Crystal Structure of Tetra-arsenic Tetraselenide

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The title compound has been shown by X-ray single-crystal study to be isostructural with α-realgar, As_4S_4. Least-squares refinement of the structure gave R 0·11 for 1008 observed photographic reflections. The far-i.r. spectrum consists of As–Se stretching (205—253) and bending bands (93—135 cm^{-1}). Mean distances: As–As 2·56$_5$ and As–Se 2·39 Å. Crystals are monoclinic, space group $P2_1/n$, $Z = 4$, $a = 9{\cdot}63 \pm 0{\cdot}02$, $b = 13{\cdot}80 \pm 0{\cdot}04$, $c = 6{\cdot}73 \pm 0{\cdot}02$ Å, $\beta = 107{\cdot}8 \pm 0{\cdot}5°$.

THERE exists some confusion in the literature concerning the n.q.r. spectrum of diarsenic triselenide, As_2Se_3, and tetra-arsenic tetraselenide, As_4Se_4. As_2Se_3 forms a stable semiconducting glass whose optical and electronic properties have been the subject of much study. The glass begins to soften at 180 °C, crystallization occurs at above 280 °C, and melting of the crystals at 380 °C.[1] As_2Se_3 crystals are isomorphous with As_2S_3,[2] having a layer structure.

The far-i.r. spectrum of As_2Se_3 has been previously reported.[3,4] Pen'kov and Safin [5] observe four n.q.r. resonances (at 79·80, 81·63, 82·02, and 82·38 MHz) for crystals considered to be As_2Se_3, whereas only two resonances are to be expected for the two arsenic atoms in the asymmetric unit of the crystal structure. Kravchenko *et al.*[6] observed only two n.q.r. resonances (at 56·07 and 60·25 MHz) for As_2Se_3 crystals at 77 K but found four resonances for As_4Se_4 at 77 K with frequencies identical with those reported by Pen'kov and Safin for As_2Se_3. We have synthesized As_2Se_3 and As_4Se_4 crystals and characterized them by single-crystal X-ray and by far-i.r. spectral study and confirm the n.q.r. results of Kravchenko. As the crystal data and spectra of As_4Se_4 have not previously been recorded we report them here.

EXPERIMENTAL

Sample Preparation.—As_4Se_4 was prepared by allowing arsenic and selenium powders in stoicheiometric proportions to react in an evacuated ampoule at 500 °C, and then annealing for 48 h at 255 °C.

Crystal Data.—As_4Se_4, $M = 615{\cdot}52$, Monoclinic, $a = 9{\cdot}63 \pm 0{\cdot}02$, $b = 13{\cdot}80 \pm 0{\cdot}04$, $c = 6{\cdot}73 \pm 0{\cdot}02$ Å, $\beta = 107{\cdot}8 \pm 0{\cdot}5°$, $U = 851{\cdot}6$ Å^3, $D_m = 4{\cdot}75 \pm 0{\cdot}05$ g cm^{-3}, $Z = 4$, $D_c = 4{\cdot}80$ gm cm^{-3}, space group $P2_1/n$. Cu-K_α radiation, $\lambda = 1{\cdot}5418$ Å; μ(Cu-K_α) = 421 cm^{-1}.

A needle-shaped crystal with dimensions 0·05 × 0·05 × 0·1 mm was mounted about its longest dimension (parallel to the c axis) and multiple-film equi-inclination Weissenberg data were obtained by use of Ni-filtered Cu-K_α radiation for the layers $hk0$—4. Intensities were estimated visually by comparison with a calibrated series of spots and were corrected for Lorentz, polarization, and spot extension, but not for absorption or extinction. From inspection of Weissenberg photographs it was evident that As_4Se_4 is isostructural with realgar As_4S_4, whose crystal structure is known.[7] Structure factors for As_4Se_4 were calculated by use of the atomic co-ordinates reported for As_4S_4. Least-squares refinement of these co-ordinates using isotropic temperature factors gave R 0·107 for 1008 observed reflections of As_4Se_4. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 20719 (3 pp., 1 microfiche).†

The far-i.r. spectrum in the range 80—400 cm^{-1} of a finely powdered sample of As_4Se_4 dispersed in yellow petroleum jelly was recorded as described previously.[3]

The n.q.r. spectra of As_4Se_4 and of a sample of As_2Se_3 characterized by X-ray powder diffraction and far-i.r. spectrum were measured in an apparatus described previously.[8]

RESULTS AND DISCUSSION

The positional and thermal parameters of the atoms of the asymmetric unit of the unit cell are listed in Table 1, and the interatomic distances and bond angles in Table 2. A view of the molecule is shown in the Figure.

TABLE 1

Positional and thermal parameters with standard deviations in parentheses

Atom	x/a	y/b	z/c	B/Å^2
As(1)	0·1141(4)	0·0182(3)	−0·2452(8)	1·34(8)
As(2)	0·4271(4)	−0·1405(3)	−0·1367(8)	1·13(7)
As(3)	0·3256(4)	−0·1312(3)	0·1752(8)	1·28(8)
As(4)	0·0363(4)	−0·1603(3)	−0·2962(9)	1·37(8)
Se(1)	0·3485(4)	0·0101(3)	−0·3065(8)	1·33(8)
Se(2)	0·2132(4)	0·0252(3)	0·1245(8)	1·40(8)
Se(3)	0·2414(4)	−0·2323(3)	−0·3729(9)	1·60(8)
Se(4)	0·1018(5)	−0·2178(3)	0·0526(9)	1·64(8)

The mean As–As bond distance (2·56$_5$ Å) in As_4Se_4 is close to the values obtained for α-As_4S_4 (2·59),[7] β-As_4S_4 (2·60),[9] As_4S_5 (2·55),[9] and the $As_4S_6^{2-}$ ion (2·58 Å).[10] The mean value for the As–Se bond (2·39 Å) agrees with the sum of the covalent bond radii of As (1·21) and Se

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† For details see Notice to Authors No. 7 in *J.C.S. Dalton*, 1972, Index issue. (Items less than 10 pp. are sent as full-sized copies.)

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TABLE 2

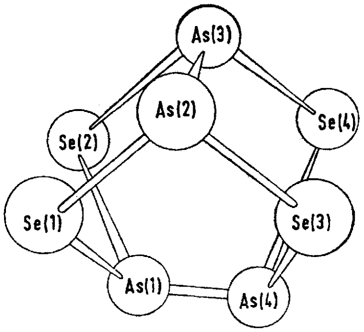
Distances and angles with standard deviations in parentheses

(*a*) Distances (Å)

As(1)–As(4)	2·567(9)	As(2)–Se(3)	2·365(9)
As(2)–As(3)	2·575(10)	As(3)–Se(2)	2·392(8)
As(1)–Se(1)	2·419(8)	As(3)–Se(4)	2·381(8)
As(1)–Se(2)	2·379(11)	As(4)–Se(3)	2·404(8)
As(2)–Se(1)	2·381(8)	As(4)–Se(4)	2·374(10)

(*b*) Angles (°)

Se(1)–As(1)–Se(2)	94·8(4)	As(4)–As(1)–Se(1)	100·5(2)
Se(1)–As(2)–Se(3)	94·7(3)	As(4)–As(1)–Se(2)	100·7(3)
Se(2)–As(3)–Se(4)	94·7(3)	As(3)–As(2)–Se(1)	101·7(3)
Se(3)–As(4)–Se(4)	95·0(3)	As(3)–As(2)–Se(3)	100·2(3)
As(1)–Se(1)–As(2)	97·7(3)	As(2)–As(3)–Se(2)	101·3(3)
As(1)–Se(2)–As(3)	97·6(3)	As(2)–As(3)–Se(4)	102·8(3)
As(2)–Se(3)–As(4)	97·8(3)	As(1)–As(4)–Se(3)	101·6(2)
As(3)–Se(4)–As(4)	96·5(4)	As(1)–As(4)–Se(4)	102·1(3)



Perspective view of the As_4Se_4 molecule

(1·17 Å). Mean values of bond angles are As–Se–As 97·2, As–As–Se 101·5, and Se–As–Se 94·7°.

I.r. absorption frequencies for As_4Se_4 are listed in Table 3, together with the frequencies found for α-realgar, As_4S_4.

TABLE 3

I.r. frequencies (cm^{-1}) for α-As_4S_4 and As_4Se_4

ν(As_4S_4)	ν(As_4Se_4)	νAs_4Se_4/νAs_4S_4
168·5s	93s	0·55
182·5w	104·5m	0·57
193w	114·5w	0·59
203·5w		
210w	129w	0·61
224s	134·5m	0·60
329w	205m	0·62
341vs	220m	0·65
359m	235m	0·65
367m	241·5vs	0·66
374m	252·5m	0·67

The far-i.r. spectrum of As_4Se_4 consists of 10 peaks in the range 93—253 cm^{-1}. The peaks between 205 and 253 cm^{-1} are assigned to As–Se stretching modes and those between 93 and 135 cm^{-1} to Se–As–Se bending modes in accord with the assignments of frequencies in arsenic sulphides and arsenic triselenide.[3,4] Four n.q.r. resonances were observed for As_4Se_4 and two resonances for As_2Se_3 at the frequencies reported by Kravchenko *et al.*[6]

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