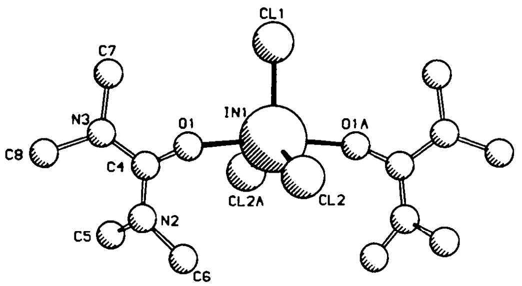

Fig. 1. Molecular structure and atomic numbering of $InCl_3(tmu)_2$.

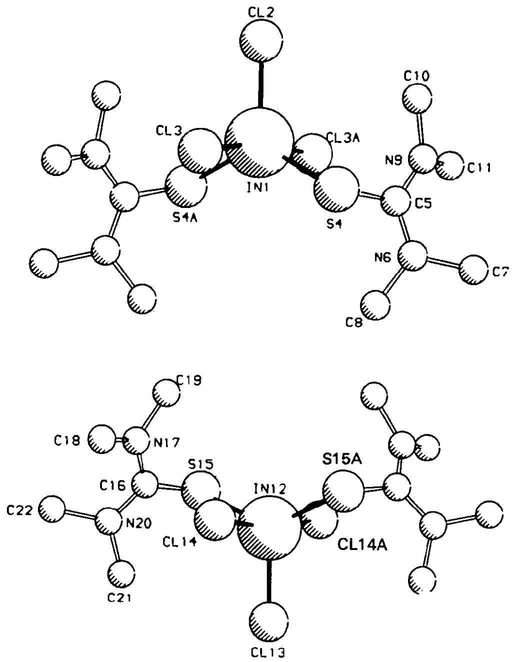

Fig. 2. Molecular structures and atomic numbering of the two independent molecules in $InCl_3(tmtu)_2$.

independent molecules in (2) show small but significant differences in the detailed coordination geometry about the In atoms. The In—Cl lengths involving the unique Cl atoms show a difference of *ca* 0·027 Å. There are also significant differences in interatomic angles between otherwise equivalent atoms. Thus the S—In—S angles differ significantly, S(4)—In(1)—S(4*A*) = 130·7 (1) whilst S(15)—In(12)—S(15*A*) = 136·1 (1)°. Similar but smaller differences occur for other bond angles, for example Cl(3)—In(1)—S(4) = 81·2 (1) compared with Cl(14)—In(12)—S(15*A*) = 82·8 (1)°, whilst Cl(3)—In(1)—S(4*A*) = 94·2 (1) compared with Cl(14)—In(12)—S(5) = 93·5 (1)°. Similarly Cl(2)—In(1)—S(4) = 114·7 (1) compared with Cl(3)—In(12)—S(15) = 112·0 (1)°.

We are grateful to SERC for the award of a Research Studentship (to JT), to the Royal Society for support (DC) and to Mr O. S. Mills for the design and provision of software required for the solution of crystal structures.

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Acta Cryst. (1991). C47, 61–63

Structure of Bis(tetraphenylphosphonium) Decaarseniotriselenate: an Example of a Two-Site-Disordered Globular Anion

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(*Received* 17 *August* 1989; *accepted* 13 *June* 1990)

Abstract. $[P(C_6H_5)_4]_2[As_{10}Se_3]$, $[P(Ph)_4]_2[As_{10}Se_3]$, M_r = 1664·5, triclinic, $P\bar{1}$, a = 9·291 (3), b = 10·554 (5), c = 27·038 (6) Å, α = 90·10 (3), β = 95·64 (2), γ = 91·33 (4)°, V = 2637 (4) Å^3, Z = 2, D_x = 2·095 Mg m^{-3}, Mo $K\alpha$, λ = 0·71069 Å, μ = 8·1 mm^{-1}, T = 293 K, $F(000)$ = 1580, final R =

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0·057, $wR = 0·059$ for 3337 observed reflections. The compound contains the polycyclic anion $As_{10}Se_3^{2-}$ which displays an orientational disorder over two symmetrical arrangements (with 85·4% and 14·6% occupancy) around the $\frac{1}{4}, \frac{1}{2}, \frac{3}{4}$ position.

Introduction. In the course of our general study of naked Zintl anions, we have reported the structures of As_4^{2-} and As_6^{2-} (Roziere, Seigneurin, Belin & Michalowicz, 1985), As_7^{3-} (Belin, Mercier, Bonnet & Mula, 1988), As_{11}^{3-} (Belin, 1980), $As_{11}Te^{3-}$ (Belin & Mercier, 1987), $As_2Se_6^{2-}$ (Belin & Charbonnel, 1982) and $As_2Te_6^{2-}$ (Belin, 1984). These anions were obtained either by complexation of the corresponding Zintl phases (alloys with alkali metals), by the bicyclic {2,2,2} cryptand ligand according to the procedure already described (Corbett, Adolphson, Merryman, Edwards & Armatis, 1975), or by oxidation of Zintl anions by chalcogens.

Heteropolyatomic anions can also be synthesized by reduction of polychalcogenates by an alkali metal in ethylenediamine (en), as in the case of $As_{10}Te_3^{2-}$ (Haushalter, 1987) and $As_7Se_4^-$ (Angilella, Mercier & Belin, 1989).

Experimental. As_4Se_4 was obtained by alloying the elements at 823 K and annealing for two days at 500 K. Approximately 70 mg of powdered As_4Se_4 was allowed to react with 34 mg of potassium in ethylenediamine; the solution was stirred until reaction was complete, and then filtered to eliminate the yellow K_2Se solid product. The red solution was complexed with tetraphenylphosphonium bromide, filtered again to remove KBr and, after a few weeks, small crystals deposited irreversibly on the bottom of the reactor. These crystals were analysed by atomic absorption spectrometry and an atomic ratio As/Se of 3·45 was found.

A suitable single crystal (parallelepiped needle of dimensions: 0·40 × 0·18 × 0·10 mm) was mounted on an Enraf–Nonius CAD-4 diffractometer using graphite-monochromatized Mo $K\alpha$ radiation, data were collected using an ω–2θ scan in the octants $(-h,h)$ $(-k,k)$ (l) in the range $2 \leq \theta \leq 25°$; 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 $K\alpha_1$ and $K\alpha_2$ splitting, A and B were chosen as 1·2 and 0·35°, respectively; maximum scan times of 60 s were programmed. Three monitored standard reflections showed no intensity variations greater than 3%. Of 9861 measured reflections $(-10 \leq h \leq 10, -12 \leq k \leq 12, 0 \leq l \leq 31; \sin\theta/\lambda \leq 0·595$ Å$^{-1})$, 3337 independent reflections with $I > 3\sigma(I)$ were retained as observed and used in the refinements. Once the composition of the crystal was known the intensities were corrected for absorption ($\mu = 8·1$ mm^{-1}) using

Table 1. *Positional and thermal parameters for atoms in* $As_{10}Se_3^{2-}$

$$U_{eq} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	k†	U_{eq}(Å^2)
As(1)	0·2974 (4)	0·3039 (2)	0·7641 (1)	0·854 (3)	0·044 (2)
As(2)	0·0952 (4)	0·5698 (4)	0·6911 (2)	0·854 (3)	0·051 (2)
As(3)	0·3065 (4)	0·6901 (2)	0·7290 (1)	0·854 (3)	0·051 (2)
As(4)	0·4346 (5)	0·4393 (4)	0·8273 (2)	0·854 (3)	0·048 (2)
As(5)	0·2018 (3)	0·4334 (2)	0·6323 (1)	0·854 (3)	0·047 (2)
As(6)	0·4066 (3)	0·3604 (2)	0·6879 (1)	0·854 (3)	0·042 (2)
As(7)	0·0609 (3)	0·4050 (2)	0·7509 (1)	0·854 (3)	0·052 (2)
As(8)	0·5134 (3)	0·5712 (3)	0·7032 (1)	0·854 (3)	0·053 (2)
As(9)	0·0645 (3)	0·5491 (3)	0·8231 (1)	0·854 (3)	0·058 (2)
As(10)	0·3084 (3)	0·6390 (2)	0·8172 (1)	0·854 (3)	0·052 (2)
Se(1)	0·3443 (4)	0·5786 (3)	0·5926 (1)	0·854 (3)	0·058 (2)
Se(2)	0·1300 (9)	0·4146 (7)	0·8891 (3)	0·854 (3)	0·085 (3)
Se(3)	0·6308 (3)	0·5135 (3)	0·7833 (1)	0·854 (3)	0·060 (2)
As(1*)	0·781 (3)	0·304 (3)	0·262 (1)	0·146 (3)	0·071 (8)
As(2*)	0·586 (5)	0·581 (4)	0·192 (2)	0·146 (3)	0·130 (2)
As(3*)	0·794 (3)	0·691 (2)	0·226 (1)	0·146 (3)	0·067 (7)
As(4*)	0·921 (4)	0·448 (3)	0·330 (1)	0·146 (3)	0·080 (1)
As(5*)	0·684 (2)	0·439 (2)	0·1297 (8)	0·146 (3)	0·063 (6)
As(6*)	0·892 (3)	0·361 (3)	0·1864 (9)	0·146 (3)	0·056 (5)
As(7*)	0·540 (3)	0·409 (2)	0·2473 (9)	0·146 (3)	0·079 (6)
As(8*)	−0·006 (3)	0·574 (2)	0·2057 (9)	0·146 (3)	0·073 (6)
As(9*)	0·546 (4)	0·558 (4)	0·320 (1)	0·146 (3)	0·099 (8)
As(10*)	0·785 (3)	0·640 (2)	0·3142 (9)	0·146 (3)	0·079 (6)
Se(1*)	0·838 (6)	0·586 (5)	0·092 (2)	0·146 (3)	0·070 (1)
Se(2*)	0·595 (4)	0·405 (3)	0·379 (1)	0·146 (3)	0·110 (1)
Se(3*)	0·102 (3)	0·511 (3)	0·282 (1)	0·146 (3)	0·092 (7)

* Atoms in the alternative disordered anion.
† k is the site occupancy factor.

Table 2. *Distances* (Å) *and angles* (°) *in the* $As_{10}Se_3^{2-}$ *anion*

As(1)—As(6)	2·452 (4)	As(6)—As(8)	2·433 (4)
As(1)—As(7)	2·459 (4)	As(6)—As(5)	2·446 (4)
As(1)—As(4)	2·464 (6)	As(6)—As(1)	2·455 (4)
As(2)—As(7)	2·414 (7)	As(7)—As(2)	2·414 (5)
As(2)—As(3)	2·449 (5)	As(7)—As(1)	2·459 (4)
As(2)—As(5)	2·441 (5)	As(7)—As(9)	2·468 (4)
As(3)—As(10)	2·444 (6)	As(8)—Se(3)	2·414 (4)
As(3)—As(2)	2·449 (5)	As(8)—As(6)	2·433 (4)
As(3)—As(8)	2·476 (5)	As(8)—As(3)	2·476 (5)
As(4)—Se(3)	2·390 (6)	As(9)—Se(2)	2·326 (8)
As(4)—As(10)	2·439 (5)	As(9)—As(10)	2·456 (4)
As(4)—As(1)	2·474 (6)	As(9)—As(7)	2·468 (4)
As(5)—Se(1)	2·333 (4)	As(10)—As(4)	2·439 (5)
As(5)—As(2)	2·441 (5)	As(10)—As(3)	2·444 (4)
As(5)—As(6)	2·446 (4)	As(10)—As(9)	2·456 (4)
Se(1)—As(5)	2·333 (4)	Se(3)—As(4)	2·390 (6)
Se(2)—As(9)	2·326 (8)	Se(3)—As(8)	2·413 (4)

As(4)—As(1)—As(6)	102·8 (2)	As(1)—As(6)—As(8)	105·4 (2)
As(4)—As(1)—As(7)	103·7 (2)	As(5)—As(6)—As(8)	94·7 (2)
As(6)—As(1)—As(7)	102·1 (2)	As(1)—As(7)—As(2)	104·4 (2)
As(3)—As(2)—As(5)	102·2 (2)	As(1)—As(7)—As(9)	102·9 (2)
As(3)—As(2)—As(7)	103·4 (2)	As(2)—As(7)—As(9)	95·5 (2)
As(5)—As(2)—As(7)	95·5 (2)	As(3)—As(8)—As(6)	101·9 (2)
As(2)—As(3)—As(8)	103·5 (2)	As(3)—As(8)—Se(3)	100·4 (2)
As(2)—As(3)—As(10)	103·0 (2)	As(6)—As(8)—Se(3)	93·1 (2)
As(8)—As(3)—As(10)	103·0 (2)	As(7)—As(9)—As(10)	96·6 (2)
As(1)—As(4)—Se(3)	101·3 (2)	As(7)—As(9)—Se(2)	102·1 (2)
As(1)—As(4)—As(10)	102·0 (2)	As(10)—As(9)—Se(2)	95·8 (2)
As(10)—As(4)—Se(3)	93·1 (2)	As(3)—As(10)—As(4)	105·1 (2)
As(2)—As(5)—As(6)	98·0 (2)	As(3)—As(10)—As(9)	103·0 (2)
As(2)—As(5)—Se(1)	101·5 (2)	As(4)—As(10)—As(9)	96·3 (2)
As(6)—As(5)—Se(1)	93·2 (2)	As(4)—Se(3)—As(8)	103·3 (2)
As(1)—As(6)—As(5)	103·5 (2)		

the numerical absorption correction facilities provided by *SHELX76* (Sheldrick, 1976), the transmission factors ranged from 0·25 to 0·55. Partial structure was solved by direct methods using *MULTAN80* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) and the full structure by Fourier and difference Fourier syntheses. The structure was refined by full-matrix least-squares refinement, *SHELX76*, with minimization of $\sum w(|F_o| - |F_c|)^2$, $w = 0{\cdot}3857/[\sigma^2(F) + 0{\cdot}00541F^2]$, anisotropic temperature factors for As, Se and P atoms, isotropic for remaining C atoms and the alternative set of atoms in the disordered anion. Final $R(F) = 0{\cdot}057$, $wR(F) = 0{\cdot}059$, H atoms were not taken into account in the calculation. Maximum/minimum peak height in the final difference map does not exceed ± 1 e Å^{-3}, $\Delta/\sigma_{max} = 0{\cdot}05$. Atomic scattering factors were from Cromer & Mann (1968).

Discussion. The final positional parameters of atoms in the $As_{10}Se_3^{2-}$ anion are listed in Table 1,* bond lengths and angles in Table 2. The atomic numbering scheme is given in Fig. 1.

The geometry of the anion is identical to that of $As_{10}Te_3^{2-}$. It is based on the As_{11}^{3-} homopolyatomic anion, with symmetry D_3, where one of the waist bicoordinated As atoms has been replaced by Se(3) and the other two are coordinated to exocyclic Se(1) and Se(2). $As_{10}Se_3^{2-}$ displays a symmetry close to C_2 with a twofold axis passing through Se(3) and the middle of the As(2)—As(7) bond. The distances and angles are similar to those found in As_{11}^{3-}. The exocyclic As—Se bond lengths (2·33 Å) are slightly larger than those observed in $As_2Se_6^{2-}$ (2·28 Å). An interesting feature of the crystal structure is the orientational disorder of the anion over two symmetrical arrangements about the $\frac{1}{4}, \frac{1}{2}, \frac{3}{4}$ position, of which the occupancies were refined to 85·4% and 14·6%. No interaction has been found between the main anionic set and the cations; on the other hand, a weak interaction (through hydrogen bonding) is found between Se(3*) and C(232) of a phenyl ring; in fact, Se(3*)—C(232) [3·38 (4) Å] and Se(3*)—H(232) (2·49 Å, obtained from calculated H position) are relatively short with respect to the sum of the van der Waals radii of the elements (3·60 and 3·10 Å respectively) (Bondi, 1964).

Such disorder problems have already been encountered for globular anions in compounds where the counter cations are nearly spherical; for example in the compound $(\text{cryptNa}^+)_2Sn_5^{2-}$ (Edwards & Corbett, 1977), a rotational disorder is observed for 14% of the tin groups. In fact, reaction of potassium with arsenic chalcogenides produces several varieties of well sized single crystals, but many of them are poorly diffracting; we suspect these crystals contain drastically disordered globular anions.

* Lists of structure factors, anisotropic thermal parameters, parameters of atoms in the cations, and angles within these cations have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53288 (32 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

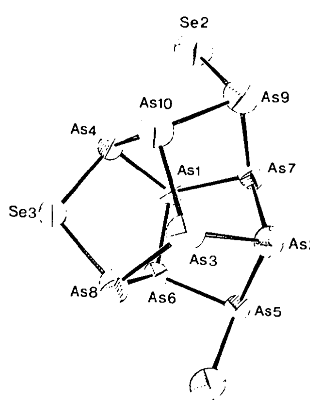

Fig. 1. *ORTEP* drawing (Johnson, 1965) of the $As_{10}Se_3^{2-}$ anion in $[P(Ph)_4]_2As_{10}Se_3$. Thermal ellipsoids are drawn at the 50% probability level.

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