

Oxidatively Coupled Polyarsenide Clusters: Synthesis and Structures of SnAs_{14}^{4-} and As_{22}^{4-}

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The synthesis and X-ray crystal structures of the anions SnAs_{14}^{4-} and As_{22}^{4-} , which represent the largest polyarsenides characterized to date, are reported.

A wide variety of polyphosphorus clusters have been characterized during the last few decades^{1,2} however the corresponding arsenic systems have received much less attention. Recently, some polyarsenic anions have been crystallographically characterized, including As_6^{4-} ,^{2,3} As_7^{3-} ,^{4,5} and As_{11}^{3-} ⁶ which are isostructural with their phosphorus analogues, but larger homoatomic polyarsenide clusters were unknown. Furthermore, with the exception of the mixed arsenic-chalcogen anions, such as $\text{As}_{10}\text{Te}_3^{2-}$ (ref. 7) and $\text{As}_{11}\text{Te}^{3-}$ (ref. 8), examples of heteroatomic arsenide clusters are also quite rare. Here, we describe the synthesis and structures of two new polyarsenides, As_{22}^{4-} and SnAs_{14}^{4-} , found in the compounds $(\text{Rb}\cdot\text{crypt})_4\text{As}_{22}^{4-}\cdot\text{DMF}$ (crypt = 4,7,13,16,21,24-hexaoxa-1,10-diazatricyclo[8.8.8]hexacosane; DMF = dimethylformamide) and $(\text{K}\cdot\text{crypt})_4\text{SnAs}_{14}^{4-}$, respectively. These clusters represent new structure types for the group 15 polyanions and are the largest molecular polyarsenides characterized to date.

During our recent investigations of the ternary alloys formed between the alkali metals and the group 14 and 15 elements, we discovered the new compounds KSnAs and KSnSb^9 that contain the anions $\mathbb{Z}[\text{Sn}_{3/3}\text{As}_{3/3}^{1-}]$ and $\mathbb{Z}[\text{Sn}_{3/3}\text{Sb}_{3/3}^{1-}]$, respectively. These materials contain puckered, infinite two-dimensional nets reminiscent of those in CaSi_2 ¹⁰ but with the Sn and As (or Sb) segregated on opposite sides of the nets. It was not possible to extract any soluble species from KSnAs using ethylenediamine (en), but by changing the ratio of the elements in the K–Sn–As system, we were able to isolate the new tin–arsenide polyanion SnAs_{14}^{4-} . The elements K, Sn, and As, in a molar ratio of 1.5 : 1.0 : 3.5 ($\text{K}_3\text{As}_7 + 2\text{Sn}$), were fused for 5 min under a He atmosphere. Extraction of the resulting solid with en gave dark red–orange crystals of $(\text{K}\cdot\text{crypt})_4\text{SnAs}_{14}^{4-}$ in ca. 15% yield after partial evaporation of the solvent. One mole equivalent of crypt per potassium was used to facilitate dissolution.

The solution of the single-crystal X-ray data† revealed the unusual geometry of the SnAs_{14}^{4-} anion as shown in Figure 1. The structure consists of two As_7 cages, similar to those found in $\text{Ba}_3\text{As}_{14}^{4-}$ or $\text{Rb}_3\text{As}_7\cdot 6/2\text{en}$,⁵ which are asymmetrically linked by a single tin atom. The tin atom is three-co-ordinate forming one bond to one of the As_7 cages [$\text{Sn}(1)\text{--As}(1)$ 2.84(1) Å] and two bonds to the other cage [$\text{Sn}(1)\text{--As}(12)$ 2.90(1), $\text{Sn}(1)\text{--As}(8)$ 2.98(1) Å]. These Sn–As bond lengths are significantly longer than those observed for the three-co-ordinate Sn atoms in KSnAs^9 [$\text{Sn}\text{--As}$ 2.72 Å]. The As–As distances within the two As_7 cages are in the range 2.3–2.5 Å, quite similar to those observed in $\text{Ba}_3\text{As}_{14}^{4-}$.⁴ The formation of SnAs_{14}^{4-} may be viewed as an oxidative coupling of two As_7^{3-} cages in the presence of (or promoted by) Sn metal. The nature of the remaining insoluble components of the melt are currently unknown.

In addition to the p-block heteropolyarsenic clusters, we have been pursuing the synthesis of transition-metal polyarsenic clusters by a variety of methods. One such reaction between $\text{Fe}_2(\text{CO})_9$ and two equivalents of Rb_3As_7 in en at

† Crystal data for $(\text{K}\cdot\text{crypt})_4\text{SnAs}_{14}^{4-}$: space group $P\bar{1}$, $a = 16.959(7)$, $b = 25.74(9)$, $c = 14.084(5)$ Å, $\alpha = 98.47(3)$, $\beta = 97.42(3)$, $\gamma = 77.43(3)^\circ$, $U = 5906(8)$ Å³, $Z = 2$, $D_c = 1.59$ g cm⁻³. For 4236 reflections with $(I) > 3\sigma(I)$, $R = 0.121$, $R_w = 0.131$. For Mo- K_α , $\mu = 45.25$ cm⁻¹, and an empirical absorption correction was applied.

Crystal data for $(\text{Rb}\cdot\text{crypt})_4\text{As}_{22}^{4-}\cdot\text{DMF}$: space group $P\bar{1}$, $a = 15.230(4)$, $b = 16.404(4)$, $c = 17.223(4)$ Å, $\alpha = 63.14(2)$, $\beta = 72.33(2)$, $\gamma = 63.34(2)^\circ$; $U = 3403(1)$ Å³, $Z = 1$, $D_c = 1.85$ g cm⁻³. For 3585 reflections with $F_o \geq 5\sigma(F_o)$, $R = 0.0618$, $R_w = 0.0681$. Mo- K_α , $\mu = 71.8$ cm⁻¹ and an empirical absorption correction was applied.

Atomic co-ordinates, bond lengths and angles, and thermal parameters for both compounds have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

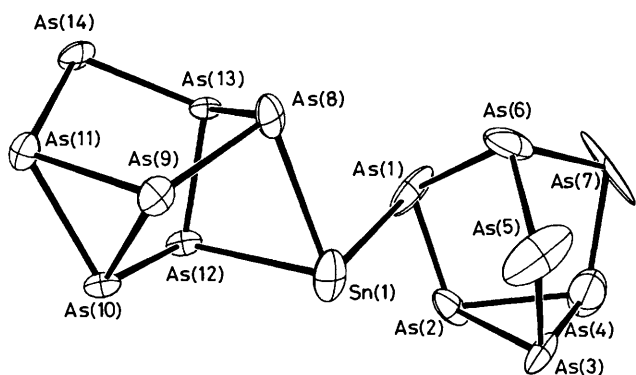


Figure 1. A view of the SnAs_{14}^{4-} anion in $(\text{K}\cdot\text{crypt})_4\text{SnAs}_{14}$. Pertinent bond distances; $\text{Sn}(1)\text{--As}(8)$ 2.983(9), $\text{Sn}(1)\text{--As}(12)$ 2.898(8), $\text{Sn}(1)\text{--As}(1)$ 2.84(1); $\text{As}(5)\text{--As}(6)$ 2.27(1), $\text{As}(5)\text{--As}(3)$ 2.36(1), $\text{As}(9)\text{--As}(11)$ 2.473(8), $\text{As}(11)\text{--As}(14)$ 2.376(9), $\text{As}(13)\text{--As}(8)$ 2.425(8), $\text{As}(1)\text{--As}(6)$ 2.37(1) Å.

100°C produced wafer-thin, orange, hexagonally shaped plates which displayed CO bands at 1873 and 1732 cm^{-1} in their i.r. spectrum. In an attempt to produce X-ray quality crystals of this compound, a recrystallization was performed in dimethylformamide. Surprisingly, iron-free, red, crystalline $(\text{Rb}\cdot\text{crypt})_4\text{As}_{22}\cdot 4\text{DMF}$ was produced in a fair yield.‡ The fate of the iron in this reaction is currently unknown.

The X-ray structure† of the polyarsenide revealed the 22 atom cluster anion As_{22}^{4-} (Figure 2), which may be formed from oxidative coupling of two As_{11}^{3-} cages. The two As_{11} subunits are linked by a single As–As bond [$\text{As}(1)\text{--As}(1')$ 2.432(6) Å]. The structure of the As_{11} subunits and As–As distances within each cage are virtually identical to those found in $(\text{K}\cdot\text{crypt})_3\text{As}_{11}$.⁶ Each As_{11} subunit possesses the trishomocubane structure found in P_{11}^{3-} ,¹¹ As_{11}^{3-} ,⁶ and [*cyclo*-($\text{C}_6\text{H}_5\text{As}$)₉ $\text{Mo}_2(\text{CO})_6$].¹² In As_{22}^{4-} , the three cube edges^{11,12} are bridged by As(1), As(4), and As(7). The As–As bond distances occur in two ranges. Distances to the two-coordinate atoms As(4) and As(7) average 2.38(1) Å, whereas the remaining distances between the three-co-ordinate As atoms average 2.45(1) Å. The latter average is typical of normal As–As distances such as those observed for *cyclo*-($\text{C}_6\text{H}_5\text{As}$)₆ [$\text{As}\text{--As}$ 2.459(2) Å av.]. The distances to As(4) and As(7) are significantly shorter, but are typical for

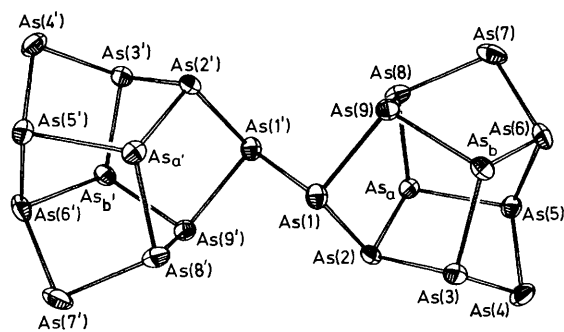


Figure 2. A view of the As_{22}^{4-} anion in $(\text{Rb}\cdot\text{crypt})_4\text{As}_{22}\cdot 4\text{DMF}$. Pertinent bond distances: $\text{As}(1)\text{--As}(1')$ 2.432(6), $\text{As}(1)\text{--As}(2)$, 2.438(4), $\text{As}(2)\text{--As}(3)$ 2.433(4), $\text{As}(3)\text{--As}(4)$ 2.375(4), $\text{As}(4)\text{--As}(5)$ 2.377(4), $\text{As}(5)\text{--As}(6)$ 2.436(4), $\text{As}(6)\text{--As}(7)$ 2.379(4), $\text{As}(7)\text{--As}(8)$ 2.400(4), $\text{As}(8)\text{--As}(9)$ 2.411(5), $\text{As}(9)\text{--As}(1)$ 2.464(3), $\text{As}_a\text{--As}(2)$ 2.451(4), $\text{As}_a\text{--As}(5)$ 2.494(3), $\text{As}_a\text{--As}(8)$ 2.455(3), $\text{As}_b\text{--As}(3)$ 2.451(3), $\text{As}_b\text{--As}(6)$ 2.484(5), $\text{As}_b\text{--As}(9)$ 2.441(4) Å.

two-co-ordinate As atoms in other polyarsenide clusters.^{4–6} The As_{22}^{4-} anion may be structurally related to the recently reported P_{22}H_4 cluster,¹ and is the largest molecular polyarsenide characterized to date.

Received, 2nd March 1988; Com. 8/00841H

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‡ Ca. 20 mg of $(\text{Rb}\cdot\text{crypt})_4\text{As}_{22}\cdot 4\text{DMF}$ crystals were obtained from 50 mg of the initial hexagonal crystals. The i.r. spectrum of $(\text{Rb}\cdot\text{crypt})_4\text{As}_{22}\cdot 4\text{DMF}$ showed a single DMF CO band at 1670 cm^{-1} (KI pellet).