transition is about 10^2 that observed for the most allowed transition of Bi^+ in melts.[14]

Note was made earlier of the fact that the presence of excess liquid bismuth in these experiments meant that equilibrium measurements could not distinguish $BiAlCl_4$ from Bi_xAlCl_4. This could include in particular the attractive Bi_3^+ which has been suggested to be stable in solution in $BiCl_3$.[5] However incorporation of the two additional metal atoms would make the entropy change for the formation reaction more negative by roughly 24 eu according to the same estimation methods just used for $BiAlCl_4$. This change would yield a K_p of 1.9×10^{-6} and a preposterous value for ϵ, $>10^9$ l. mol^{-1} cm^{-1}. Even the Bi_2AlCl_4 alternative appears to give an unreasonable result for ϵ and so it is concluded that only $BiAlCl_4$ will satisfy the experimental data.

Spectroscopic investigations of the gas phase in the ternary system were also carried out at lower temperatures (400–600°) but these generally gave unsatisfactory results, evidently because of partial condensation to the very stable, reduced tetrachloroaluminate melts.[7] With decreasing temperature the values of K_a deduced become increasingly erratic and low when compared with those expected according to parameters deduced at higher temperatures, but no observable differences in the spectra measured were noted other than in overall intensity. At a given temperature, deviations from absorbances calculated according to the high-temperature data were found to correlate well with the total moles of the two trichlorides added, a reasonable result for a system undergoing partial and roughly congruent condensation together with reduction by the excess metal present.

Although the conversion of some metal chlorides to their gaseous tetrachloroaluminate salts is large and accompanied by substantial alteration in volatility,[16-18] BiCl remains the major component even in the presence of more than 1 atm of $AlCl_3$. Much of this may be attributed to the extra stability of BiCl associated with covalency. The value of 71.8 ± 1 kcal mol^{-1} for $\Delta H°_{298}$ for its dissociation to atoms,[12] together with standard ionization and affinity data and the coulomb energy of the simple ion pair at 2.83[12] to 3.1 Å,[8,9] indicates the real molecule is of the order of 40–50 kcal mol^{-1} more stable than the ionic model. On the other hand the stability of $BiAlCl_4$ can apparently be satisfactorily accounted for with a simple ionic entity, adding to the above data for the formation of gaseous Bi^+ and Cl^- the chloride ion affinity of $AlCl_3$, -78 ± 7 kcal mol^{-1},[19] and the coulomb energy of a model ion pair. For the last the tetrahedral $AlCl_4$ unit with the usual Al–Cl distances of 2.12 Å[15] is employed since substantial angular distortion is not likely with Cl–Cl distances already reduced to 3.45 Å (compared with twice the van der Waals radius of ~3.6 Å). The Bi^+ ion is again placed on a triangular face of the anion at Bi–Cl distances of 3.1 Å.[8,9] For the point charge calculation employed the inherent charge asymmetry of the Al–Cl bonds and the charge polarization of the anion caused by the cation cannot both be uniquely established. However, plausible combinations yield the coulomb energy of the ion pair (-109 ± 7 kcal mol^{-1}) necessary to account for observed data, for example, charges on aluminum, each of the three chlorine atoms next to Bi^+, and the fourth chlorine atom of +1, −0.55, −0.35 or +0.33, −0.42, −0.08, respectively. Although the estimation methods are drastically simplified, the results are gratifying. Measurements of the moment of inertia of $BiAlCl_4$ and of the stability of simple and more ideal examples such as $NaAlCl_4(g)$ would be illuminating.

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The Crystal Structure of Octaselenium(2+) Tetrachloroaluminate, $Se_8^{2+}(AlCl_4^-)_2$[1]

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The crystal structure of the compound $Se_8(AlCl_4)_2$ formed in the pseudobinary Se–($SeCl_4$ + 4$AlCl_3$) system has been determined from three-dimensional X-ray diffraction data. The crystals are orthorhombic (space group $Pca2_1$) with $a = 14.92$ (2), $b = 10.67$ (1), and $c = 13.22$ (1) Å and four $Se_8(AlCl_4)_2$ units per cell. The model was derived by Patterson and Fourier methods and refined to a conventional R index of 0.077 by full-matrix least squares (Se anisotropic, Al and Cl isotropic) on 721 observed reflections $>2\sigma(I)$. The structure consists of approximately tetrahedral $AlCl_4^-$ ions and Se_8^{2+} ions of novel geometry. The angles in the $AlCl_4^-$ groups average 109.5°, and the Al–Cl distances, 2.12 Å. The Se_8^{2+} ion (approximate symmetry C_s) has a [3.3.0] bicyclic structure derived from an eight-membered ring in the endo,exo configuration through shortening of one transannular separation to form a weak Se–Se bond at 2.84 Å, which compares with 2.29–2.36 Å about the ring and in the element. The structure of Se_8^{2+} is discussed in relation to those of S_4N_4, Se_4N_4, and Se_8.

Introduction

Earlier successes in preparing new polybismuth cations as their tetrachloroaluminate salts[2] led to an examination of the analogous tellurium and selenium systems and to the preparation of five new polyatomic compounds of these elements.[3] In this study rather poor liquidus data characterized one of the selenium compounds as having a Se:$AlCl_4$ ratio in the neighborhood of 4, and infrared data seemed to support rather

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[1] Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

[2] J. D. Corbett, *Inorg. Chem.*, **7**, 198 (1968).

[3] D. J. Prince, J. D. Corbett, and B. Garbisch, *ibid.*, **9**, 2731 (1970).

clearly the occurrence of the $AlCl_4^-$ ion therein. A preliminary report of the present structural identification of the phase as $Se_8^{2+}(AlCl_4^-)_2$ together with comment on the unique configuration of the cation has appeared.[4] Gillespie and coworkers[5,6] have also obtained evidence for a cation of this molecular weight in sulfuric acid media and for other solid salts which exhibit the proper spectra for the component ions.

Experimental Section

The preparation of $Se_8(AlCl_4)_2$ from the stoichiometric mixture of Se, $SeCl_4$, and $AlCl_3$ was accomplished in a sealed Pyrex tube of 10-mm diameter and 20-cm length. For a sample weighing *ca.* 5 g the complete reaction of the metal with the fused mixture required about 3 hr at 250°. The black liquid freezes at about 192° to give a glasslike or poorly crystalline solid which is also black or intensely colored. On exposure to air, this material rapidly becomes coated with an orange-brown deposit, apparently as a result of oxidation and/or hydrolysis. Crystals for the diffraction study were obtained from the black liquid by vapor-phase transport through a temperature gradient of 195° at the sample to 140° where crystals formed. Specimens of the crystals were sealed in capillary tubes in an argon-filled drybox.

The X-ray powder pattern of the composition Se_4AlCl_4 which had been melted, solidified, and annealed could be completely indexed on the basis of the single-crystal parameters obtained from the transported phase. There was therefore strong evidence in the absence of elemental analyses that the single crystals and the melt from which they were obtained were of the same composition, in agreement with the phase relationships.[3] The far-infrared spectrum showed that the crystals contain the $AlCl_4^-$ ion; features attributable to Se–Se vibrations were however very weak. A rod of composition $Se_4(AlCl_4)$ was qualitatively diamagnetic.

The crystal chosen for the diffraction study was in the form of a rectangular prism of dimensions 0.157 × 0.105 × 0.188 mm. Weissenberg and precession photographs provided initial unit cell parameters and information for the space group assignment. More accurate values for the cell constants were obtained from 2θ values measured on a diffractometer using Cu Kα radiation (λ 1.5418 Å). Integrated intensities were obtained with Zr-filtered Mo radiation by the θ–2θ scan technique on a General Electric diffraction unit equipped with a single-crystal orienter, scintillation counter, and pulse height analyzer. Stationary background measurements were made at the start and finish of each scan. A standard reflection was measured each after 40 reflections and was found to show no systematic variation in intensity such as would result from decomposition or changes in alignment. All independent reflections up to $2\theta = 50°$ were examined. Very few of adequate intensity were observed at the higher angles; only about one-third (737) of those examined were found to have intensities above $2\sigma(I)$. The standard deviations $\sigma(I)$ were based on counting statistics. The intensities corrected first for background were then corrected for Lorentz–polarization and absorption effects ($\mu = 160$ cm^{-1} for Mo radiation). Transmission coefficients were evaluated by numerical integration.

Crystal Data.—Crystals of this compound are often of a hexagonal form and appear dark reddish brown when viewed in transmitted light. They are orthorhombic with lattice dimensions $a = 14.92 \pm 0.02$, $b = 10.67 \pm 0.01$, $c = 13.22 \pm 0.01$ Å. The systematic absences ($0kl$ for l odd and $h0l$ for h odd) are characteristic of space groups *Pcam* or $Pca2_1$; the latter space group (no. 29) was established by the structure analysis. The simplest formula unit consistent with the observed diamagnetism and expected composition is $Se_8(AlCl_4)_2$. A cast rod with this composition had a density of 3.2 ± 0.2 g cm^{-3}, as compared with the value of 3.06 g cm^{-3} calculated assuming four $Se_8(AlCl_4)_2$ units per cell.

Structure Determination and Refinement

A sharpened three-dimensional Patterson function was evaluated from the intensity data. A solution of the Patterson map was sought briefly in space group *Pcam* but without success. It was then observed that the concentration of vectors on sections $^1/_2vw$, $u0w$, $uv^1/_2$ indicated the correct choice of space groups to be $Pca2_1$. Subsequently the most prominent vector peaks were all interpreted by placing eight nonequivalent selenium atoms in the general 4(a) sites of $Pca2_1$ and fitting the 24 positional parameters to the Patterson distribution. The selenium atoms were found to form a reasonable structure consisting of Se_8 units (Figure 1) arranged in a pattern of approximate *Pcam* symmetry. The three-dimensional electron density map from which the selenium atoms had been subtracted thus had quasi-mirror symmetry in the c direction, because of the selenium phasing model, and showed twice the expected number of prominent peaks required to place the lighter atoms. Positions of the aluminum and chlorine atoms forming two nonequivalent $AlCl_4$ groups were readily located from this map in the 4(a) sites of $Pca2_1$ by selecting the higher peak of each prominent mirror-related pair as the correct one. On the other hand, it was impossible to devise a plausible ordered structure in *Pcam*, even allowing for large variations from the expected stoichiometry, because of the close proximity of chlorine positions related by the mirror planes in *Pcam*. The atomic parameters of the trial structure in $Pca2_1$ were adjusted in three isotropic cycles of least-squares refinement, and this reduced the reliability index $R\ (= \Sigma||F_o| - |F_c||/\Sigma|F_o|)$ from the initial value 0.28 to 0.19. The following difference electron density map showed no features that indicated either positional disorder or omission of atoms, from

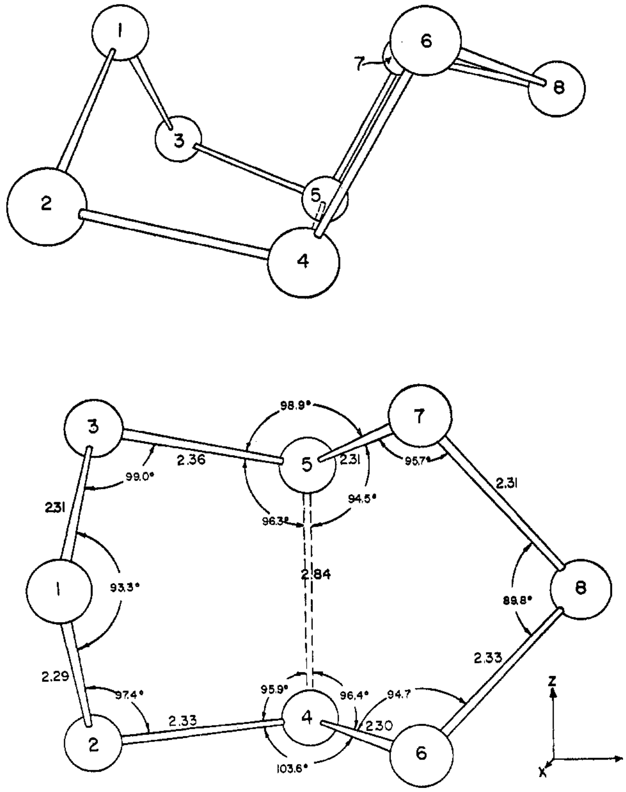

Figure 1.—Perspective views of the cation Se_8^{2+}, with bond distances and angles and key to atomic notation used in text: top, projection approximately down the c axis; bottom, projection down a axis.

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TABLE I

FINAL POSITIONAL AND THERMAL PARAMETERS[a]

Atom	x/a	y/b	z/c	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Se(1)	0.1467 (5)	0.0677 (7)	0.2500[b]	0.0029 (4)	0.0076 (6)	0.0067 (6)	0.0019 (4)	−0.0005 (6)	0.0003 (8)
Se(2)	0.0384 (9)	0.0621 (9)	0.1277 (13)	0.0070 (7)	0.0073 (9)	0.0110 (9)	−0.0006 (7)	−0.0036 (7)	−0.0002 (9)
Se(3)	0.0440 (8)	0.0869 (8)	0.3798 (10)	0.0071 (7)	0.0074 (9)	0.0070 (7)	0.0021 (7)	0.0032 (6)	0.0042 (7)
Se(4)	0.0003 (7)	0.2736 (8)	0.1324 (12)	0.0053 (7)	0.0057 (8)	0.0099 (9)	0.0002 (6)	−0.0038 (6)	0.0014 (8)
Se(5)	−0.0064 (6)	0.2920 (8)	0.3467 (11)	0.0034 (6)	0.0084 (9)	0.0075 (7)	0.0022 (6)	0.0024 (6)	0.0018 (7)
Se(6)	0.1357 (9)	0.3744 (9)	0.1126 (11)	0.0068 (8)	0.0088 (10)	0.0072 (8)	−0.0004 (7)	0.0033 (6)	−0.0006 (8)
Se(7)	0.1290 (8)	0.3962 (8)	0.3599 (11)	0.0062 (7)	0.0086 (9)	0.0058 (7)	−0.0006 (6)	−0.0022 (6)	−0.0004 (7)
Se(8)	0.1028 (5)	0.5336 (6)	0.2278 (10)	0.0042 (4)	0.0050 (6)	0.0069 (7)	−0.0002 (4)	0.0005 (6)	0.0002 (6)

Atom	x/a	y/b	z/c	B, Å^2	Atom	x/a	y/b	z/c	B, Å^2
Al(1)	0.7630 (16)	0.2401 (18)	0.5125 (20)	2.8 (5)	Al(2)	0.3863 (14)	0.2633 (20)	0.3214 (19)	2.5 (4)
Cl(1)	0.6890 (16)	0.0877 (19)	0.5721 (21)	4.8 (5)	Cl(5)	0.3062 (16)	0.1590 (21)	0.4178 (20)	5.2 (5)
Cl(2)	0.7043 (13)	0.4107 (17)	0.5479 (17)	3.5 (4)	Cl(6)	0.3552 (15)	0.4570 (19)	0.3377 (19)	4.9 (5)
Cl(3)	0.8957 (12)	0.2297 (17)	0.5730 (16)	3.3 (4)	Cl(7)	0.3700 (20)	0.2136 (26)	0.1693 (22)	6.3 (7)
Cl(4)	0.7781 (13)	0.2134 (18)	0.3510 (18)	3.9 (4)	Cl(8)	0.5239 (13)	0.2375 (18)	0.3667 (18)	4.3 (5)

[a] Corresponding standard deviations in the last figures are given in parentheses. The anisotropic temperature factors are expressed as $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$. [b] Fixed to define origin.

which it was concluded that structure was of correct symmetry with the atoms of the formula $Se_8(AlCl_4)_2$ forming the asymmetric unit.

The refinement was continued by the method of full-matrix least squares. The quantity minimized was $\Sigma w(|F_o| - |F_c|)^2$, where the weights w were assigned by the Hughes scheme.[7] The atomic scattering factors used were those for neutral Al and Cl atoms listed in ref 8 and that for Se was given by Hanson, *et al.*[9] Corrections for the real and imaginary components of anomalous dispersions for the Se atoms were taken from ref 8 and applied in the subsequent refinement. The z parameter of Se(1) was held constant during the refinement to define the origin since this is arbitrary along the [c] direction in $Pca2_1$. After three additional least-squares cycles in which the (72 − 1) positional and isotropic thermal parameters plus one scale factor were varied, the index R converged at the value 0.116 for the 737 reflections observed with intensities greater than twice their standard deviations. The difference map prepared at this stage showed evidence of anisotropic thermal motion at the selenium positions, where electron density errors as large as 2.5 e$^-$ Å^{-3} were observed. An attempted anisotropic refinement of the complete model was unsuccessful, probably because of the paucity of reliable data. When the selenium atoms alone were allowed anisotropic temperature parameters and the light atoms were permitted to vary isotropically, the refinement then proceeded satisfactorily. After four cycles, shifts of the 104 parameters were all less than half the estimated standard deviations, and the refinement was terminated. The final refinement was based on 721 reflections obtained when 16 reflections at the $2\sigma(I)$ threshold were excluded from the original set, and the final R value was 0.077. The largest residual features in the final difference map were errors of ± 1.0 e$^-$ Å^{-3} in the vicinity of the selenium atoms.

All calculations were carried out on the IBM 360/65 computer of the Iowa State University Computer Center with the following programs: SCO 6 for goniometer orientation,[10] ABCOR for absorption corrections,[11] ALF for Fourier summation,[12] ORFLS for least-squares parameter refinement,[13] ORFFE for molecular parameters and estimates of error,[14] and ORTEP for figure illustrations.[15]

Results and Discussion

The final atomic and thermal parameters and their estimated standard deviations are given in Table I.[16] The bond lengths and valence angles are listed in Table II and those for the Se_8^{2+} ion are shown in Figure 1, where the selenium atom notation used in the text is given. (A different numbering was used in ref 4.) The packing of the ionic clusters Se_8^{2+} and $AlCl_4^-$ found in the structure is shown stereoscopically in Figure 2.

The Se_8^{2+} group has a cyclic structure with approximately C_s symmetry. The most striking structural difference between the Se_8^{2+} ion and the cyclic Se_8 molecules found in α- and β-selenium[17,18] is the transannular closure at Se(4)–Se(5) to the distance 2.84 Å which is significantly less than the van der Waals separation; *cf.* distances Se(2)–Se(3) and Se(6)–Se(7) in Figure 1 and Table II. To attribute due significance to this feature, the Se_8^{2+} configuration may be described as one of two fused five-membered rings. Four atoms in each ring, excluding Se(1) and Se(8), are coplanar to almost the limits of their positional errors, Table III. Atoms Se(1) and Se(8) are displaced 1.49 and 1.60 Å from their respective rings to occupy endo and exo positions relative to opposite rings. The dihedral angles along the fold lines Se(2)–Se(3), Se(4)–Se(5), and Se(6)–Se(7) are, respectively, 109.0, 101.9, and 102.9°. The torsion angles listed in Table IV provide a more

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(15) C. K. Johnson, "A FORTRAN Thermal Ellipsoid Plot Program for Crystal Structure Illustration," USAEC Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965.

(16) The observed and calculated structure factor amplitudes will appear following these pages in the microfilm edition of the journal. Single copies may be purchased from the Reprint Department, ACS Publications, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to author, title of article, volume, and page number. Remit $3.00 for photocopy or $2.00 for microfiche.

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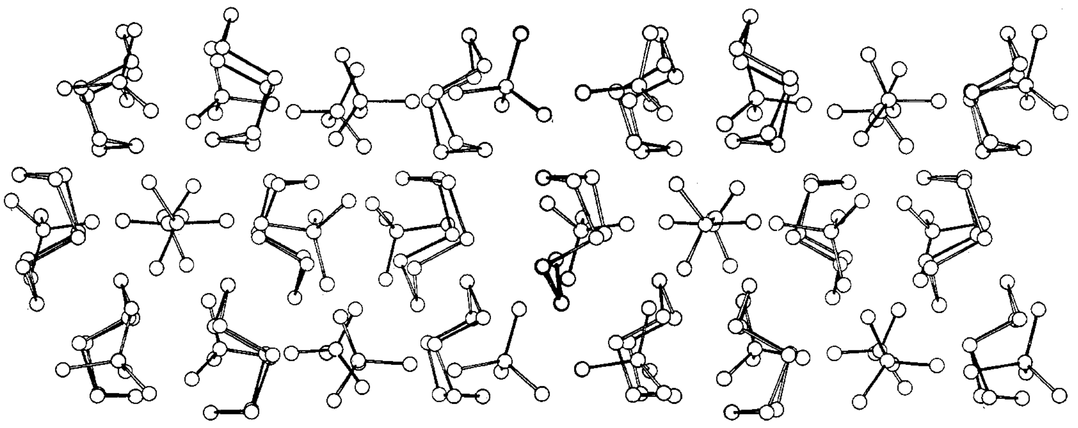

Figure 2.—Stereographic view of the structure of $Se_8(AlCl_4)_2$ looking down *c* axis. The *a* axis is horizontal.

Table II

Bond Lengths (Å) and Angles (deg)[a]

Se(1)-Se(2)	2.29 (1)	Se(3)-Se(1)-Se(2)	93.3 (3)
Se(2)-Se(4)	2.33 (1)	Se(1)-Se(2)-Se(4)	97.4 (4)
Se(4)-Se(6)	2.30 (1)	Se(2)-Se(4)-Se(6)	103.6 (5)
Se(6)-Se(8)	2.33 (1)	Se(2)-Se(4)-Se(5)	95.9 (4)
Se(8)-Se(7)	2.31 (1)	Se(6)-Se(4)-Se(5)	96.4 (4)
Se(7)-Se(5)	2.31 (1)	Se(4)-Se(6)-Se(8)	94.7 (4)
Se(5)-Se(3)	2.36 (1)	Se(6)-Se(8)-Se(7)	89.8 (3)
Se(3)-Se(1)	2.31 (1)	Se(8)-Se(7)-Se(5)	95.7 (4)
Se(2)-Se(3)	3.35 (1)[b]	Se(7)-Se(5)-Se(3)	98.9 (5)
Se(4)-Se(5)	2.84 (1)	Se(7)-Se(5)-Se(4)	94.5 (4)
Se(6)-Se(7)	3.29 (1)[b]	Se(3)-Se(5)-Se(4)	96.3 (4)
		Se(5)-Se(3)-Se(1)	99.0 (5)
Al(1)-Cl(1)	2.12 (3)		
Al(1)-Cl(2)	2.07 (2)	Cl(1)-Al(1)-Cl(2)	112 (1)
Al(1)-Cl(3)	2.14 (2)	Cl(1)-Al(1)-Cl(3)	108 (1)
Al(1)-Cl(4)	2.17 (3)	Cl(1)-Al(1)-Cl(4)	109 (1)
		Cl(2)-Al(1)-Cl(3)	111 (1)
Al(2)-Cl(5)	2.07 (3)	Cl(2)-Al(1)-Cl(4)	112 (1)
Al(2)-Cl(6)	2.13 (2)	Cl(3)-Al(1)-Cl(4)	105 (1)
Al(2)-Cl(7)	2.09 (2)		
Al(2)-Cl(8)	2.16 (2)	Cl(5)-Al(2)-Cl(6)	109 (1)
		Cl(5)-Al(2)-Cl(7)	113 (1)
		Cl(5)-Al(2)-Cl(8)	108 (1)
		Cl(6)-Al(2)-Cl(7)	109 (1)
		Cl(6)-Al(2)-Cl(8)	108 (1)
		Cl(7)-Al(2)-Cl(8)	110 (1)

[a] Estimated standard deviations in the last figures are given in parentheses. [b] Nearest-neighbor nonbonding distances which are included for comparison.

Table III

Least-Squares Planes in the Se_8^{2+} Ion

Equations of Planes

(Referred to the Crystallographic Axes, *X*, *Y*, *Z* in Å)

Plane 1 $0.0434X + 0.9958Y - 0.0802Z = 0.5494$

Plane 2 $0.9588X + 0.2832Y - 0.0211Z = 0.7441$

Plane 3 $-0.4760X + 0.8761Y - 0.0772Z = 2.4209$

Plane 4 $-0.9631X - 0.2691Y - 0.0103Z = -3.0401$

Displacements from Planes, Å

Atom	Plane 1	Plane 2	Plane 3	Plane 4
Se(1)	0.00[a]	1.49	−3.08	0.70
Se(2)	0.00[a]	−0.04[a]	−2.24	2.29
Se(3)	0.00[a]	0.04[a]	−2.31	2.11
Se(4)	2.22	0.05[a]	0.00[a]	2.23
Se(5)	2.18	−0.05[a]	0.00[a]	2.25
Se(6)	3.40	2.30	0.00[a]	0.00[a]
Se(7)	3.36	2.20	0.00[a]	0.00[a]
Se(8)	4.95	2.28	1.60	0.00[a]

[a] Atoms forming plane.

Table IV

Torsion Angles[a] in Se_8^{2+}

Atoms h i j k	Angle, deg	Atoms h i j k	Angle, deg
Se(3)-Se(1)-Se(2)-Se(4)	73.9	Se(2)-Se(1)-Se(1)-Se(5)	−69.7
Se(4)-Se(6)-Se(8)-Se(7)	76.5	Se(5)-Se(7)-Se(8)-Se(6)	−77.5
Se(1)-Se(2)-Se(4)-Se(6)	52.9	Se(1)-Se(3)-Se(5)-Se(7)	−58.8
Se(2)-Se(4)-Se(6)-Se(8)	−141.2	Se(3)-Se(5)-Se(7)-Se(8)	141.3
Se(1)-Se(2)-Se(4)-Se(5)	−45.2	Se(1)-Se(3)-Se(5)-Se(4)	36.7
Se(5)-Se(4)-Se(6)-Se(8)	−43.6	Se(4)-Se(5)-Se(7)-Se(8)	44.2
Se(2)-Se(4)-Se(5)-Se(3)	5.0		
Se(6)-Se(4)-Se(5)-Se(7)	−0.1		
Se(2)-Se(4)-Se(5)-Se(7)	104.4		
Se(6)-Se(4)-Se(5)-Se(3)	−99.5		

[a] Defined as the angle, measured clockwise, that the projection of bond (jk) makes with reference to bond (hi) when viewed in direction i → j.

detailed description of the conformation of the ion. The Se–Se bond lengths, other than the transannular Se(4)–Se(5), vary between 2.29 and 2.36 Å, *i.e.*, over a range of 7σ, and average to 2.318 Å, a value in good agreement with twice the conventional single-bond radius of selenium. Bond lengths varying between 2.30 and 2.36 Å are found in the α and β forms of the element.[17,18] The valence angles in Se_8^{2+} tend to be smaller than in Se_8 and to vary over a wider range, namely, 89.9–103.6° *vs.* 101.6–109.0°. Internal angles of the five-membered ring containing Se(1) are with one exception (at Se(4)) significantly larger than the corresponding angles in the other (Figure 1), but there appears to be no systematic correlation between the variation of bond lengths and valence angles.

The presence of pseudomirror symmetry in Se_8^{2+} can be further seen from a comparison of those dimensions (Figure 1; Tables II and IV) which might be expected to be equal in the observed conformation if they were unaltered by external forces. The pairs of bonds so related show a maximum deviation of 0.03 Å or 3σ. Although the external angles at Se(4) and Se(5) differ by 4.7°, differences between the four other pairs of comparable angles are smaller, being on the average 1.2°. The internal consistency of these values does not encourage discussion in which individual differences are attributed solely to intramolecular forces.

The conformational changes accompanying the transformation of the crown form of Se_8 to Se_8^{2+} may be envisaged as follows. One transannular distance of Se_8 decreases from the average value of 5.2 Å to the bicylic closure value of 2.84 Å in Se_8^{2+}; one apical atom, Se(1), "flips" from the exo to endo position in the bicylic system, which amounts to a twist of *ca.* 148° about axes Se(2)–Se(4) and Se(3)–Se(5). The first change might reasonably be associated with the loss of one electron each by Se(4) and Se(5) followed by a weak pairing of electrons in those orbitals directed approximately along the line of atomic centers. The second change, resulting in the observed exo,endo conformation, is also probably a consequence of internal forces. A Dreiding model constructed with the observed torsion and valence angles suggests that the endo of the two possible apical positions results in fewer nonbonding electron repulsions. However, the endo,endo conformation also requires prohibitively short contact distances between apical atoms 1 and 8 and so exo,endo is the favored form for $Se_8{}^{2+}$. A model ion in the endo,endo form with D_{2h} symmetry and average dimensions as observed with $Se_8{}^{2+}$ has a Se(1)–Se(8) separation of 2.81 Å, which agrees with the observed Se(4)–Se(5) bonding distance of 2.84 Å within the internal consistency of the bond lengths. The stability of an ion of this form would thus seem to require removal of two more electrons and the formation of a second weak Se–Se bond to give an $Se_8{}^{4+}$ species. Such a cation has not been shown to exist; rather this oxidation state is to date known only as the tetrameric $Se_4{}^{2+}$.[5,19] However, an endo,endo bonded form with the same number of valence electrons is well known in S_4N_4, Se_4N_4, and As_4N_4[20–23] where the sulfur, selenium, or arsenic atoms, respectively, occupy positions 1, 4, 5, 8. It will be noted that the $Se_8{}^{2+}$ ion is in the same valence sense isoelectronic with bicyclo[3.3.0]octane.

The two symmetry-independent $AlCl_4{}^-$ ions have approximately tetrahedral configurations in which the mean value of the Cl–Al–Cl angles equals 109.5° with a maximum deviation from the average of 3.5° (3.5σ). The Al–Cl bond distances in the two ions collectively average 2.12 Å and also vary between similar extremes, *i.e.*, 2.07–2.16 and 2.07–2.17 Å or about 3.5σ. Structure analyses providing more accurate dimensions for $AlCl_4{}^-$ also show similarly large variations in the bond length; *cf.* 2.10–2.19 Å in $Co(AlCl_4)_2$[24] and 2.08–2.14 Å in $Te_4(AlCl_4)_2$,[25] apparently as a result of differences in the coordination environments of chlorine. The apparent thermal motion of both nonequivalent $AlCl_4$ groups is reasonable in that the temperature factors of the Al atoms are smaller than those of the Cl atoms. The comparatively smaller factors for the Cl atoms about Al(1) (Table I) indicate a somewhat tighter environment for that group, consistent, in general, with the observed Se–Cl contact distances.

TABLE V

INTERIONIC DISTANCES LESS THAN 4.0 Å

Se(1)–Cl(1)	3.78
Cl(3)	3.99
Cl(4)	3.82
Cl(5)	3.40
Cl(7)	3.83
Se(2)–Se(3)	3.85
Cl(1)	3.48
Cl(3)	3.34
Cl(5)	3.76
Cl(7)	3.91
Se(3)–Cl(1)	3.82
Cl(3)	3.71
Cl(8)	3.48
Se(4)–Cl(1)	3.54
Cl(2)	3.56
Cl(8)	3.55
Se(5)–Cl(3)	3.40
Cl(4)	3.32
Cl(6)	3.38
Se(6)–Cl(2)	3.42
Cl(5)	3.56
Cl(6)	3.74
Cl(7)	3.96
Se(7)–Cl(2)	3.42
Cl(5)	3.74
Cl(6)	3.45
Se(8)–Cl(2)	3.78
Cl(3)	3.25
Cl(6)	3.97
Cl(8)	3.28
Cl(1)–Cl(4)	3.95
Cl(5)	3.76
Cl(7)	3.57
Cl(8)	3.99
Cl(2)–Cl(6)	3.84
Cl(3)–Cl(7)	3.73
Cl(4)–Cl(6)	3.70
Cl(8)	3.81

The packing of ions in the crystal is shown in Figure 2; the shortest interionic distances are listed in Table V. The anion–anion and cation–cation separation distances all exceed the sum of Pauling's van der Waals radii, 1.80 Å for Cl and 2.00 Å for Se, except the one Cl–Cl contact of 3.57 Å and the Se–Se distance of 3.85 Å considered below. There are 22 Se–Cl anion–cation distances in Table V less than the above radius sum of 3.80 Å, some as much as 0.55 Å less, a fact which warrants special attention since it appears to suggest unusual attractive interactions. The customary use of the ionic radius for Se^{2-} for the approximate value of the van der Waals distance probably places too high a value on the minimum interatomic contact distance in this structure and thereby exaggerates the significance of these observations. A similar situation evidently also arises with the intermolecular separations in α- and β-selenium.[17,18] Estimates of the selenium nonbonding contact radius from nearest-neighbor distances between molecules in α- and β-selenium and between chains in trigonal selenium[26] put this quantity in the range 1.72–1.76 Å, a value perhaps slightly too large for the ion $Se_8{}^{2+}$ but much more realistic than that of Se^{2-}.[27] The intercationic distance Se(2)–Se(3) of 3.85 Å thus does not appear exceptional.

With the revised minimum Se–Cl distance of 3.52 Å there remain twelve unusual contacts, two being *ca.* 0.25 Å below this value. Clearly, there are attractive interactions operating at distances less than conservatively estimated hard-shell ionic dimensions. Consistent with this are the observations that the shapes of the clusters $Se_8{}^{2+}$ and $AlCl_4{}^-$ appear perturbed from greater regularity by these contacts, the angular distortions being appreciable and the changes in bond lengths of lesser significance. Further structure studies on the $Se_8{}^{2+}$ ion with anions of varying shapes and bonding properties will be necessary before decisions can be made regarding the relative importance of external bonding on the conformation of the cluster and on the weak transannular interaction.

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