pyramidal, such as $[IrCl(CO)(NO)(PPh_3)_2]^+BF_4$ (Hodgson & Ibers, 1968) or trigonal bipyramidal such as $IrCl(CO)_2(PPh_3)_2$ (Payne & Ibers, 1969), whilst some have intermediate arrangements of ligands. This analysis shows that the $[Ir(CO)_3(PMe_2Ph)_2]^+$ ion has the trigonal bipyramidal arrangement with the phosphine ligands in the axial positions. Selected bond lengths and angles of the cation are given in Table 2, and Fig. 1 shows the structure of the complex cation with the atom numbering indicated. The two phosphine ligands are oriented so that each has its substituents staggered with respect to the equatorial carbonyl groups so that the two phosphines are almost mutually eclipsed. The cation has approximate twofold symmetry with the twofold axis ideally passing through Ir, C(3) and O(3). The mean C–C bond length is 1·40 (2) Å and the Cl–O bonds average 1·30 (3) Å. The latter bond length is undoubtedly shortened from its true value as a result of librational motion of the ion; the chlorine atom has $U_{iso}=0{\cdot}087$ Å^2 whilst O(4) to O(7) have U_{iso} of 0·17–0·24 Å^2.

Table 2. *Bond lengths and angles with their e.s.d.'s*

Dimensions related by the approximate twofold axis of the cation are given on the same line.

Ir——P(1)	2·34 (2) Å	Ir——P(2)	2·29 (2) Å
Ir——C(1)	1·81 (5)	Ir——C(2)	1·89 (5)
Ir——C(3)	1·94 (6)		
P(1)–C(4)	1·84 (5)	P(2)–C(7)	1·74 (6)
P(1)–C(5)	1·86 (7)	P(2)–C(6)	1·78 (5)
P(1)–C(8)	1·72 (6)	P(2)–C(14)	1·85 (4)
C(1)–O(1)	1·19 (6)	C(2)–O(2)	1·24 (6)
C(3)–O(3)	1·04 (9)		
P(1)–Ir——P(2)	177·4 (5)°		
P(1)–Ir——C(1)	92 (2)	P(2)–Ir——C(2)	98 (2)°
P(1)–Ir——C(2)	80 (2)	P(2)–Ir——C(1)	87 (2)
P(1)–Ir——C(3)	93 (2)	P(2)–Ir——C(3)	89 (2)
C(1)–Ir——C(2)	126 (2)		
C(1)–Ir——C(3)	116 (2)	C(2)–Ir——C(3)	118 (2)
Ir——P(1)–C(4)	109 (2)	Ir——P(2)–C(7)	110 (2)
Ir——P(1)–C(5)	115 (2)	Ir——P(2)–C(6)	115 (2)
Ir——P(1)–C(8)	113 (2)	Ir——P(2)–C(14)	112 (2)
Ir——C(1)–O(1)	172 (4)	Ir——C(2)–O(2)	154 (4)
Ir——C(3)–O(3)	169 (7)		

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Tetra-arsenic Tetraselenide

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Abstract. As_4Se_4 is monoclinic, $P2_1/n$, $a=9{\cdot}55$ (1), $b=13{\cdot}80$ (1), $c=6{\cdot}74$ (2) Å, $\beta=106{\cdot}4$ (2)°, $Z=4$, $D_x=4{\cdot}82$ g cm^{-3}. Crystals were prepared by fusion of a 1 : 1 As : Se mixture followed by sublimation in vacuum. The structure is isostructural with α-As_4S_4, and consists of discrete As_4Se_4 molecules which possess almost exact $\bar{4}2m$ (D_{2d}) symmetry. Mean bond lengths (corrected for libration) and angles are: As–As 2·564, As–Se 2·388 Å; Se–As–As 101·2, Se–As–Se 94·1 and As–Se–As 98·1°.

Introduction. The mass spectra and X-ray powder photographs of the sublimation products of fused arsenic–selenium mixtures provide evidence for the existence of molecular arsenic selenides analogous to the established As_4S_3 and As_4S_4. The abundant positive ions in the mass spectra are: As_4S_3 ($As_4S_3^+$ 100, $As_3S_2^+$ 59, As_3S^+ 71, AsS^+ 88); As_4Se_3 ($As_4Se_3^+$ 100, As_3Se^+ 94, $AsSe^+$ 51); As_4S_4 ($As_4S_4^+$ 100, $As_3S_3^+$ 68, AsS^+ 90); and As_4Se_4 ($As_4Se_4^+$ 46, $As_4Se_3^+$ 100).

Experimental. A crystal of As_4Se_4 elongated along [001] with approximate dimensions 0·02 × 0·008 × 0·06 mm was sealed into a Lindemann glass capillary tube. Intensities were determined on a Stoe Stadi-2 two-circle diffractometer (layers *hk*0 to *hk*7) with Mo $K\alpha$ radiation. The data were collected in an approximately 'constant count' mode; where a prescan indicated that the count could not be achieved within a specified time, the reflexion was ignored. 1484 reflexions were measured, of which 223 were rejected because of background imbalance or because the net count was less than 3σ based on counting statistics; averaging of equivalent reflexions led to 684 unique reflexions. Systematic absences were observed for $h0l$ ($h+l$ odd) and $0k0$ (k odd). Absorption, Lorentz and polarization corrections were applied. Consistent unit-cell dimensions were obtained from diffractometer measurements ($\lambda=0{\cdot}71069$ Å), and by least-squares analysis of $\sin^2\theta$ values from powder photographs taken with a Guinier focusing camera and silicon internal calibrant (d= 5·4306 Å).

The unit-cell dimensions and space group indicated that the crystal was isostructural with realgar, α-As_4S_4 ($P2_1/n$, $a=9{\cdot}32$, $b=13{\cdot}55$, $c=6{\cdot}58$ Å, $\beta=106{\cdot}5°$; Ito, Morimoto & Sadanaga, 1952; Porter & Sheldrick, 1972). The structure was refined by full-matrix least-squares calculations starting from the α-As_4S_4 atomic coordinates; in the final cycles, anisotropic temperature factors were employed for all atoms. The final weighted residual $R'=\sum w^{1/2}\Delta/\sum w^{1/2}F_o$ was 0·070, with a corresponding unweighted R of 0·074. The weighting scheme employed was $w=(42{\cdot}39+|F_o|+0{\cdot}00572F_o^2)^{-1}$. Neutral atom scattering factors were used (Cromer, 1965; Cromer & Waber, 1965). Final atomic coordinates are given in Table 1 and anisotropic temperature factors in Table 3. The full covariance matrix was used in estimating the standard deviations in the bond lengths (Table 2) and bond angles (Table 4).*

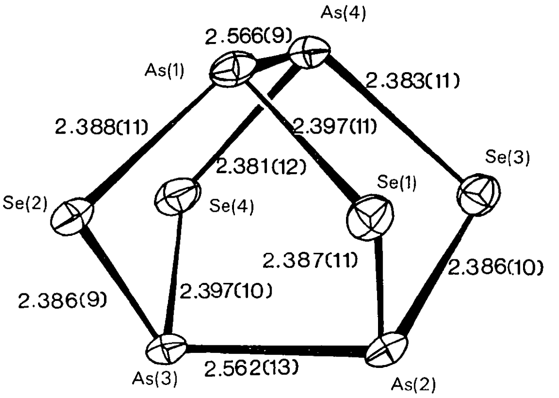

Fig. 1. View of one molecule perpendicular to [133], showing 50% probability thermal ellipsoids with principal axes, and librationally corrected bond lengths.

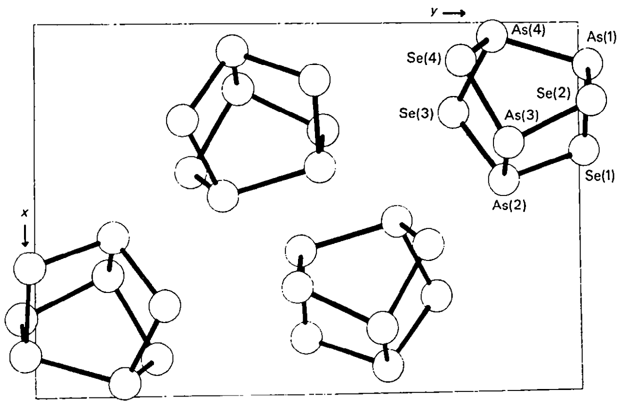

Fig. 2. Projection of the structure perpendicular to [001].

Table 1. *Fractional coordinates* (× 10^4)

	x	y	z
As(1)	1141 (4)	182 (3)	−2436 (8)
As(2)	4270 (4)	−1403 (3)	−1360 (9)
As(3)	3254 (4)	−1306 (3)	1763 (8)
As(4)	366 (3)	−1599 (3)	−2966 (8)
Se(1)	3484 (4)	98 (3)	−3060 (8)
Se(2)	2125 (4)	249 (3)	1230 (8)
Se(3)	2419 (4)	−2324 (3)	−3718 (9)
Se(4)	1015 (4)	−2181 (3)	494 (8)

Table 2. *Bond lengths* (Å) *before correction for libration*

As(1)–Se(2)	2·384 (10)	As(1)–As(4)	2·563 (9)
As(1)–Se(1)	2·394 (9)	As(2)–As(3)	2·558 (12)
As(2)–Se(1)	2·383 (9)		
As(2)–Se(3)	2·384 (9)	Average corrected bond lengths	
As(3)–Se(2)	2·382 (8)		
As(3)–Se(4)	2·394 (8)	As–As	2·564
As(4)–Se(3)	2·380 (9)	As–Se	2·388
As(4)–Se(4)	2·378 (10)		

Table 3. *Anisotropic temperature factors* (Å^2 × 10^3)

The anisotropic temperature factor takes the form:

$$\exp\left[-2\pi^2(U_{11}h^2a^{*2}+U_{22}k^2b^{*2}+U_{33}l^2c^{*2}+2U_{23}klb^*c^*+2U_{31}lhc^*a^*+2U_{12}hka^*b^*)\right].$$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
As(1)	14 (2)	24 (2)	21 (3)	3 (2)	2 (2)	2 (1)
As(2)	10 (2)	25 (2)	27 (3)	−1 (2)	4 (2)	1 (1)
As(3)	12 (1)	27 (2)	21 (3)	3 (2)	1 (2)	1 (1)
As(4)	10 (2)	25 (2)	26 (3)	−3 (2)	−2 (2)	−5 (1)
Se(1)	18 (2)	24 (2)	26 (3)	1 (2)	4 (2)	−3 (1)
Se(2)	15 (2)	30 (2)	24 (3)	−4 (2)	2 (2)	1 (1)
Se(3)	20 (2)	28 (2)	27 (3)	−6 (2)	5 (2)	−3 (1)
Se(4)	15 (2)	33 (2)	28 (3)	2 (2)	7 (2)	−5 (1)

Table 4. *Bond angles* (°)

Se(1)–As(1)–As(4)	100·1 (3)	As(2)–Se(1)–As(1)	98·1 (3)
Se(2)–As(1)–As(4)	101·3 (3)	As(3)–Se(2)–As(1)	98·7 (3)
Se(1)–As(2)–As(3)	102·1 (3)	As(4)–Se(3)–As(2)	97·7 (3)
Se(2)–As(3)–As(2)	100·6 (3)	As(4)–Se(4)–As(3)	98·0 (3)
Se(3) As(2)–As(3)	101·1 (5)		
Se(3)–As(4)–As(1)	102·2 (3)	Average bond angles	
Se(4)–As(3)–As(2)	100·8 (3)	Se–As–As	101·2
Se(4)–As(4)–As(1)	101·7 (3)	Se–As–Se	94·1
		As–Se–As	98·1
Se(2)–As(1)–Se(1)	94·0 (3)		
Se(3)–As(2)–Se(1)	94·0 (3)		
Se(4)–As(3)–Se(2)	94·6 (3)		
Se(4)–As(4)–Se(3)	93·7 (3)		

Discussion. The relatively poor agreement index (for diffractometer data) is almost certainly accounted for by the poor quality of the crystal used. The anisotropic temperature factors in β-As_4S_4 (Porter & Sheldrick, 1972) were in good agreement with the rigid-body motion model of Schomaker & Trueblood (1968), so the temperature factors for As_4Se_4 were analysed in the same way, leading to the librationally corrected bond lengths given in Fig. 1. Librational tensors, with respect to axes parallel to x^*, y and z, were L_{11} 15 (2), L_{12} O(2), L_{13} 2 (2), L_{22} 16 (3), L_{23} 1 (1), L_{33} 12 (3) 10^{-4} rad^2; S_{11}

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* The list of structure factors has been deposited with the National Lending Library, England, as Supplementary Publication No. SUP 30121. Copies may be obtained through the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

−4 (10), S_{12} −4 (2), S_{13} −1 (2), $\bar{S}_{22}$ 1 (11), $\bar{S}_{23}$ −3 (2), $\bar{S}_{33}$ 3 (11) 10^{-4} rad. Å; T_{11} 77 (10), $\bar{T}_{12}$ −11 (7), T_{13} −11 (7), T_{22} 222 (9), T_{23} −2 (6), T_{33} 193 (9) 10^{-4} Å^2 (relative to an origin at $x/a=0{\cdot}2514$, $y/b=-0{\cdot}0871$, $z/c=-0{\cdot}1070$ which makes S symmetric). The generalized index $R_g=[\sum\Delta^2/\sum U^2]^{1/2}$ for the agreement between the observed and calculated orthogonal U_{ij} was 0·079.

The asymmetric unit consists of one molecule, with approximately $\bar{4}2m$ (D_{2d}) symmetry; chemically equivalent bond lengths are equal within experimental error. The vectors As(1)–As(4) and As(2)–As(3) make angles of 89·7 and 89·9° with the normal to the mean plane through the four selenium atoms, and an angle of 90·2° with each other. The As–As bond length is within the range found in α-As_4S_4 (2·59 Å), β-As_4S_4 (2·59 Å) α-As_4S_3 (2·45 Å, Whitfield, 1970), and $As_4S_6^{2-}$ (2·58 Å, Porter & Sheldrick, 1971). The intermolecular distances are slightly longer than those in realgar, whose structure has been discussed in detail by Ito, Morimoto & Sadanaga (1952).

Table 5. *Non-bonded distances* (Å)

Intramolecular

As(1)–As(2)	3·61
As(1)–As(3)	3·62
As(1)–Se(3)	3·85
As(1)–Se(4)	3·83
As(2)–As(4)	3·59
As(2)–Se(2)	3·80
As(2)–Se(4)	3·82
As(3)–As(4)	3·60
As(3)–Se(1)	3·84
As(3)–Se(3)	3·83
As(4)–Se(1)	3·80
As(4)–Se(2)	3·83
Se(1)–Se(2)	3·49
Se(1)–Se(3)	3·48
Se(1)–Se(4)	4·94
Se(2)–Se(3)	4·93
Se(2)–Se(4)	3·51
Se(3)–Se(4)	3·47

Intermolecular (less than 4·4 Å)

Molecules related by 2_1 axis

As(1)–Se(3)	3·71
Se(1)–Se(3)	3·93
Se(2)–Se(3)	3·83

Moleules related by centre of symmetry

As(1)–As(4)	3·60
As(1)–Se(2)	3·49
As(1)–Se(4)	3·88
As(2)–Se(1)	3·62
As(2)–Se(2)	3·77
As(3)–Se(1)	3·42
As(4)–Se(2)	3·47
Se(1)–Se(2)	4·05
Se(2)–Se(2)	3·99
Se(2)–Se(4)	3·93

Molecules related by *n* glide

As(2)–As(4)	3·55
As(2)–Se(3)	3·50
As(2)–Se(4)	3·62
As(3)–As(4)	3·50
As(3)–Se(4)	3·73
Se(3)–Se(4)	3·68
As(4)–Se(4)	4·33
Se(1)–Se(4)	4·18
Se(2)–Se(4)	4·29

Molecules related by cell translation

As(3)–Se(1)	4·03
As(3)–Se(3)	3·64

A projection of the structure perpendicular to [001] is shown in Fig. 2.

We are grateful to the Science Research Council for providing the diffractometer, and for a maintenance grant to E.J.S. The calculations were performed on the Cambridge University IBM 370/165 computer with programs written by G.M.S. When this determination was almost complete, we learnt that a determination of the same structure had been completed independently by Bastow & Whitfield (1973).

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(±)-4α,8α,14β-Trimethyl-18-nor-5α,13β-androst-9(11)-en-3,17-dione, a Synthetic Precursor of Fusidic Acid*

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Abstract. Crystals of the title compound are monoclinic, $C2/c$, $a=19{\cdot}562$ (6), $b=11{\cdot}915$ (4), $c=15{\cdot}623$ (4) Å, $\beta=107{\cdot}84$ (4)°, 24°C; $C_{21}H_{30}O_2$, $M=314{\cdot}47$, $Z=8$, $D_x=1{\cdot}208$ g cm^{-3}; the racemic material was prepared by Dauben, Ahlgren, Leitereg, Schwarzel & Yoshioka [*J. Amer. Chem. Soc.* (1972). **94**, 8593–8594] and crystallized from a cyclohexane–methanol solution. Unusual stereochemistry is exhibited by the 8α configuration and by the 13β, 14β *cis C*/*D* ring junction.

Introduction. Fusidic acid has been shown to be effective in combating infections caused by staphylococci. The total synthesis of the tetracyclic nucleus of fusidic

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