Synthesis and *X*-Ray Structure of $[Ag_2(Ph_2X_2)_4][AsF_6]_2$ (X = S or Se); Six-membered Silver–Sulphur and Silver–Selenium Rings †

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The reaction of diphenyl disulphide with $AgAsF_6$ in liquid SO_2 leads to $[Ag_2(Ph_2S_2)_4][AsF_6]_2$. The *X*-ray structure [space group $P\bar{1}$, a = 10.902(4), b = 10.976(6), c = 13.308(7) Å, α = 112.82(4), β = 92.43(3), γ = 107.69(3)°, Z = 1, and R = 0.041 for 5 139 unique observed reflections] shows a centrosymmetric six-membered ring, in which two silver atoms are connected by two bridging Ph_2S_2 ligands; further unidentate sulphur ligands complete irregular three-co-ordination at silver. The analogous reaction with diphenyl diselenide leads to the isostructural $[Ag_2(Ph_2Se_2)_4][AsF_6]_2$ [space group $P\bar{1}$, a = 10.676(3), b = 11.253(3), c = 13.625(4) Å, α = 66.40(2), β = 89.67(2), γ = 71.40(2)°, Z = 1, and R = 0.044 for 4 439 reflections].

We have recently reported the tendency of Ag^+, especially with AsF_6^- as counter ion, to form complexes by co-ordination through sulphur and selenium.[1–3] These studies were, however, restricted to cyclic ligands. We have now investigated the reaction of $AgAsF_6$ with the acyclic ligands diphenyl disulphide and diphenyl diselenide.

Experimental

Reaction with Diphenyl Disulphide.—A mixture of $AgAsF_6$ (0.5 g, 1.7 mmol) and Ph_2S_2 (0.74 g, 3.4 mmol) was cooled to −190 °C in a pressure flask and liquid SO_2 (20 cm^3) was added. The flask was allowed to warm to room temperature and was stirred for an additional 15 h. Evaporation of SO_2 yielded a pale yellow product (1) which was recrystallized from methylene chloride (decomp. 118—120 °C). I.r. absorptions (Nujol mull: 1 577w, 1 445s, 1 072w, 1 022w, 1 000w, 760s, 752s, 745s, 702s, 684s, 674s, 505w, 480w, 468w, and 339s cm^{-1}) and Raman bands (1 574s, 1 469w, 1 072s, 1 069s, 1 022s, 999s, 673w, 615w, 512s, 488m, 458s, and 303m cm^{-1}) indicated that complex formation had taken place, but *X*-ray analysis was necessary to elucidate the exact nature of the product (1), which is air stable but sensitive towards daylight and moisture.

Table 1. Crystal data and details of data collection and refinement for compounds (1) and (2)

	(1)	(2)
Formula	$C_{48}H_{40}Ag_2As_2F_{12}S_8$	$C_{48}H_{40}Ag_2As_2F_{12}Se_8$
M	1 466.88	1 804.10
Space group	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)
a/Å	10.902(4)	10.676(3)
b/Å	10.976(6)	11.253(3)
c/Å	13.308(7)	13.625(4)
α/°	112.82(4)	66.40(2)
β/°	92.43(3)	89.67(2)
γ/°	107.69(3)	71.40(2)
Z	1	1
U/Å^3	1 374.9	1 407.5
D_c/g cm^{-3}	1.77	2.13
μ/mm^{-1}	2.3	7.0
F(000)	724	868
Crystal size/mm	0.7 × 0.45 × 0.2	0.4 × 0.15 × 0.1
Total reflections	7 687	6 496
Unique reflections	6 301	6 453
Observed reflections [$F > 4\sigma(F)$]	5 139	4 439
Transmission factors	0.62—0.94	0.52—0.65
Structure solution	Heavy atom	Isostructural (see Discussion)
R	0.041	0.044
R'	0.041	0.039
g	0.000 15	0.000 2

Reaction with Diphenyl Diselenide.—The analogous reaction between $AgAsF_6$ (0.3 g, 1.0 mmol) and Ph_2Se_2 (0.62 g, 2.0 mmol), followed by repeated recrystallization of the crude product from liquid SO_2, yielded yellow crystals of the product (2) (decomp. 143—144 °C). I.r. absorptions (Nujol mull): 1 570w, 1 440s, 1 068w, 1 020w, 1 001m, 756s, 740s, 700s, 683s, 672m, 470w, 459m, and 399s cm^{-1}. Raman bands: 1 572s, 1 164w, 1 064s, 1 020s, 1 000s, 678w, 614w, 302s, 274s, 254s, and 234s cm^{-1} (Found: C, 31.2; H, 2.3; F, 12.6. $C_{48}H_{40}Ag_2As_2F_{12}Se_8$ requires C, 31.3; H, 2.3; F, 12.4%). Compound (2) was also subjected to *X*-ray structure determination.

X-Ray Structure Determinations of Compounds (1) *and* (2).—The following features were common to both investigations. Profile-fitted[4] intensities were measured on a Stoe–Siemens four-circle diffractometer in the range 7 < 2θ < 55° (monochromated Mo-K_α radiation, λ = 0.710 69 Å). After Lorentz, polarisation, and empirical absorption corrections, equivalent reflections were merged. Cell constants were refined from 2θ values of selected strong reflections in the range 20—24°. The program system SHELXTL (written by G.M.S.) was used for

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† Di-μ-(diphenyl disulphide-*SS'*)-bis[(diphenyl disulphide-*S*)silver(I)] bis(hexafluoroarsenate) and di-μ-(diphenyl diselenide-*SeSe'*)-bis[(diphenyl diselenide-*Se*)silver(I)] bis(hexafluoroarsenate).

Supplementary material available (SUP 23939; 88 pp.): thermal parameters, H-atom co-ordinates, full bond distances and angles, structure factors. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.

Table 2. Fractional atomic co-ordinates (× 10⁴) for compound (1)

Atom	*x*	*y*	*z*	Atom *	*x*	*y*	*z*
Ag	785(1)	1 434(1)	1 498(1)	C(35)	3 623(4)	6 047(5)	5 957(3)
S(1)	1 583(1)	395(1)	−1 169(1)	C(36)	2 597(4)	4 764(4)	5 422(3)
S(2)	1 477(1)	2 232(1)	20(1)	C(41)	−350(4)	4 082(4)	2 851(3)
S(3)	1 031(1)	2 482(1)	3 591(1)	C(42)	−1 119(4)	3 468(4)	1 795(3)
S(4)	−567(1)	3 156(1)	3 704(1)	C(43)	−981(5)	4 212(5)	1 161(3)
C(11)	1 834(3)	767(3)	−2 346(3)	C(44)	−78(5)	5 564(5)	1 561(4)
C(12)	2 885(4)	527(4)	−2 824(3)	C(45)	688(5)	6 174(4)	2 593(4)
C(13)	3 075(5)	693(5)	−3 788(4)	C(46)	545(4)	5 446(4)	3 244(3)
C(14)	2 234(5)	1 111(5)	−4 257(4)	As	3 132(1)	−419(1)	1 769(1)
C(15)	1 196(4)	1 347(5)	−3 789(3)	F(1)	3 240(4)	1 291(3)	2 132(2)
C(16)	973(4)	1 173(4)	−2 828(3)	F(2)	1 565(4)	−923(5)	1 069(5)
C(21)	3 147(3)	3 371(3)	556(3)	F(3)	2 913(5)	−2 130(3)	1 398(3)
C(22)	4 166(4)	2 896(4)	630(3)	F(4)	2 412(7)	−290(6)	2 885(4)
C(23)	5 411(4)	3 869(5)	1 101(4)	F(5)	3 565(6)	−609(6)	549(4)
C(24)	5 612(4)	5 295(5)	1 511(3)	F(6)	4 594(5)	122(6)	2 431(6)
C(25)	4 595(4)	5 747(4)	1 434(3)	F(1′)	2 450(12)	−294(13)	756(9)
C(26)	3 348(4)	4 799(4)	955(3)	F(2′)	1 729(16)	−1 476(17)	1 738(13)
C(31)	2 391(3)	4 073(4)	4 281(3)	F(3′)	3 820(12)	−406(13)	2 902(10)
C(32)	3 202(4)	4 630(4)	3 686(3)	F(4′)	4 614(15)	431(17)	1 690(14)
C(33)	4 226(4)	5 900(5)	4 238(4)	F(5′)	3 577(16)	−1 698(19)	949(14)
C(34)	4 414(4)	6 609(5)	5 359(4)	F(6′)	2 800(20)	902(22)	2 789(17)

* For fluorine atoms, site occupation factor: unprimed atoms 0.8, primed atoms 0.2.

Table 3. Fractional atomic co-ordinates (× 10⁴) for compound (2)

Atom	*x*	*y*	*z*	Atom*	*x*	*y*	*z*
Ag	4 305(1)	1 460(1)	3 503(1)	C(35)	1 222(6)	5 987(7)	−910(5)
Se(1)	3 209(1)	383(1)	6 212(1)	C(36)	2 248(6)	4 710(6)	−395(4)
Se(2)	3 576(1)	2 355(1)	4 963(1)	C(41)	5 542(6)	4 090(5)	2 208(4)
Se(3)	4 024(1)	2 426(1)	1 392(1)	C(42)	6 256(6)	3 480(6)	3 239(4)
Se(4)	5 899(1)	3 130(1)	1 290(1)	C(43)	6 016(7)	4 209(7)	3 870(5)
C(11)	3 048(5)	745(5)	7 480(4)	C(44)	5 117(8)	5 502(8)	3 475(5)
C(12)	2 017(6)	464(6)	8 048(5)	C(45)	4 404(8)	6 127(7)	2 467(5)
C(13)	1 909(7)	613(7)	9 011(6)	C(46)	4 633(6)	5 400(6)	1 821(5)
C(14)	2 808(7)	1 015(7)	9 391(5)	As	1 835(1)	−387(1)	3 261(1)
C(15)	3 795(6)	1 302(6)	8 828(5)	F(1)	1 672(10)	1 271(7)	2 885(8)
C(16)	3 947(5)	1 150(5)	7 866(4)	F(2)	3 383(14)	−800(20)	3 894(16)
C(21)	1 768(5)	3 596(5)	4 337(4)	F(3)	2 120(12)	−2 039(8)	3 673(8)
C(22)	785(6)	3 163(6)	4 160(5)	F(4)	2 545(22)	−276(14)	2 186(10)
C(23)	−478(7)	4 156(8)	3 657(5)	F(5)	1 404(17)	−555(16)	4 468(10)
C(24)	−688(7)	5 516(8)	3 378(5)	F(6)	319(12)	196(17)	2 696(14)
C(25)	320(7)	5 942(7)	3 563(5)	F(1′)	3 293(12)	−1 418(19)	3 282(16)
C(26)	1 553(6)	4 968(6)	4 052(4)	F(2′)	2 461(17)	−159(14)	4 206(10)
C(31)	2 578(5)	4 165(6)	705(4)	F(3′)	1 184(12)	−558(17)	2 220(10)
C(32)	1 894(6)	4 824(7)	1 292(5)	F(4′)	322(10)	562(15)	3 252(11)
C(33)	885(7)	6 069(8)	784(6)	F(5′)	1 382(17)	−1 659(16)	4 125(15)
C(34)	555(7)	6 658(7)	−313(5)	F(6′)	2 177(16)	876(21)	2 285(13)

* For all fluorine atoms, site occupation factor 0.5.

structure solution and refinement; the AsF_6^- ions displayed disorder and the F atoms were refined on two alternative sites. Hydrogen atoms were included in the refinement using a riding model [C–H 0.96 Å, H on external bisector of appropriate C–C–C angle, $U(H) = 1.2\ U_{iso.}(C)$]. The weighting scheme was $w^{-1} = \sigma^2(F) + gF^2$. For further details and crystal data, see Table 1. Atomic co-ordinates and derived parameters are given in Tables 2—5.

Results and Discussion

The compounds (1) and (2) are isostructural; this is not immediately apparent from the cell constants for the reduced cells, but converting α and γ of (2) to 180 − α°, 180 − γ° respectively (using the matrix $\bar{1}00/010/00\bar{1}$) makes the relationship clear. The co-ordinates of compound (1) were transformed to give a successful trial structure for (2) using the same matrix.

The structures consist of centrosymmetric $[Ag_2(Ph_2X_2)_4]^{2+}$ cations; these contain six-membered Ag_2X_4 rings with the chair conformation (Figure 1). The X_2 unit of one independent Ph_2X_2 ligand bridges the silver atoms; the other ligand co-ordinates in an exocyclic manner to silver *via* only one X atom.

The sulphur compound (1) contains a major (site occupancy factor of fluorine atoms 0.8) and a minor component of the disordered AsF_6^- ion. Two F atoms of the major component form weak contacts to silver (2.82 and 2.84 Å); these distances are comparable to those in $[Ag(S_3N_2O)_2][AsF_6]$.[5] In the selenium analogue (2) the disorder ratio of the two AsF_6^- components is 1 : 1, the F atom thermal parameters are appreciably higher, and there is only one Ag · · · F contact of <3 Å. The co-ordination at silver (excluding these weak

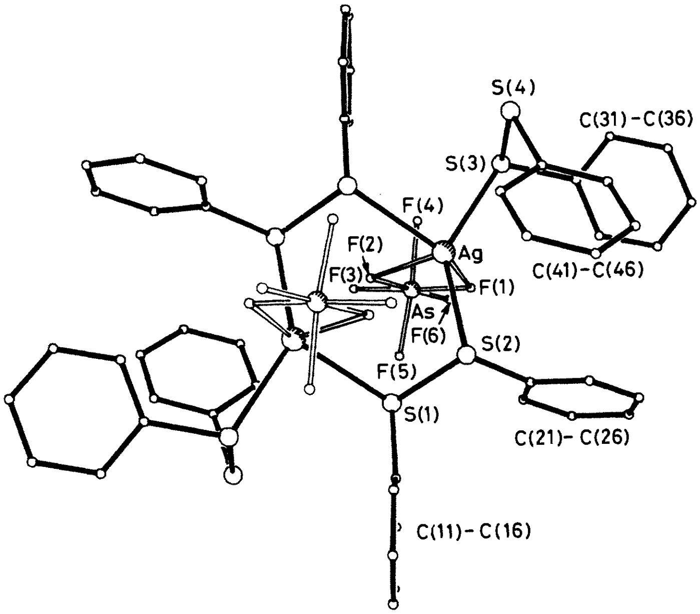

Figure. The centrosymmetric $[Ag_2(Ph_2S_2)_4][AsF_6]_2$ unit, showing the atom numbering scheme and the weak Ag–F contacts

Table 4. Bond lengths (Å) and angles (°) for compound (1)

Ag–S(2)	2.503(2)	S(1)–S(2)	2.065(2)
Ag–F(1)	2.841(5)	C(11)–S(1)	1.779(5)
Ag–S(1^{I})	2.638(2)	C(21)–S(2)	1.789(4)
S(3)–S(4)	2.080(3)	C(31)–S(3)	1.777(4)
Ag–S(3)	2.534(2)	C(41)–S(4)	1.774(6)
Ag–F(2)	2.824(7)		
S(2)–Ag–F(1)	95.3(2)	S(2)–Ag–S(1^{I})	119.8(2)
S(2)–Ag–F(2)	104.9(2)	F(1)–Ag–S(1^{I})	128.7(2)
F(1)–Ag–F(2)	49.7(2)	S(2)–S(1)–C(11)	104.0(2)
S(3)–Ag–S(1^{I})	94.1(2)	C(11)–S(1)–Ag^{I}	110.8(2)
F(2)–Ag–S(1^{I})	83.8(2)	Ag–S(2)–C(21)	104.7(2)
S(2)–S(1)–Ag^{I}	102.6(2)	Ag–S(3)–S(4)	97.5(2)
Ag–S(2)–S(1)	100.3(2)	S(4)–S(3)–C(31)	103.6(3)
S(1)–S(2)–C(21)	104.5(2)	S(1)–C(11)–C(12)	116.7(4)
Ag–S(3)–C(31)	113.9(2)	S(2)–C(21)–C(22)	123.5(4)
S(3)–S(4)–C(41)	103.1(2)	S(2)–C(21)–C(26)	115.0(4)
S(1)–C(11)–C(16)	122.6(4)	S(3)–C(31)–C(32)	120.5(3)
S(2)–Ag–S(3)	138.4(2)	S(3)–C(31)–C(36)	119.0(4)
S(3)–Ag–F(1)	78.5(2)	S(4)–C(41)–C(42)	120.3(4)
S(3)–Ag–F(2)	101.9(2)	S(4)–C(41)–C(46)	120.3(4)

* Symmetry operator: I $-x$, $-y$, $-z$.

Table 5. Bond lengths (Å) and angles (°) for compound (2) *

Ag–Se(2)	2.580(2)	C(11)–Se(1)	1.923(7)
Ag–Se(1^{I})	2.711(2)	C(21)–Se(2)	1.936(6)
Se(3)–Se(4)	2.360(2)	C(31)–Se(3)	1.927(6)
Ag–Se(3)	2.616(2)	C(41)–Se(4)	1.922(8)
Se(1)–Se(2)	2.344(2)		
Se(2)–Ag–Se(3)	138.3(2)	C(11)–Se(1)–Ag^{I}	106.9(2)
Se(3)–Ag–Se(1^{I})	94.3(2)	Se(1)–Se(2)–C(21)	101.6(3)
Ag–Se(2)–Se(1)	97.5(2)	Se(4)–Se(3)–C(31)	102.3(3)
Se(2)–Se(1)–C(11)	101.7(3)	Se(1)–C(11)–C(12)	116.0(6)
Ag–Se(2)–C(21)	101.5(3)	Se(2)–C(21)–C(22)	123.0(5)
Ag–Se(3)–C(31)	112.5(3)	Se(2)–C(21)–C(26)	115.5(6)
Se(3)–Se(4)–C(41)	101.0(3)	Se(3)–C(31)–C(32)	121.2(5)
Se(1)–C(11)–C(16)	123.0(5)	Se(3)–C(31)–C(36)	117.9(6)
Se(2)–Ag–Se(1^{I})	119.8(2)	Se(4)–C(41)–C(42)	120.0(5)
Se(2)–Se(1)–Ag^{I}	97.9(2)	Se(4)–C(41)–C(46)	119.5(5)
Ag–Se(3)–Se(4)	92.5(2)		

* Symmetry operator: I $1 - x$, $-y$, $1 - z$.

interactions) is distorted pyramidal, the silver atom lying 0.39 Å out of the X_3 plane in compound (1) and 0.40 Å in (2). The Ag–S bond lengths (2.503—2.638 Å) correspond to the lower end of the range previously observed;[1–3] the Ag–Se bond lengths (2.580—2.711 Å) are appreciably shorter than in the six-co-ordinated silver complex[3] $[Ag\{(CH_2Se)_3\}_2]^+$ (2.78 Å).

A comparison of X–X bond lengths and C–X–X–C torsion angles in (1), (2), the free ligands,[6–8] and the rhenium complexes $[Re_2Br_2(CO)_6(Ph_2X_2)]$[9,10] (as far as we are aware, the only other metal complexes of Ph_2X_2 to have been crystallographically characterized) shows no very clear pattern. The X–X bonds are significantly longer in the metal complexes than in the free ligands, consistent with the suggestion[9] of repulsion between partial positive charges on the X atoms. For compounds (1) and (2), however, the bidentate ligand unexpectedly has a significantly shorter X–X bond than its unidentate counterpart; the wide spread of Ag–X bond lengths may contribute to this pattern, since each bidentate ligand forms one long Ag–X bond.

Acknowledgements

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