Heteroatomic Polyanions of Post-transition Elements. Synthesis and Structure of a Salt containing the Undeca-arsenictellurate(3−) Anion, $As_{11}Te^{3-}$

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Reaction of the $K_{1.6}\,As_{1.6}\,Te$ alloy with the <2.2.2> cryptand ligand $N([CH_2]_2O[CH_2]_2O[CH_2]_2)_3N$ in ethylenediamine (en) results in the formation of a compound formulated as $[K(crypt<2.2.2>)]_3\,As_{11}Te{\cdot}en$, the anion geometry of which has been established by *X*-ray analysis.

The following results were obtained in a general study of Zintl phases,[1,2] and specifically of 'naked polyanionic clusters' such as $As_2Te_6^{2-}$, $As_2Se_6^{2-}$, and As_{11}^{3-} which have recently been synthesized and characterized crystallographically.[3—5] Important progress in the isolation of such polyatomic anions from alloys containing alkali metals has been made after a novel route for stabilization was developed by Corbett using the bicyclic <2.2.2.> cryptand ligand to complex the alkali metal cation.[6] Early investigations have shown that novel compounds such as $As_{11}Te_2$ or $As_{11}Te_3$ may exist, but we have as yet been unable to determine the crystal structure of these clusters, which appear highly disordered. In the present work, we report the synthesis and *X*-ray crystal analysis of a new phase $[K(crypt<2.2.2.>)]_3As_{11}Te{\cdot}en$, containing the $As_{11}Te^{3-}$ anion {crypt<2.2.2> = $N([CH_2]_2O[CH_2]_2O[CH_2]_2)_3N$}. It will be used as a reference in EXAFS studies of the preceding heteroanions.

An alloy of stoicheiometry $K_{1.6}As_{1.6}\,Te$ was prepared from the elements in an argon weld-sealed tantalum tube heated to 700 °C. Distillation of dried ethylenediamine (en) onto the alloy in a Pyrex reactor produced an initial solution which turned almost instantaneously red–brown copper on contact with the 2.2.2 cryptand ligand. Very slow evaporation of en led to the formation of deep red crystals. The composition of the title compound was established by full elemental flame analysis giving a stoicheiometry for heavy atoms close to $K_3As_{11}Te$.†

The structures of two cations are similar to those determined elsewhere[3—5] while the third cation is fairly disordered. The most interesting feature of the structure, the $As_{11}Te^{3-}$ anion, is illustrated in Figure 1. Owing to the binding of a

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† *Crystal data:* $[K(cryptand<2.2.2>)]_3As_{11}Te{\cdot}en$, $M = 2\,198.5$, triclinic, space group $P\bar{1}$, $a = 14.052(4)$, $b = 14.336(3)$, $c = 24.650(6)$ Å, $\alpha = 91.07(2)$, $\beta = 92.39(3)$, $\gamma = 102.70(2)°$, $Z = 2$, $F(000) = 2\,180$, $D_c = 1.506$ g cm^{-3}, μ(Mo-$K_{\bar{\alpha}}$) = 44.105 cm^{-1}. Intensity data were collected by the ω–θ scan technique on a Nonius CAD-4 diffractometer in the range $4 \leqslant 2\theta \leqslant 36°$ [7430 unique reflections of which 3259 had $I > 3\sigma(I)$]. The data were corrected for background and Lorentz–polarisation effects but no absorption correction was applied. The structure was solved by direct methods and refined by full-matrix least-squares to a final R of 0.0726 (R_w 0.136) with anisotropic thermal parameters for As, Te, and K atoms and isotropic thermal parameters for the other non-hydrogen atoms.[7] 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.

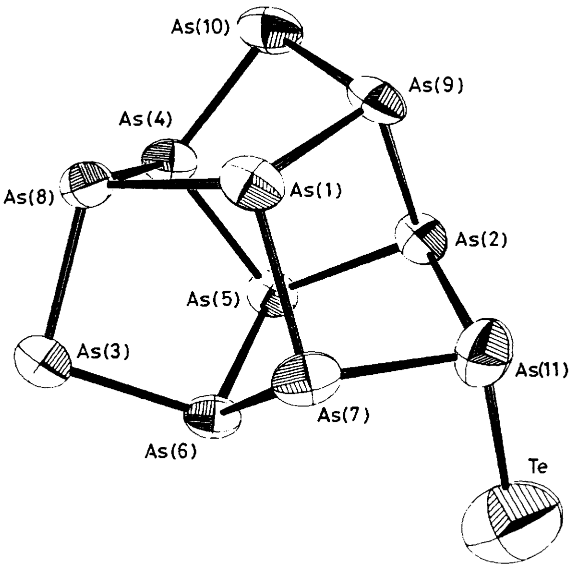

Figure 1. Geometry of the $As_{11}Te^{3-}$ anion in [K(crypt<2.2.2.>)]$_3$ $As_{11}Te$·en. Bond distances (Å): As(1)–As(7) 2.432(5), As(1)–As(8) 2.464(5), As(1)–As(9) 2.464(5), As(2)–As(9) 2.417(5), As(2)–As(11) 2.428(5), As(2)–As(5) 2.436(5), As(3)–As(8) 2.372(5), As(3)–As(6) 2.380(5), As(4)–As(10) 2.380(5), As(4)–As(8) 2.427(5), As(4)–As(5) 2.475(5), As(6)–As(7) 2.419(5), As(7)–As(11) 2.416(5), As(9)–As(10) 2.366(5), As(6)–As(5) 2.449(5), As(11)–Te 2.491(5).

tellurium atom to a waist arsenic, this anion has no symmetry although the frame As_{11}^{3-} from which it derives displays a symmetry close to D_3 [the threefold axis passing through As(1) and As(5)]. Nine As atoms are three-co-ordinated (one of them is co-ordinated to the tellurium atom) while the other two are two-co-ordinated on the waist of the cluster. Except for the part which is related to the tellurium atom, the distances and angles are similar to those found in As_{11}^{3-}.[5] The exocyclic As–Te bond length is close to that observed in $As_2Te_6^{2-}$ (2.506 Å), although in this case each arsenic atom is surrounded by three tellurium atoms. Compared to bond lengths involving the waist two-co-ordinated arsenic atoms, the electron transfer through bonding to the tellurium atom induces an increase of about 0.05 Å in the As–As bond lengths around As(11).

In this anion, the bonding scheme follows the classical valence rules with two centre–two electron bonds and one or two free electron pairs located respectively on three- or two-co-ordinated arsenic atoms; this description is in accordance with that already proposed for $P_{11}R_3$ and As_7R_3.[8] The vicinity of the free electron pair on As(11) induces a distortion of the As(11)–Te exocyclic bond with respect to As(7) and As(2), as seen by the angles As(2)–As(11)–Te, As(2)–As(11)–As(7), and As(7)–As(11)–Te with values of 112, 97, and 102°, respectively. This distortion evidently results from the combination of repulsions between bonding and free electron pairs; in $As_2Te_6^{2-}$, where the arsenic atom is bonded to two cyclic and one exocyclic tellurium atoms, these repulsions act more symmetrically, with a more expanded free electron pair and angles around the central arsenic atom close to 97°.

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