The Molecular Configuration of the Se_8^{2+} Ion in $Se_8(AlCl_4)_2$†

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Summary The molecular configuration of the Se_8^{2+} ion in $Se_8(AlCl_4)_2$ is described and compared with those of the related bicyclo-octane, Se_8, and S_4N_4.

DURING recent investigations into the possible existence of homopolyatomic cations of heavy main-group elements in tetrachloroaluminate systems, we have isolated a number of crystalline selenium and tellurium compounds believed to contain such polyatomic ions.[1] Gillespie and his co-workers[2–4] have investigated the formation of similar species in fluorosulphuric acid media and have reported the existence of Se_4^{2+} and Se_8^{2+} as well as a square model for the former based on a tentative interpretation of two-dimensional X-ray diffraction data. The two reduced selenium tetrachloroaluminate phases have compositions consistent with the presence of these cations. We report that a detailed structure determination of the more reduced of these allows a description of the unusual bicyclic Se_8^{2+}.

Black crystals of $Se_8(AlCl_4)_2$ were grown by vapour-phase transport and were mounted under anaerobic conditions. Examination of Weissenberg photographs showed that the crystals were orthorhombic ($a = 14{\cdot}92 \pm 0{\cdot}02$; $b = 10{\cdot}67 \pm 0{\cdot}01$; $c = 13{\cdot}22 \pm 0{\cdot}01$ Å) and that the extinction conditions were consistent with the space groups *Pcam* (No. 57) or $Pca2_1$ (No. 29). The latter non-centrosymmetric symmetry was established by the structure determination. D_m for a cast rod of the composition $Se_8(AlCl_4)_2$ is $3{\cdot}2 \pm 0{\cdot}2$ g. cm.$^{-3}$, and D_c is $3{\cdot}06$ g. cm.$^{-3}$ for $Z = 4$. Three-dimensional intensity data were collected with Mo-K_α radiation using a G.E. single-crystal orienter and were corrected for adsorption, Lorentz, and polarization effects.

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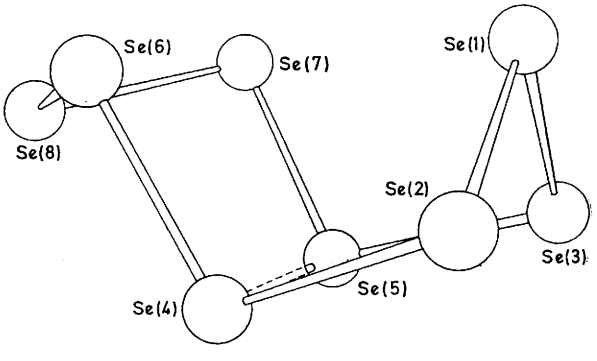
Trial positions for the eight non-equivalent selenium atoms were deduced from the three-dimensional Patterson function, and difference Fourier syntheses phased by this model revealed the positions of the lighter atoms. At the present stage of the analysis, the full matrix least-squares refinement with isotropic thermal parameters has converged at a conventional R value of 11·6% for 737 reflections observed to be greater than the 2σ level established from counting statistics.

The structure consists of discrete Se_8^{2+} and $AlCl_4^-$ ions with the three ions of the formula unit being the non-equivalent groups of the unit cell. The configuration of the Se_8^{2+} ion is that of a ring with approximate m symmetry, as shown in the Figure. The Se–Se–Se angles in the ring average 98° excluding the angles subtended at atoms 1 and 8 which are nearer 90°. The average Se–Se distance around the ring is $2{\cdot}32 \pm 0{\cdot}03$ Å, substantially the same as in elemental selenium.[5,6] The distances between atoms related by the plane of pseudo-symmetry are $3{\cdot}36 \pm 0{\cdot}02$, $2{\cdot}83 \pm 0{\cdot}01$, and $3{\cdot}30 \pm 0{\cdot}01$ Å, with the larger Se(2)–Se(3) and Se(6)–Se(7) distances, respectively, being fairly normal van der Waals' contacts but with the Se(4)–Se(5) distance appearing to have a highly significant reduction of this value. Considering this to be a bonding interaction between Se(4) and Se(5) confers a bicyclic structure to Se_8^{2+} reminiscent of bicyclo[3,3,0]octane. In fact, if the carbon atoms in the bicyclo-octane are replaced by selenium atoms and the hydrogen atoms by lone electron pairs, the bicyclo-octane and Se_8^{2+} have basically the same valence electronic configuration. A Dreiding model of Se_8^{2+} constructed with the observed parameters is quite rigid, suggesting that the conformation adopted is not dictated by interionic forces on a more flexible ion.

The structure and bonding of Se_8^{2+} appears directly related to those of two better known entities, Se_8 and S_4N_4. Atoms 2, 3, 6, and 7 constitute an invariant reference plane throughout these changes. The observed Se_8^{2+} may be obtained from the normal "crown" conformation of monocyclic Se_8[5,6] (48 valence electrons) by loss of two electrons followed by the transannular closing of Se(4)–Se(5) and a ring flip of Se(1) to the observed conformation (*syn-cis-anti*). Further loss of two electrons with a ring flip of Se(8) plus a Se(8)–Se(1) closure will give a Se_8^{4+} ion with D_{2d} symmetry. Such a hypothetical Se_8^{4+}, with 44 valence electrons, will be recognized as having a molecular and electronic structure like S_4N_4,[7,8] or a structure like As_4S_4[9] where sulphur rather than nitrogen comprises the plane of atoms 2, 3, 6, and 7.



FIGURE

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[1] D. J. Prince and J. D. Corbett, unpublished results.

[2] I. D. Brown, D. B. Crump, R. J. Gillespie, and D. P. Santry, *Chem. Comm.*, 1968, 853.

[3] J. Barr, R. J. Gillespie, R. Kapoor, and K. C. Malhotra, *Canad. J. Chem.*, 1968, **46**, 149.

[4] J. Barr, R. J. Gillespie, R. Kapoor, and G. P. Pez, *J. Amer. Chem. Soc.*, 1968, **90**, 6855.

[5] R. D. Burbank, *Acta Cryst.*, 1951, **4**, 140.

[6] R. E. Marsh, L. Pauling, and J. D. McCullough, *Acta Cryst.*, 1953, **6**, 71.

[7] D. B. Sharma and J. Donohue, *Acta Cryst.*, 1963, **16**, 891.

[8] A. G. Turner and F. S. Mortimer, *Inorg. Chem.*, 1966, **5**, 906.

[9] T. Ito, N. Morimoto, and R. Sadanaga, *Acta Cryst.*, 1952, **5**, 775.