Heteroatomic Polyanions of Post-transition Elements. Synthesis and Structure of a Salt containing the Novel Hybrid Hepta-arsenic Tetraselenate(1−) Anion, $As_7Se_4^-$

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Reduction of As_4Se_4 by potassium in ethylenediamine in the presence of tetraphenylphosphonium bromide resulted in the formation of the compound $P(C_6H_5)_4{\cdot}As_7Se_4$ whose structure has been determined crystallographically.

We report the results of our general study of naked Zintl anions such as As_4^{2-}, As_6^{4-}, As_{11}^{3-}, $As_{11}Te^{3-}$, $As_2Se_6^{2-}$, and $As_2Te_6^{2-}$.[1—5] These anions were obtained either by complexation of the corresponding Zintl phases containing alkali metals, by the bicyclic [2.2.2] cryptand ligand according to the procedure described by Corbett,[6] or by oxidation of Zintl anions by chalcogens. On the other hand, heteropolyanions can also be synthesized by reduction of polychalcogenates by an alkali metal in ethylenediamine (en), as performed by Haushalter for $As_{10}Te_3^{2-}$.[7]

Reaction of As_4Se_4 with potassium in ethylenediamine yielded a yellow precipitate (potassium selenide). The orange-brown filtrate, which was treated with $P(C_6H_5)_4Br$, instantaneously turned red; after a week, a few flat red crystals deposited on the wall of the reactor, the elemental analysis of which indicated an As/Se ratio of 1.73. On evaporation of this solution, a large amount of parallelepipedic crystals with an As/Se ratio of 2.51 were obtained; only the former crystals were suitable for *X*-ray analysis.†

The structure of the $P(C_6H_5)_4{\cdot}As_7Se_4$ compound reveals the

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† *Crystal data*: $P(C_6H_5)_4{\cdot}As_7Se_4$, M = 1179.5, triclinic, space group $P\bar{1}$, a = 11.159(3), b = 12.135(4), c = 13.113(3) Å, α = 106.13(2), β = 108.97(2), γ = 96.72(2)°, Z = 2, $F(000)$ = 1092, D_c = 2.49 g cm^{-3}, μ(Mo-$K_{\bar{\alpha}}$) = 128 cm^{-1}. Intensity data were collected by the $w - 1/3\ \theta$ technique on a Nonius CAD-4 diffractometer in the range $4 \leqslant 2\theta \leqslant 46°$ [4142 unique reflexions of which 2461 had $I > 3\sigma(I)$]. The data were corrected for background and Lorentz polarisation and numerical absorption corrections were applied. The structure was solved by direct methods and refined by full-matrix least-squares to a final R of 0.0603 (R_w = 0.0626) with anisotropic thermal parameters for all atoms, calculated hydrogen positions were introduced. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

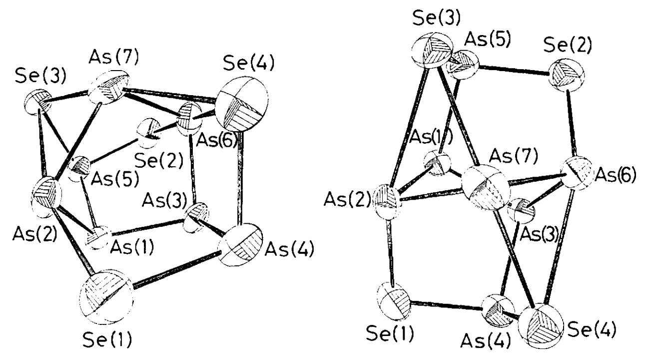

Figure 1. Two views of the geometry of the $As_7Se_4^-$ anion in the $P(C_6H_5)_4 \cdot As_7Se_4$ compound. Bond distances (Å): As(1)–As(2) 2.406(2), As(1)–As(3) 2.442(2), As(1)–As(5) 2.487(3), Se(1)–As(2) 2.378(3), Se(1)–As(4) 2.391(3), As(2)–As(7) 2.475(3), As(2)–Se(3) 3.158(3), As(3)–As(6) 2.418(3), As(3)–As(4) 2.484(3), As(4)–Se(4) 2.335(3), As(5)–Se(3) 2.366(3), As(5)–Se(2) 2.382(3), Se(2)–As(6) 2.383(3), As(6)–As(7) 2.457(3), As(6)–Se(4) 3.127(3), Se(3)–As(7) 2.639(3), As(7)–Se(4) 2.734(3).

novel hybrid heteropolyanion $As_7Se_4^-$ which is represented in Figure 1. The co-ordination around both As and Se atoms is greater than that which is generally observed in cage or cyclic anions: $As_xCh_y^{z-}$ where the number of arsenic–chalcogen exocyclic bonds is y if $y < z$ [$As_{11}Te^{3-}$ (ref. 3)] and z if $y > z$ [$As_2Se_6^{2-}$ (ref. 4); $As_{10}Te_3^{2-}$ (ref. 7)].

In the present structure there is no evidence of exocyclic bonds; Se(4) has a medium bond length to As(4) of 2.335 Å, intermediate between exocyclic (2.276 Å) and ring Se–As (2.414 Å) bonds. Furthermore Se(4) is in bonding interaction with As(7) and As(6) at 2.734 and 3.127 Å, respectively, which is, even in the latter case, below the sum of the van der Waals radii of the elements (3.75 Å[8]). In the same way Se(3) is found to be trico-ordinated, while the bridging Se(1) and Se(2) atoms are bico-ordinated to arsenic atoms (mean length 2.384 Å). Among the arsenic atoms, As(2), As(6), and As(7) are found to be tetraco-ordinated and the anion displays a pseudo two-fold axis passing through the As(7) atom and the middle of the As(1)–As(3) bond.

The co-ordination observed for both arsenic and selenium atoms is unusual in this kind of anion. It appears that the structure is intermediate between a cage and a cluster. The anion contains 60 valence electrons of which 34 can, in a simplified manner (localized electrons), be allocated to the 17 internal bonds, the remaining 26 electrons being allocated to external non-bonding pairs [one pair for As, Se(3), and Se(4) atoms, two pairs for the bico-ordinated Se(1) and Se(2) atoms]. Nevertheless, it would be better to discuss the electronic structure in terms of partially delocalized electrons about the As(2), Se(3), As(7), Se(4), and As(6) atoms.

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