The purity of the perxenate was very high when the hydrolysis was carried out with pure NaOH in a closed system and the product dried under vacuum at 22 °C. A typical iodimetric analysis indicated a purity of 99.0% with the assumption of anhydrous Na_4XeO_6. Since samples dried under vacuum will contain some water, the actual purity may be somewhat greater than 99.0% and is very near 100% if one assumes 0.6 waters of hydration. The latter is believed to be the degree of hydration for Na_4XeO_6 dried under vacuum at 22 °C.[3c] Both the yields and purity of Na_4XeO_6 were lower if less pure NaOH was used for hydrolysis, if the solution was not adequately protected from the atmosphere, or if the perxenate was dried at elevated temperatures.

In conclusion, the reaction of XeF_6 with $HOPOF_2$ presents a more safe and convenient method for synthesis of small amounts of XeO_3.[9] In turn, excellent yields of sodium perxenate are possible with minimal handling of the trioxide.

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Registry No. XeO_3, 13776-58-4; Na_4XeO_6, 13721-44-3; XeF_6, 13693-09-9; $HOPOF_2$, 13779-41-4.

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(9) The scale described here is only 3 mmol. However, the same procedure has been successfully carried out on both larger (6–7 mmol) and smaller (1 mmol) scales.

Contribution from the Laboratoire des Acides Minêraux,
Laboratoire Associê au CNRS (No. 79),
Universitê des Sciences et Techniques du Languedoc,
34060 Montpellier, France

Heteroatomic Polyanions of Post Transition Elements. Synthesis and Structure of a Salt Containing the Diarsenichexaselenate(2–) Anion, $As_2Se_6^{2-}$

Claude H. E. Belin* and Monique M. Charbonnel

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Ternary systems of the type A^I–B^V–X^{VI}, where A^I represents an alkali metal, B^V = As, Sb, or Bi, and X^{VI} = S, Se, or Te, have been extensively studied and their physicochemical properties described by Lazarev et al.[1] In these phases, as well as in the mercury compounds $Hg_2P_2S_7$,[2] $Hg_2P_2S_6$, or $Hg_2P_2Se_6$,[3] there is no evidence for isolated heteroatomic polyanions of the electronegative elements; however, the anion $As_4S_6^{2-}$ was isolated by action of piperidine on a solution of As_4S_4 in $MeNH(CH_2)_2OH$[4] and its structure described by Porter.[5] In fact, such anions generally can exist only in compounds with relatively large and nonpolarizing cations. Recently, a general route to stabilize homopolyatomic anions of post transition elements from their alloys with alkali metals was found by Corbett and co-workers[6] in using the bicyclic 2,2,2-crypt[7] to complex the alkali cation and to prevent the electron transfer back from the anion to the cation in the solid state. This procedure has now allowed the isolation and characterization of the stable homopolyatomic anions such as Sn_9^{4-},[8,9] Pb_5^{2-} and Sn_5^{2-},[10] Sb_7^{3-},[11] Te_3^{2-},[12] Ge_9^{4-} and Ge_9^{2-},[13] Bi_4^{2-},[14] and As_{11}^{3-}.[15] More recently, the heteroatomic polyanion $Tl_2Te_2^{2-}$ was so synthesized and its structure described by Burns and Corbett.[16]

The purpose of our work was to isolate large heteroatomic polyanions from Na–As–Se ternary alloys, and the procedure described above still seemed to us the easiest and most appropriate way.

Experimental Section

Synthesis. Arsenic, selenium, the 2,2,2-crypt ligand, and sodium were obtained from Merck Laboratories. Although selenium and crypt were used without further purification, arsenic was purified through sublimation and sodium through several fractional crystallizations. Ethylenediamine (en) was first dried with CaH_2 and then distilled onto and stored over molecular sieve and again distilled from there for utilization.

An alloy of composition $NaAs_2Se_3$ was prepared in two steps: As_4Se_4 was first prepared by allowing arsenic and selenium to react in stoichiometric proportion in an evacuated Vycor ampule at 550 °C and then annealed for 1 day at 225 °C. Then, As_4Se_4, Se, and Na in the above composition were allowed to react at 700 °C in a tantalum tube previously weld-sealed in argon atmosphere and in turn enclosed in an evacuated Vycor jacket; after 2 days, the reactor was allowed to cool slowly to room temperature in the hope of obtaining single crystals, but the resulting black product crystallizes poorly, leaving a dark brown smear when ground to a very fine powder in the mortar. The product dissolved easily in ethylenediamine, particularly when crypt was added, giving a dark brown solution which, within 1 day, turned orange while a large amount of amorphous and green material deposited on the bottom of the Pyrex reactor. The solution was left to stand for at least 2 weeks and then evaporated very slowly, leaving a few parallelepipedic and, in larger quantity, needle-shaped, orange crystals. Preliminary oscillation and Weissenberg photographs showed that the parallelepipedic crystals possessed triclinic symmetry, while the others were demonstrated to be hexagonal; in this case, the rapidly falling intensities of diffraction spots when $(\sin\theta)/\lambda$ was greater than 0.30 seemed characteristic of highly disordered systems such as found in plastic crystals. Only the triclinic form was investigated. The crystals were selected under argon atmosphere with use of a microscope and wedged in Lindemann glass capillaries. A truncated block-shaped crystal of dimensions 0.23 × 0.30 × 0.30 mm which gave the best diffraction spots was mounted on a Nonius CAD4 automated diffractometer.

Since the compound was obtained in small yield, the arsenic and selenium ratio was verified by microanalysis[17] of a few single crystals. Anal. Calcd for $(2,2,2\text{-crypt-}Na^+)_2As_2Se_6^{2-}$: As, 10.53; Se, 33.30. Found: As, 8.87; Se, 28.46.

Data Collection and Reduction. Integrated diffraction intensities were collected at ambient temperature (25 °C). The profile analysis of a few low-angle reflections indicated that an ω–$^5/_3\theta$ scan method was the most appropriate for data collection. Scan ranges were calculated from the formula $Sr = A + B \tan\theta$, where A depends on the mosaic spread of the crystal and B allows for increasing peak width due to the $K\alpha_1$ and $K\alpha_2$ splitting; A and B were chosen as 1.2 and

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Table I. Final Parameters for Atoms in (2,2,2-crypt-Na$^+$)$_2$As$_2$Se$_6$$^{2-}$

	x	y	z		x	y	z
As	−0.1745 (1)	0.0237 (2)	0.0442 (1)	C(12)	0.259 (1)	0.756 (2)	0.166 (1)
Se(1)	0.0532 (2)	0.1443 (2)	0.9430 (2)	O(13)	0.3946 (8)	0.7832 (9)	0.2056 (8)
Se(2)	−0.0057 (2)	0.2025 (2)	0.1247 (2)	C(14)	0.426 (1)	0.795 (2)	0.104 (1)
Se(3)	−0.2000 (2)	0.0867 (2)	0.2382 (2)	C(15)	0.567 (1)	0.785 (1)	0.132 (1)
Na	0.5377 (5)	0.6781 (5)	0.3306 (5)	O(16)	0.5764 (9)	0.6559 (9)	0.1223 (9)
N(1)	0.818 (1)	0.671 (1)	0.324 (1)	C(17)	0.685 (1)	0.608 (1)	0.092 (1)
C(2)	0.857 (1)	0.546 (2)	0.317 (1)	C(18)	0.813 (1)	0.683 (1)	0.207 (1)
C(3)	0.816 (1)	0.511 (2)	0.409 (2)	C(19)	0.905 (1)	0.782 (1)	0.444 (1)
O(4)	0.6803 (9)	0.4967 (9)	0.3770 (9)	C(20)	0.841 (1)	0.903 (2)	0.478 (1)
C(5)	0.611 (1)	0.386 (1)	0.253 (1)	O(21)	0.7258 (9)	0.8797 (9)	0.4992 (9)
C(6)	0.480 (1)	0.355 (1)	0.256 (1)	C(22)	0.750 (1)	0.863 (2)	0.616 (1)
O(7)	0.4128 (9)	0.4585 (9)	0.2514 (9)	C(23)	0.632 (1)	0.895 (1)	0.654 (1)
C(8)	0.293 (1)	0.444 (1)	0.270 (1)	O(24)	0.5231 (9)	0.7946 (8)	0.5490 (8)
C(9)	0.218 (1)	0.545 (1)	0.246 (1)	C(25)	0.408 (1)	0.832 (1)	0.565 (1)
N(10)	0.2892 (9)	0.676 (1)	0.333 (1)	C(26)	0.299 (1)	0.717 (1)	0.467 (1)
C(11)	0.231 (1)	0.769 (2)	0.286 (2)				

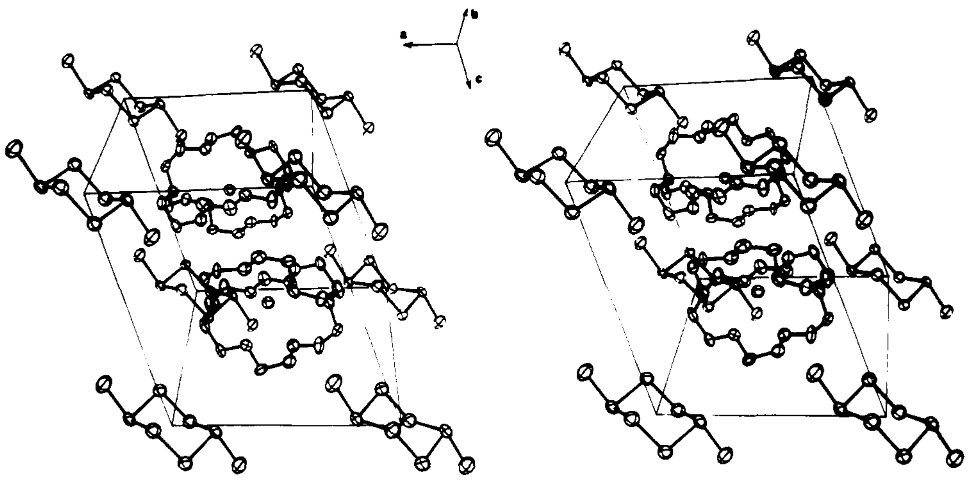

Figure 1. Stereoview of the unit cell of (2,2,2-crypt-Na$^+$)$_2$As$_2$Se$_6$$^{2-}$, approximately down the $\vec{b}$ axis. Thermal ellipsoids are shown at the 50% probability level.

0.35°, respectively. For each reflection, the calculated scan angle was extended by 25% on either side to estimate the background count. Cell parameters were obtained by least-squares refinement of the angular positions of 25 reflections automatically centered on the diffractometer: $a = 11.249$ (3) Å, $b = 11.573$ (3) Å, $c = 12.159$ (3) Å, $\alpha = 114.97$ (2)°, $\beta = 109.36$ (2)°, $\gamma = 90.65$ (2)°, and $V = 1332.45$ Å^3.

The data were collected in the four octants hkl, $h\bar{k}l$, $hk\bar{l}$, $h\bar{k}\bar{l}$ with graphite-monochromated Mo K$\bar{\alpha}$ radiation ($\lambda = 0.71069$ Å), in the range $4 \leq 2\theta \leq 50°$. During data collection, the intensities of three standard reflections were checked after every 50 reflections and no significant decay was observed. The data were corrected for background and Lorentz–polarization effects. Once the composition of the compound was known, the data were corrected for the effects of absorption by Gaussian integration[18] with $\mu = 57.6$ cm^{-1}. From 4861 recorded reflections, the final data set consisted of 2188 independent reflections with $I > 3\sigma(I)$. The initial structure solution and preliminary refinements were carried out with the data in the range $4 \leq 2\theta < 36°$, while all the data were used in final refinement cycles.

Structure Solution and Refinement. With reference to the mean volume of 630 Å^3 occupied by the cryptated sodium cation in similar compounds and with the assumption that the volume occupied by the anion is comparatively small, the cell was found to contain two cations; then, the measured density of 1.76 g cm^{-3} for the crystal clearly indicated the presence of eight arsenic or selenium heavy atoms in the cell.

The structure was solved by conventional heavy-atom Patterson methods; with the assumption that the space group was $P\bar{1}$, the Patterson map indicated the presence of four independent heavy atoms forming a nonplanar six-membered ring bonded to two exocyclic atoms, conforming to the C_i point symmetry. According to the chemical analysis, the single three-coordinate atom was considered as arsenic while the other three were attributed to selenium atoms.

Table II. Bond Distances (Å) and Angles (Deg) in the Anion As$_2$Se$_6$$^{2-}$

As–Se(3)	2.276 (2)	As–Se(1)	2.416 (2)
As–Se(2)	2.412 (2)	Se(1)–Se(2)	2.345 (2)
Se(3)–As–Se(2)	95.10 (8)	Se(1)–Se(2)–As	101.04 (8)
Se(3)–As–Se(1)	96.51 (8)	Se(2)–Se(1)–As	101.09 (7)
Se(2)–As–Se(1)	101.32 (7)		

After a few cycles of positional and isotropic thermal parameters refinement, $R = \sum[|F_o| - |F_c|]/\sum|F_o| = 0.29$. At this stage, a Fourier map indicated, in addition to the heavy-atom peaks, the sodium and 14 nonhydrogen atoms of the cryptated cation; after refinement of these positions, R was 0.19 and a subsequent difference Fourier synthesis clearly indicated the remaining atoms. Finally, all atomic positional parameters and anisotropic temperature factors were refined by full-matrix least-squares, and convergence was obtained by minimizing the function $w(|F_o| - |F_c|)^2$ with $w^{-1} = \sigma^2_{\text{count}}(F^2)/4F^2 + (0.02F)^2$. The final agreement factors were $R = 0.050$ and $R_w = 0.065$; the goodness-of-fit, defined as $[w(|F_o| - |F_c|)^2/(N - M)]^{1/2}$, where N is the number of observations (2188) and M the number of parameters varied (280), was 1.42. The final difference Fourier map was flat, except for some spurious peaks less than 1.5 e Å^{-3} close to the As and Se(1) atoms. In the final refinement cycle, the shift in heavy-atom parameters was $<0.06\sigma$ (esd) while the changes in light atoms parameters were $<0.12\sigma$. A total of 36 hydrogen atoms in the asymmetric unit, representing 13% of the total electron density, were not located or their estimated positions included in the structure factors calculation. Corrections for the anomalous dispersion effects were included in the neutral atom scattering factors for heavy atoms.[19] The crystallographic programs used were as previously reported.[15]

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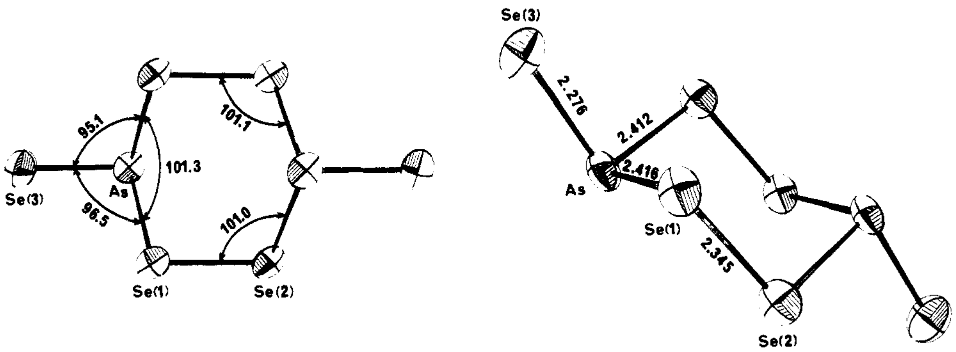

Figure 2. Two views of polyanion $As_2Se_6^{2-}$ in $(2,2,2\text{-crypt-}Na^+)_2As_2Se_6^{2-}$: (a) view perpendicular to cyclic Se plane showing the C_i symmetry; (b) view approximately down the pseudo-twofold axis. Thermal ellipsoids are shown at the 50% probability level.

Results and Discussion

The final positional parameters for the 31 nonhydrogen atoms in $(\text{crypt-}Na^+)_2As_2Se_6^{2-}$ are listed in Table I. Bond distances and angles inside the anion are given in Table II. Thermal parameters for all atoms, bond distances and some angle data for the cation (Tables A and B), as well as the listing of observed and calculated structure factors are given in the supplementary material. The packing in the unit cell is represented on Figure 1. The structure of the cation is similar to those described in other crypt-Na^+ compounds with cells of low symmetry.[9,11] Since the Na^+ ion is considered undersized for the 2,2,2-crypt cavity, this introduces some strain in the ligand, as reflected by nonnegligible differences in distances between sodium and oxygen atoms (2.48, 2.51, 2.62, 2.66, and 2.79 Å; $\sigma = 0.01$ Å) as well as in distances with nitrogen (2.81 (1) and 3.18 (1) Å) while the sodium is off the midpoint of the N–N axis by 0.20 (1) Å with a $N-Na^+-N$ angle of 178.2 (4)°.

As it was previously reported for $(\text{crypt-}K^+)_2Bi_4^{2-}$,[14] the two centrosymmetry-related cations nearly adopt a hexagonal stacking with y and z coordinates of sodium and both nitrogen atoms close to $^1/_3$ and $^2/_3$, corresponding to a position on the threefold axis of a proper hexagonal cell, causing the pseudoequality of b and c parameters and the angle α to be close to 120°.

The most interesting feature of the structure is the hitherto unknown $As_2Se_6^{2-}$ polyanion which is represented on Figure 2. It consists of a six-membered ring in chair conformation (As_2Se_4) bonded, through the trans arsenic atoms, to two exocyclic selenium atoms in equatorial position, so the molecule is bound by six heteroatomic As–Se and two homoatomic Se–Se bonds. As indicated by Figure 2a,b, the anion displays a symmetry close to C_{2h} with a pseudo-twofold axis passing through the midpoint of the Se(1)–Se(2) bonds and a mirror plane perpendicular to it, which would contain the As and Se(3) atoms.

In this anion, the bonding scheme conforms to the classical valence rules; the value of 2.345 (2) Å for Se–Se agrees with twice the covalent radius of selenium (1.17 Å).[20] For the As–Se cyclic bonds, distances of 2.412 (2) and 2.416 (2) Å are not much larger than the sum of the covalent radii of the elements (2.38 Å) and close to those observed in As_4Se_4[21] with a mean value of 2.39 Å. On the other hand, the arsenic to terminal selenium bond length of 2.276 (2) Å indicates some multiple-bond character as observed for exo As–S bonds in the anion $As_4S_6^{2-}$.[5] The shortest contacts between selenium and carbon atoms in the cation are greater than 3.71 Å and obviously exceed the sum of the van der Waals radii of the atoms (3.60 Å, Bondi[22]); this excludes any, even very weak, hydrogen-bonding interaction, especially to the exocyclic selenium atoms.

Registry No. $(2,2,2\text{-crypt-}Na^+)_2As_2Se_6^{2-}$, 81205-87-0.

Supplementary Material Available: Listings of thermal parameters for all atoms, bond distances and some angle data for the cation (Tables A and B), and observed and calculated structure factors (13 pages). Ordering information is given on any current masthead page.

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Contribution from the Department of Chemistry,
Virginia Polytechnic Institute and State University,
Blacksburg, Virginia 24061

Reactions of ((Pentafluorosulfanyl)imino)difluorosulfane, $SF_5N{=}SF_2$, with Titanium(IV) Chloride, $TiCl_4$, Tin(IV) Chloride, $SnCl_4$, and Antimony(V) Chloride, $SbCl_5$. Preparation and Characterization of ((Pentafluorosulfanyl)imino)chlorofluorosulfane, $SF_5N{=}SClF$

Joseph S. Thrasher, Narayan S. Hosmane, Donald E. Maurer, and Alan F. Clifford*

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((Pentafluorosulfanyl)imino)dichlorosulfane, $SF_5N{=}SCl_2$, was first synthesized[1] by the reaction between pentafluorosulfanylamine, SF_5NH_2, and sulfur dichloride, SCl_2. A yield of 90% was reported; however, all subsequent attempts to repeat this reaction have resulted in <10% yield of $SF_5N{=}SCl_2$.[2] It is also curious to note that Clifford and Goel recovered only 4.26% of the expected quantity of sulfur in the initial reaction.

Aluminum chloride,[3] phosphorus pentachloride,[4] and silicon tetrachloride[5] were used in the chlorination of ((perfluoroalkyl)imino)difluorosulfanes. Recently $SF_5N{=}SCl_2$ was synthesized in 75% yield by the reaction between $SF_5N{=}SF_2$ and PCl_5.[6,7] However, the purification of the main product is rendered difficult by the byproduct chlorofluorophosphoranes. These compounds have physical properties

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