportionation was not ascertained, but it may be tentatively described by the equation

$$4Se_8(AlCl_4)_2 \rightarrow 3Se_{10}(AlCl_4)_2 + Se_2Cl_2 + 2AlCl_3$$

No evidence was obtained in any of the above preparations for the formation of the previously claimed species Se_{12}^{2+} and Se_{16}^{2+}.[12]

Electronic Spectrum of the Se_{10}^{2+} Cation. The electronic absorption spectrum of $Se_{10}(AsF_6)_2$ in 95.5% H_2SO_4 and the diffuse reflectance of $Se_{10}(SbF_6)_2$ are shown in

Table IV. Electronic Absorption and Diffuse Reflectance Spectra of the Se$_{10}^{2+}$ and Se$_8^{2+}$ Cations[a]

	Se$_{10}^{2+}$ species			Se$_8^{2+}$ species[b]	
	abs spectrum[c] Se$_{10}$(AsF$_6$)$_2$ (95.5% H$_2$SO$_4$)			abs spectrum[c] (H$_2$SO$_4$, HSO$_3$F, H$_2$S$_2$O$_7$)	
λ, nm	$10^{-2}\epsilon$, dm^3 cm^{-1} mol^{-1}	reflectance spectrum Se$_{10}$(SbF$_6$)$_2$[d] λ, nm		λ, nm	$10^{-2}\epsilon$, dm^3 cm^{-1} mol^{-1}
680	1.10	475 br[e]		685	2.50[f]
455	1.61	280		470	2.00
320 sh	7.81			295	8.90
280 sh	10.02				

[a] All spectra recorded at room temperature. [b] Data for Se$_8^{2+}$ taken from ref 1. [c] Molar extinction coefficients expressed in g-atom of Se/L. [d] The reflectance spectrum of Se$_{10}$(AsF$_6$)$_2$ is identical with that of Se$_{10}$(SbF$_6$)$_2$. [e] Key: br = broad, sh = shoulder. [f] Molar extinction coefficients taken from spectra recorded in 100% H$_2$SO$_4$.

Figure 1, while the band maxima and relevant extinction coefficients, together with some data on the Se$_8^{2+}$ cation in highly acidic media, are given in Table IV. It may also be noted that the absorption spectrum of the Se$_8^{2+}$ cation in an NaCl–AlCl$_3$ melt at 150 °C has been recently reported[21] and, except for the expected shift in the spectrum, is quite similar to that previously reported.[1] The absorption spectrum of the Se$_{10}^{2+}$ cation seems to be independent of the solvent as a virtually identical spectrum was obtained from an SO$_2$ solution of Se$_{10}$(AsF$_6$)$_2$. The absorption spectrum of Se$_{10}^{2+}$ is very similar to that of Se$_8^{2+}$ as is suggested by their respective green-brown and green colors in solution. This similarity appears to be coincidental and is not due to oxidation of Se$_{10}^{2+}$ to Se$_8^{2+}$ since the Se$_{10}^{2+}$ cation was found to be stable in 95.5% H$_2$SO$_4$ and gave the same spectrum as that in SO$_2$, a nonoxidizing solvent, although it was fairly rapidly oxidized in 100% H$_2$SO$_4$. Furthermore, recent ^{77}Se NMR studies using selenium enriched to 92.4% in ^{77}Se have also indicated that the Se$_{10}^{2+}$ cation is stable both in 95.5% H$_2$SO$_4$ and in SO$_2$ as solvents.[22] In oleum solution, or in HSO$_3$F, we observed, however, that Se$_{10}^{2+}$ was immediately oxidized to the Se$_8^{2+}$ species. Hence, as selenium will not dissolved in 95% H$_2$SO$_4$ at room temperature without the addition of an oxidizing agent, it is not surprising that the existence of this cation was overlooked during the previous studies of Barr et al.[1] on solutions of selenium in H$_2$SO$_4$, HSO$_3$F, and H$_2$S$_2$O$_7$ (45% oleum).

It should also be noted that there is a considerable difference between the solution and solid-state electronic spectra of the Se$_{10}^{2+}$ cation (Figure 1). This suggests that the same structure may not be retained in solution. The above ^{77}Se NMR studies have also given evidence for intramolecular exchange reactions in both SO$_2$ and 95.5% H$_2$SO$_4$ solution, in accord with this suggestion.[22]

The Crystal Structure of Se$_{10}$(SbF$_6$)$_2$. There are two Se$_{10}^{2+}$ cations in the asymmetric unit, each with approximate C_2 symmetry. The equivalent distances and angles in both Se$_{10}^{2+}$ cations are the same within 2–3 standard deviations. It should be noted that the Se$_{10}^{2+}$ structure is chiral and that these two cations represent the two enantiomorphs. Each enantiomorph of Se$_{10}^{2+}$ has a bicyclo[4.2.2]decane structure and is thus isostructural with the previously determined Te$_2$Se$_8^{2+}$ cation. In the structure of Te$_2$Se$_8$(AsF$_6$)$_2$ the two possible enantiomorphs are related by the center of symmetry.[13] The bicyclo-
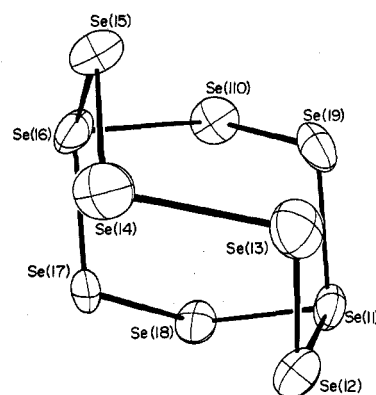
Figure 2. Perspective view of the Se$_{10}^{2+}$ cation 1 showing the atomic notation used in the structure determination, viewed approximately down the *b* axis. Thermal ellipsoids are drawn at the 50% probability level.
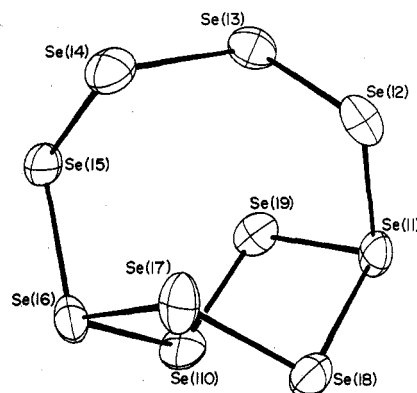
Figure 3. Perspective view of the Se$_{10}^{2+}$ cation 1 showing the atomic notation used in the structure determination, viewed approximately down the *c* axis. Thermal ellipsoids are drawn at the 50% probability level.

[4.2.2]decane structure of both Se$_{10}^{2+}$ and Te$_2$Se$_8^{2+}$ can alternatively be viewed as either a six-membered boat-shaped ring linked across the middle by a chain of four selenium atoms or as two fused eight-membered rings (Figures 2 and 3).

The bond lengths in Se$_{10}^{2+}$ were in the range 2.24–2.44 Å and they alternate in length on moving away from the two three-coordinate selenium atoms along any of the chains. The bond lengths fall into three rather distinct groups: (1) the six bonds adjacent to the three-coordinate selenium atoms (which carry a formal positive charge) are the longest, having lengths of 2.41–2.44 Å; (2) the bonds adjacent to these long bonds are shorter with lengths of 2.24–2.26 Å; and (3) the unique central bond in the four-atom backbone has an intermediate length of 2.35 Å.

Small bond length alternations have also been found in chains of four or more sulfur atoms[23] and in cyclo-S$_{10}$.[24] Rather large alternations in bond lengths are a feature of the structures of S$_7$, S$_7$I$^+$, S$_8$O, and the S$_7$ rings in S$_{19}^{2+}$, and the effect of a formal or partial positive charge in increasing the lengths of all the bonds involving this atom has been noted previously for the substituted sulfur rings mentioned above.[11] In each of these cases, the bonds formed by the three-coordinate positively charged atoms are all considerably longer than the average bond length. The adjacent bonds are then correspondingly shorter than the average length, the next bond is again longer, and so on. As has been pointed out by

(21) Fehrmann, R.; Bjerrum, N. J.; Andreasen, H. A. *Inorg. Chem.* **1975**, *14*, 2259.
(22) Burns, R. C.; Schrobilgen, G. J., unpublished results.

(23) Nickless, G. "Inorganic Sulphur Chemistry", Elsevier, Amsterdam, 1968.
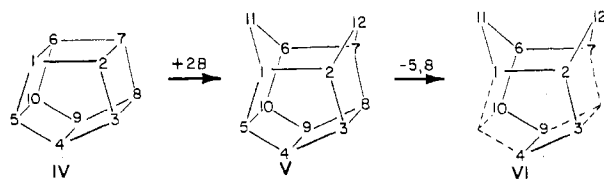(24) Reinhardt, R.; Steudel, R.; Schuster, F. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 57.

Steudel[25] these bond length alternations indicate that there is considerable interaction between adjacent bonds in these sulfur compounds. In chains of three to four selenium atoms similar bond alternations have also been observed,[26,27] and the bond interactions in Se_{10}^{2+} are even stronger, presumably due to the two positively charged atoms.

The average length of the bonds in Se_{10}^{2+} (2.36 Å) and the length of the unique bond in the tetraselane backbone (2.35 Å) are close to both the length of the selenium–selenium bond lengths in several forms of cycooctaselenium (2.335 Å)[28] and the distances in dimorpholinodiselane (2.346 (1) Å),[26] di-*tert*-butyltriselane (2.314 (1) Å),[27] and dimorpholinotriselane (2.352 (1) Å),[26] which may be regarded as "normal" single bonds.[26] In dimorpholinotetraselane and dipiperidino-tetraselane, however, the central selenium–selenium bond lengths are comparable at 2.356 (2) and 2.346 (2) Å, but the adjacent bonds in these compounds are slightly shorter (2.336 (2) and 2.328 (2) Å, respectively).[26] It is interesting to note that the four short bonds in Se_{10}^{2+} have lengths that are comparable with the lengths of the bonds in the Se_4^{2+} ion in $Se_4(HS_2O_7)_2$, 2.283 (4) Å,[5] and in $Se_4(Sb_8F_{33})(SbF_6)$, 2.236 (8) Å,[29] which according to simple valence bond considerations have bond orders of 1.25. It might be concluded therefore, that the four short bonds in Se_{10}^{2+} have comparable bond orders.

It has been shown elsewhere that the structures of ring and cage compounds of the main group elements can all be related to a number of basic cluster frameworks including the tetrahedron, the trigonal prism, the cube, the cuneane structure, and the pentagonal prism. Cages and rings can be derived from these structures by adding additional atoms across the edges and/or removing certain bonds so that some of the atoms become only two-coordinated rather than three-coordinated and the tight cluster opens up into a cage or ring.[30] In the present case the Se_{10}^{2+} structure can be related to the cuneane structure I in the following way: (1) One edge of each of the
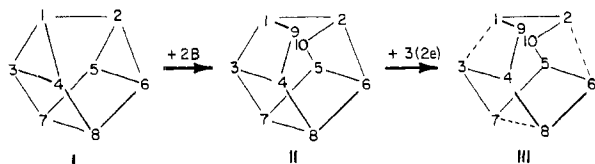
two triangular faces is bridged by the additional atoms 9 and 10 to give II. There are two alternative ways to form these bridges, each of which preserves a twofold axis down the middle of the structure and eventually give rise to the two enantiomorphs of Se_{10}^{2+}. (2) The bonds 1–3, 2–6, and 7–8 are then broken by the addition of an extra electron pair into each of these bonds, retaining the twofold axis of symmetry and giving the Se_{10}^{2+} structure III. An alternative procedure is to start with a pentagonal prism IV: (1) Two extra atoms,

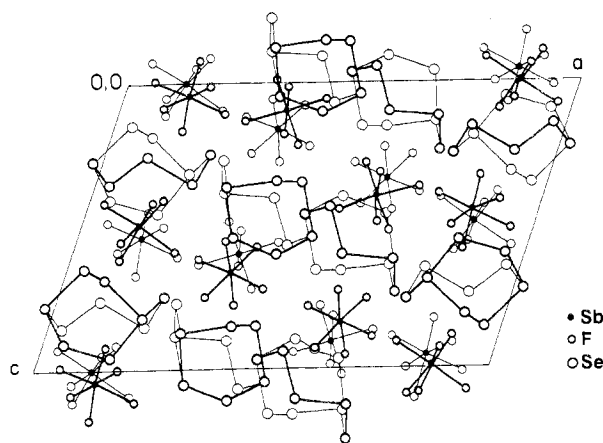11 and 12, are added by bridging across two of the adjacent

(25) Steudel, R.; Reinhardt, R.; Schuster, F. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 716.
(26) Foss, O.; Janickis, V. *J. Chem. Soc., Chem. Commun.*, **1977**, 833.
(27) McKinnon, B. J.; de Mayo, P.; Payne, N. C.; Ruge, B. *Nouv. J. Chem.*, **1978**, *2*, 92.
(28) Foss, O.; Janickis, V. *J. Chem. Soc., Chem. Commun.* **1977**, 834.
(29) Gillespie, R. J.; Sawyer, J. F.; Vekris, J. E., unpublished results.
(30) Gillespie, R. J. *Chem. Soc. Rev.* **1979**, *8*, 315.

Figure 4. The packing arrangement of $Se_{10}(SbF_6)_2$ as viewed down the *b* axis showing layers of anions and cations nearly parallel to *a**.

parallel edges, retaining a twofold axis, to give V. (2) Atoms 5 and 8 are removed to give VI. Alternatively, the removal of atoms 3 and 10 also preserves the twofold axis and gives rise to the other enantiomorph.

The bond angles in the two Se_{10}^{2+} cations are very similar and range from 96.7 to 105.9°. The angles at the three-coordinate positions are slightly smaller (96.7–103.1°) than the angles at the two-coordinate atoms (101.5–105.9°). The rather small range of the bond angles suggests that the Se_{10}^{2+} cation is relatively free of angle strain.

There are three intramolecular contacts in Se_{10}^{2+} that are worthy of note. These are in the range 3.30–3.49 Å and although they are not as short as the transannular bond in Se_8^{2+} (2.84 Å),[4] they are significantly shorter than the other intramolecular contacts in Se_{10}^{2+} which are all longer than 3.58 Å. Furthermore, these shorter contacts are ca. 0.5–0.7 Å less than the sum of the van der Waals radii for selenium (ca. 4.0 Å). There is one contact (Se(18)···Se(110) = 3.30 Å and Se(27)···Se(29) = 3.37 Å) across the middle of the six-membered ring in the base of each Se_{10}^{2+} (7–8 in III). In addition, there are two contacts (Se(13)···Se(19) = 3.39 Å and Se-(14)···Se(17) = 3.49 Å; Se(23)···Se(28) = 3.41 Å and Se-(24)···Se(210) = 3.43 Å) which bridge each eight-membered ring to form four- and six-membered rings if these contacts are considered as weak "bonds" (1–3 and 2–6 in III). The most striking feature of these short contacts is that they are in the positions of the three bonds that are broken by the addition of electron pairs in deriving the structure of Se_{10}^{2+} (and $Te_2Se_8^{2+}$) from the cuneane structure I. Similar contacts involving the same atom positions are also present in $Te_2Se_8^{2+}$ but are slightly longer (3.43, 3.52, and 3.58 Å), and there is an additional intercation contact of 3.49 Å which may be of importance.[13]

The average Sb–F bond length in the four SbF_6^- anions is 1.87 Å and cis and trans angles (with the exception of those involving F(2) and F(3) which were fixed with ideal values during the final cycle of least squares) do not deviate significantly from 90 and 180°, respectively.

The packing of the anions and cations is shown in Figure 4. It should be noted that there are layers of anions and cations nearly parallel to the *a** direction, which gave rise to the pseudosymmetry observed in early diffraction photographs.

Several intermolecular (ionic) contacts that may be of importance in stabilizing the Se_{10}^{2+} ion are noted in Table III. While all the intercation Se···Se contacts are >3.6 Å, there are several Se···F contacts to each Se_{10}^{2+} cation which are less than the sum of the van der Waals radii for selenium and fluorine (3.35 Å). The relatively high standard deviations associated with these contacts are such that quantitative comparison is probably not valid. It should be noted, however,

that similar interionic contacts less than van der Waals contact distances are found in most of the homo- and heteropolyatomic cationic species of the group 6 elements so far studied.

Structure and Solution Behavior of Palladium(II)–Thiocyanate Complexes of 1-Substituted 3,4-Dimethylphospholes

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A series of four complexes of the type $L_2Pd(CNS)_2$[2] (L = 1-R-3,4-dimethylphosphole; R = CH_3, t-C_4H_9, C_6H_5, or $CH_2C_6H_5$) have been prepared and characterized by conductance studies, infrared spectroscopy, and ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopy. The complexes appear to be cis in the solid state with the exception of R = t-C_4H_9, which is trans. The phenyl and benzyl complexes exhibit either a single mixed-linkage isomer or a mixture of N-bonded and S-bonded isomers in the solid state. Upon dissolution of the complexes in $CDCl_3$, linkage isomerism occurs in all cases and geometrical isomerism in some cases, giving mixtures of isomers in solution. The methyl and *tert*-butyl complexes are trans in solution, and the benzyl and phenyl complexes exhibit intermediate exchange between cis and trans isomers in solution at room temperature. An NMR shift reagent, $Eu(fod)_3$, was used to facilitate the identification of isomers in solution. The crystal structure of *cis*-bis(thiocyanato)bis(1,3,4-trimethylphosphole)palladium(II) was determined from three-dimensional X-ray diffraction techniques. The molecule crystallizes in the monoclinic space group $C2/c$ in a unit cell of dimensions $a = 9.212$ (1) Å, $b = 15.344$ (3) Å, $c = 14.572$ (4) Å, $\beta = 96.89$ (2)°, $\rho_{calcd} = 1.542$ g/cm³, and $\rho_{obsd} = 1.53$ (2) g/cm³. Refinement converged to $R = 0.035$, with 1195 independent reflections. The phosphole ring is planar in this complex, and short intracyclic P–C bond lengths (1.795 Å) indicate the presence of some intracyclic electron delocalization within the coordinated phosphole.

Introduction

The bonding mode of the thiocyanate ion to "soft" metals such as Pd(II) or Pt(II) has been the center of much controversy over the last decade. Both electronic effects[3,4] and steric effects[5] or a combination thereof[6] have been proposed to play the dominant role in determining the thiocyanate bonding mode. The controversy stems from the belief that either steric effects[7–9] or electronic effects[10] exclusively determine this bonding mode. In an attempt to resolve this problem, the question of whether phosphines do or do not function as π acceptors in Pd(II) and Pt(II) complexes in general was reevaluated,[11–13] as π-bonding arguments were

being invoked[14] to explain changes in thiocyanate coordination. Whatever the final outcome of this controversy, it is immediately apparent that the steric and electronic effects on the thiocyanate bonding mode are finely balanced for Pd(II) complexes, and subtle changes in either one will tip this balance and determine both linkage and geometrical isomerism.[15]

It has been shown[16] that 1-R-3,4-dimethylphospholes (I)

I
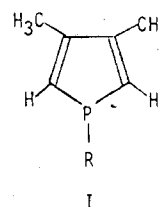
form complexes of the type L_2PdX_2 (X = Cl⁻, Br⁻, N_3^-) containing Pd–P bonds which are as strong as, if not stronger than, those in structurally similar palladium–phosphine complexes. The enhanced bonding properties of these phospholes could be a consequence of their sterically undemanding nature

(1) (a) University of Nevada. (b) University of Georgia. (c) University of Warwick. (d) Institut National de Recherche Chimique Appliquée.
(2) There are six possible square-planar isomers for the complexes $L_2Pd(CNS)_2$, viz., cis and trans N-bound, cis and trans S-bound, and cis and trans mixed-linkage isomers. Throughout the paper "metal-thiocyanate" bonding is represented as N(SCN), metal–isothiocyanate bonding is represented as M(NCS), and when no specific bonding mode is implied, M(CNS) is used; the term "mixed-linkage isomers" is used to imply the presence of two thiocyanate groups coordinated in a monodentate fashion but differing in their point of attachment to the metal.
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