Silver(I) Complexes of the Potentially Chelating Olefinic Ligands 2,2-Dimethylbut-3-enyl Methyl Sulphide and 2,2-Dimethyl-2-silabut-3-enyl Methyl Sulphide. Crystal Structure Analysis of Bis(2,2-dimethylbut-3-enyl methyl sulphide)silver(I) Tetrafluoroborate, (2,2-Dimethylbut-3-enyl methyl sulphide)silver(I) Perchlorate, (2,2-Dimethylbut-3-enyl methyl sulphide)nitratosilver(I), and (2,2-Dimethylbut-3-enyl methyl sulphide)-trifluoroacetatosilver(I)

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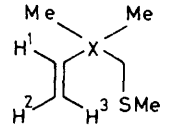
The ligands 2,2-dimethylbut-3-enyl methyl sulphide (1a) and 2,2-dimethyl-2-silabut-3-enyl methyl sulphide (1b) form analogous sets of complexes with a series of silver salts. Thus, 1 : 1 complexes have been obtained from $Ag[BF_4]$, $Ag[ClO_4]$, $Ag[NO_3]$, and $Ag[O_2CCF_3]$, 1 : 2 (Ag : ligand) complexes from $Ag[BF_4]$ and $Ag[ClO_4]$, and 2 : 1 (Ag : ligand) complexes from $Ag[NO_3]$. In the solid state (i.r. and *X*-ray) the ligands are chelated, while in solution (^1H n.m.r.) both the Ag–sulphur and Ag–olefin bonds are labile even at low temperatures (−80 °C). Crystal-structure analyses have been completed on $Ag[BF_4]\cdot 2(1a)$, $Ag[ClO_4]\cdot(1a)$, $Ag[NO_3]\cdot(1a)$, and $Ag[O_2CCF_3]\cdot(1a)$. The complex $Ag[BF_4]\cdot 2(1a)$ contains discrete $[Ag\cdot 2(1a)]^+$ cations (which have two-fold crystallographic symmetry) and disordered BF_4^- anions. Polymeric structures have been found for the remaining three complexes. In $[Ag\cdot(1a)][ClO_4]$ polymeric cation chains are present, while the perchlorate ions are not co-ordinated to silver. In $Ag[NO_3]\cdot(1a)$ the nitrato-group is bidentate (Ag–O 2.537 and 2.647 Å), whereas the carboxyl group in $Ag[O_2CCF_3]\cdot(1a)$ is predominantly unidentate (Ag–O 2.29 and 2.99 Å). In all four structures the five-membered –Ag–S–C(1)–C(2)–C(3)– ring adopts a C(2) envelope conformation. The olefin co-ordination is defined by the S–Ag–C(3)=C(4) torsion angles 148.6 in $Ag[BF_4]\cdot 2(1a)$, 140.9 in $Ag[ClO_4]\cdot(1a)$, 158.7 in $Ag[NO_3]\cdot(1a)$ and 140.2° in $Ag[O_2CCF_3]\cdot(1a)$. Crystals of $Ag[BF_4]\cdot 2(1a)$ are monoclinic, space group $C2/c$, with four formula units in a cell of dimensions a = 10.838(2), b = 11.720(2), c = 16.355(2) Å, β = 105.02(1)°, R = 0.049 for 645 observed reflections. Crystals of $Ag[ClO_4]\cdot(1a)$ are orthorhombic, space group $P2_12_12_1$, with four formula units in a cell of dimensions a = 8.229(3), b = 10.645(3), c = 13.917(3) Å, R = 0.066 for 1 259 reflections. Crystals of $Ag[NO_3]\cdot(1a)$ are monoclinic, space group $P2_1/c$, with four molecules in a cell of dimensions a = 11.049(1), b = 7.823(1), c = 14.352(3) Å, β = 118.392(7)°, R = 0.049 for 1 653 reflections. Crystals of $Ag[O_2CCF_3]\cdot(1a)$ are monoclinic, space group $P2_1/b$, with four molecules in cell of dimensions a = 10.194(3), b = 15.784(5), c = 8.125(4) Å, γ = 95.49°, R = 0.099 for 846 reflections.

THERE are few reports of the isolation of silver(I) chelates of potentially chelating olefinic ligands. Such derivatives have been obtained with (*o*-allylphenyl)dimethylarsine,[1] diphenylvinylphosphine,[2] 2-allylpyridine,[3] and *N*-allylpyrazole [4] but only with silver nitrate. Chelation of silver in solution has been inferred on the basis of stability constants for but-3-en-1-ol [5] and olefinic (but-3-en-1-yl and pent-4-en-1-yl) thioethers,[6] selenoethers,[7] and amino-acids.[8]

The present study was initiated to characterise the types of complexes that could be prepared from 2,2-dimethylbut-3-enyl methyl sulphide (1a) and 2,2-dimethyl-2-silabut-3-enyl methyl sulphide (1b) with a range of silver(I) salts and to compare the complexing abilities of the vinyl moieties in the two ligands towards silver. We have previously reported [9] the results of a similar study of palladium(II) halide complexes of these ligands which appeared to indicate that the metal–olefin bond is weaker for the vinyl silane than for its carbon analogue. A particularly interesting feature of the ^1H n.m.r. results was the observation that while the olefinic proton resonances of (1a) suffered downfield shifts upon complexation, as is usual for palladium(II) complexes, those of (1b) suffered a general upfield shift. It was suggested that this difference in behaviour is due to the possibility of more effective metal-to-olefin back-bonding for (1b). Since such back-bonding is expected [10] to be less favourable in the case of silver(I), we wished to compare the changes in chemical shifts for (1a) and (1b) induced by complexation to this metal.



(1a) X = C
(1b) X = Si

RESULTS

The ligands (1a) and (1b) gave two entirely analogous series of complexes with silver(I) tetrafluoroborate, perchlorate, nitrate, and trifluoroacetate. The 14 complexes obtained are listed in Table 1 along with relevant i.r. data. All four salts gave 1 : 1 complexes while in addition the perchlorate and tetrafluoroborate gave 1 : 2 (salt : ligand) complexes and the nitrate gave products of 2 : 1 stoicheiometry. Attempts to prepare $(Ag[ClO_4])_2\cdot(1a)$, $(Ag[O_2CCF_3])_2\cdot(1a)$, and $Ag[NO_3]\cdot 2(1a)$ resulted in the isolation of only 1 : 1 complexes, although it was noted that both $Ag[NO_3]\cdot(1a)$ and $Ag[NO_3]\cdot(1b)$ have significantly greater solubility in the presence of excess of ligand. The tetrafluoroborates, $Ag[BF_4]\cdot(1a)$ and $Ag[BF_4]\cdot(1b)$, are hygro-

TABLE 1

Infrared data (cm^{-1}) for ligands [a] and complexes [b]

Compound	Vibrations associated with vinyl groups	Vibrations associated with anion	Unassigned
(1a)	1 643ms, 1 015wm, 1 000m, 969w, 936w(sh), 908vs		
$(Ag[NO_3])_2$·(1a)	1 587vw, 1 020ms, 991vw, 984w, 947ms, 932w		
$Ag[NO_3]$·(1a)	1 599wm, 1 029w, 1 013vw, 996vw, 980wm, 950m, 931wm		
$Ag[O_2CCF_3]$·(1a)	1 592w,[c] 1 020wm, 1 009w, 980w, 969wm, 940m	1 664vs, 1 418m	
$Ag[ClO_4]$·(1a)	1 600w, 1 029w, 1 008w, 982wm, 950wm	1 113s, 1 080br (sh), 928w, 621s	
$Ag[BF_4]$·(1a) [d]	1 600wm, 1 006,[e] 984ms, 952ms	1 123(sh), 1 082vs, br, 1 050(sh), 520wm	
$Ag[ClO_4]$·2(1a)	1 598wm, 1 029w, 1 011vw, 974w, 943ms	1 095s, 1 082s, 621ms	
$Ag[BF_4]$·2(1a)	1 599wm, 1 011wm, 977w, 955w(sh), 944ms	1 097ms, 1 062s, 520w	
(1b)	1 595w, 1 010s, 957s		515ms
$(Ag[NO_3])_2$·(1b)	1 542vw, 1 020m, 1 008w, 981wm, 973wm		585ms
$Ag[NO_3]$·(1b)	1 554vw, 1 011w, 988m, 975(sh)		578ms
$Ag[O_2CCF_3]$·(1b)	1 560vw, 999m, 978m, 968m, 960m	1 664vs, 1 412m	575w
$Ag[ClO_4]$·(1b)	1 560vw, 1 003w, 988wm, 978wm, 970w	1 115s(sh), 1 090vs, 928w, 621s	575ms
$Ag[BF_4]$·(1b) [d]	1 561vvw, 1 005,[e] 989ms, 980m, 971m	1 128(sh), 1 086vs, br, 1 043(sh), 520wm	578wm
$Ag[ClO_4]$·2(1b)	1 562w, 1 003m, 988m, 976m, 967m	1 089vs, br, 928w, 621s	571m
$Ag[BF_4]$·2(1b)	1 566vw, 1 017,[e] 1 008m, 992m, 971m	1 098br (sh), 1 068vs, br, 519w	579wm

[a] Liquid film. [b] Nujol mull. [c] An apparently weaker band is present at this frequency in the spectrum of $Ag[O_2CCF_3]$·(1b). [d] Mull prepared in dry-box. [e] Intensity masked by band due to BF_4^-.

scopic as evidenced by the appearance of water bands in their i.r. spectra as mulls.

The i.r. spectra of all complexes lack the band attributable to C=C stretching in the free ligand, this being replaced by a weaker band at lower energies ($\Delta\nu$ = 33—56 cm^{-1}). Further, a marked increase in the complexity of the bands in the region associated with olefinic C–H deformations is observed upon complexation [*cf.* the corresponding palladium(II) complexes [9]]. Bands attributable to the anions are also listed in Table 1.

Hydrogen-1 n.m.r. data are collected in Table 2, from which it can be seen that in all cases complexation of the ligands leads to downfield shifts of all resonances. The changes in shifts of the resonances arising from the S–CH

TABLE 2

Hydrogen-1 n.m.r. data (p.p.m., *J*/Hz) for ligands and complexes [a]

Compound	Solvent	C(Si)–Me	S–Me	S–CH_2	H^1	H^2	H^3	$J(H^1–H^2)$	$J(H^1–H^3)$	$J(H^2–H^3)$
(1a)	$(CD_3)_2CO$	1.08	2.08	2.51	5.873	4.925	4.986	10.8	17.5	1.3
	$(CD_3)_2CO$ [b]	1.07	2.09	2.54	5.88	4.98	5.00	10.8	17.5	1.3
	$CDCl_3$	1.08	2.10	2.50	5.83	4.94	4.97	10.8	17.5	1.3
	CD_3OD	1.08	2.08	2.51	5.86	4.93	4.99	10.8	17.5	1.3
$Ag[O_2CCF_3]$·(1a)	$(CD_3)_2CO$	1.19	2.46	3.03	6.143	5.395	5.285	10.5	17.3	1.5
	$(CD_3)_2CO$ [c]	1.19	2.51	3.19	6.30	5.55	5.40	10.5	17.3	1.5
	$CDCl_3$	1.17	2.41	2.86	6.025	5.506	5.293	10.3	17.3	1.5
	$CDCl_3$ [c]	1.21	2.45	2.97	6.10	5.55	5.33	10.3	17.3	1.5
$(Ag[NO_3])_2$·(1a)	CD_3OD	1.17	2.45	2.99	6.13	5.41	5.26	10.5	17.3	1.5
$Ag[NO_3]$·(1a)	$(CD_3)_2CO$	1.18	2.44	3.02	6.16	5.38	5.28	10.5	17.3	1.5
$Ag[ClO_4]$·(1a)	$(CD_3)_2CO$ [d]	1.21	2.53	3.13	6.322	5.530	5.373	10.3	17.3	1.5
	$(CD_3)_2CO$ [c]	1.20	2.48	3.08	6.288	5.501	5.362	10.4	17.4	1.5
	$(CD_3)_2CO$ [b]	1.23	2.64	3.34	6.560	5.797	5.530	10.1	17.1	1.5
$Ag[ClO_4]$ + (1a) [f]	$(CD_3)_2CO$	1.23	2.59	3.21	6.371	5.576	5.410	10.3	17.2	1.6
	$(CD_3)_2CO$ [b]	1.28	2.76	3.51	6.56	5.79	5.57	10.2	17.2	1.5
$Ag[ClO_4]$·2(1a)	$(CD_3)_2CO$	1.18	2.47	3.07	6.273	5.450	5.312	10.4	17.4	1.5
	$(CD_3)_2CO$ [b]	1.16	2.54	3.24	6.53	5.78	5.45	10.4	17.4	1.5
$Ag[BF_4]$·(1a)	$(CD_3)_2CO$	1.20	2.51	3.14	6.35	5.56	5.39	10.3	17.3	1.5
	$(CD_3)_2CO$ [c]	1.22	2.67	3.39	6.59	5.83	5.57	10.1	17.1	1.5
$Ag[BF_4]$·2(1a)	$(CD_3)_2CO$	1.18	2.49	3.10	6.311	5.510	5.348	10.4	17.4	1.5
(1b)	$(CD_3)_2CO$	0.13	2.12	1.85	6.175	5.980	5.767	14.7	20.6	3.7
$Ag[O_2CCF_3]$·(1b)	$(CD_3)_2CO$ [g]	0.27	2.48	2.32	6.240 9	6.244 6	5.916 7	14.4	20.0	3.7
	$(CD_3)_2CO$ [c,g]	0.31	2.54	2.47	6.238 2	6.323 3	5.969 5	14.0	19.8	3.8
$(Ag[NO_3])_2$·(1b)	CD_3OD [h]	0.30	2.50	2.31	6.27	6.27	5.94	14.3	20.0	3.7
$Ag[NO_3]$·(1b)	$(CD_3)_2CO$ [g]	0.28	2.48	2.32	6.256 4	6.262 7	5.924 6	14.3	20.0	3.7
$Ag[ClO_4]$·(1b)	$(CD_3)_2CO$ [g]	0.29	2.53	2.40	6.361 4	6.382 0	6.001 2	14.2	20.1	3.8
	$(CD_3)_2CO$ [b]	0.33	2.65	2.65	6.50	6.55	6.15	14.2	20.1	3.8
$Ag[ClO_4]$·2(1b)	$(CD_3)_2CO$ [d]	0.28	2.55	2.40	6.42	6.38	6.01	14.4	20.2	3.7
$Ag[ClO_4]$ + (1b) [i]	$(CD_3)_2CO$	0.21	2.35	2.15	6.28	6.17	5.88	14.5	20.4	3.7
$Ag[BF_4]$·(1b)	$(CD_3)_2CO$	0.33	2.61	2.50	6.45	6.49	6.09	14.2	20.1	3.8
$Ag[BF_4]$·2(1b)	$(CD_3)_2CO$ [g]	0.27	2.53	2.40	6.368 5	6.371 7	6.005 2	14.4	20.2	3.7
	$(CD_3)_2CO$ [b]	0.26	2.58	2.52	6.52	6 60	6.12	14.4	20.2	3.7

[a] Unless otherwise indicated, solution concentrations were *ca.* 0.05 mol dm^{-3}. Values of chemical shifts and coupling constants for the vinyl protons have been optimised by computer matching where the chemical shifts are reported to four (400 MHz) and three (60 MHz) decimal places. In other cases the values of the coupling constants were assumed and the chemical shifts optimised to two decimal places. Experimental line positions were obtained for the 400 MHz spectra using a scale of 2 Hz cm^{-1} and for the 60 MHz spectra using a Bruker WP 60 instrument in the cursor mode with expanded display. In some low-temperature spectra line broadening and overlap made precise location difficult. [b] At 193 K. [c] At 213 K. [d] Saturated solution. [e] Sixteen-fold dilution of saturated solution. [f] Ag : (1a) = 4 : 1. [g] At 400 MHz. [h] Concentration 0.10 mol dm^{-3}. [i] Ag : (1b) = 1 : 3.

and the olefinic protons are comparable in magnitude and generally increase on cooling. The various resonance positions for the complexes show some concentration dependence, suffering small upfield shifts upon dilution.

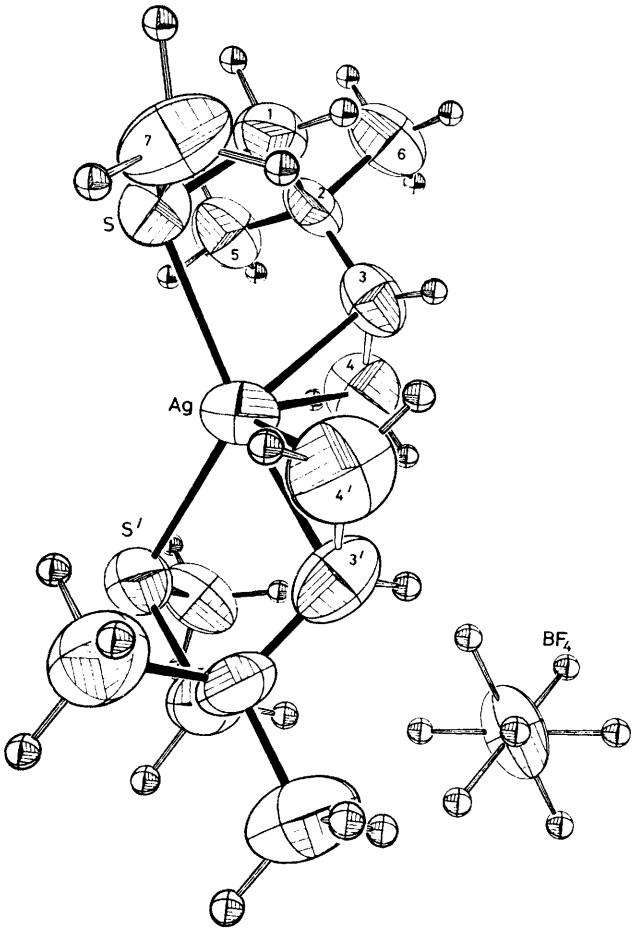


FIGURE 1 View with 50% probability ellipsoids of $Ag[BF_4]\cdot 2(1a)$ showing ring geometry and details of the numbering scheme. For clarity the fluorine and hydrogen atoms are shown as spheres of an arbitrary radius. The BF_4^- ion sits on an inversion centre and is disordered

Small decreases are observed for the *cis* and *trans* olefinic proton–proton coupling constants on complexation of (1a) and (1b), the decreases being slightly accentuated on cooling. In contrast, the geminal coupling constant appears to suffer a slight increase in most cases.

TABLE 3

Final fractional co-ordinates ($\times 10^4$) for $Ag[BF_4]\cdot 2(1a)$ with estimated standard deviations in parentheses

Atom	*x/a*	*y/b*	*z/c*
Ag	0 *	1 812(1)	2 500 *
S	276(3)	884(3)	1 180(2)
C(1)	1 520(10)	1 800(10)	955(6)
C(2)	2 506(11)	2 198(9)	1 745(7)
C(3)	1 886(11)	2 968(10)	2 238(7)
C(4)	2 063(12)	2 938(11)	3 093(8)
C(5)	3 190(12)	1 161(10)	2 249(8)
C(6)	3 450(11)	2 921(11)	1 418(8)
C(7)	−1 080(11)	1 308(11)	323(7)
B	0 *	5 000 *	0 *
F(1)	9 623(19)	4 383(16)	609(13)
F(2)	892(24)	4 411(20)	−133(17)
F(3)	9 062(20)	5 121(21)	−604(14)
F(4)	425(26)	6 002(18)	361(16)

* Fixed co-ordinate.

Solid-state structures have been determined for $Ag[BF_4]\cdot 2(1a)$ (Figures 1 and 2), $Ag[ClO_4]\cdot(1a)$ (Figures 3 and 4), $Ag[NO_3]\cdot(1a)$ (Figures 5 and 6), and $Ag[O_2CCF_3]\cdot(1a)$

TABLE 4

Final fractional co-ordinates (Ag and S $\times 10^4$, others $\times 10^3$) for $Ag[ClO_4]\cdot(1a)$ with estimated standard deviations in parentheses

Atom	*x/a*	*y/b*	*z/c*
Ag	563(1)	3 091(1)	155(1)
S	3 139(4)	2 990(3)	−854(2)
C(1)	341(2)	465(2)	−112(1)
C(2)	317(2)	546(1)	−21(1)
C(3)	142(2)	543(1)	10(1)
C(4)	89(3)	516(2)	97(2)
C(5)	439(3)	507(2)	60(2)
C(6)	356(3)	682(2)	−50(2)
C(7)	295(3)	239(2)	−205(1)
Cl	306(1)	119(1)	188(0)
O(1)	198(3)	82(2)	255(2)
O(2)	460(4)	73(4)	210(3)
O(3)	259(4)	62(3)	98(2)
O(4)	308(7)	246(6)	183(6)

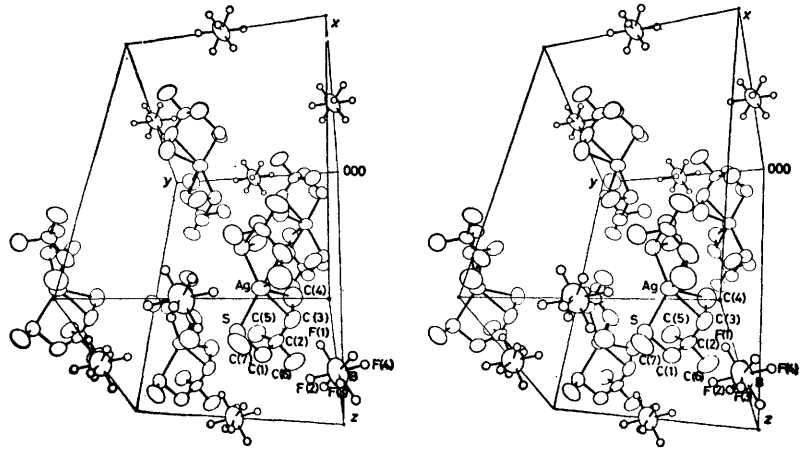


FIGURE 2 Stereoview of the molecular packing for $Ag[BF_4]\cdot 2(1a)$

TABLE 5

Final fractional co-ordinates ($\times 10^4$) for $Ag[NO_3]\cdot(1a)$ with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c
Ag	1 080(1)	286(1)	3 077(1)
S	962(1)	3 520(2)	3 281(1)
C(1)	2 376(6)	4 257(8)	3 086(5)
C(2)	3 497(6)	2 934(8)	3 273(4)
C(3)	2 834(6)	1 386(11)	2 571(5)
C(4)	3 126(8)	−234(10)	2 850(8)
C(5)	4 330(6)	2 443(10)	4 452(5)
C(6)	4 505(7)	3 769(14)	2 940(7)
C(7)	1 467(8)	4 037(11)	4 646(5)
N	1 510(7)	−1 276(8)	5 107(5)
O(1)	594(9)	−1 734(10)	4 242(5)
O(2)	2 250(10)	−157(13)	5 153(9)
O(3)	1 609(8)	−1 928(9)	5 917(4)

(Figures 7 and 8). Fractional co-ordinates for the structures are in Tables 3—6 and selected bond lengths and angles are in Table 7.

DISCUSSION

The *X*-ray structural investigations show that in all cases examined, (1a) acts as a bidentate chelating ligand. Indeed, $Ag[BF_4]\cdot 2(1a)$ {and presumably $Ag[ClO_4]\cdot 2(1a)$, $Ag[BF_4]\cdot 2(1b)$, and $Ag[ClO_4]\cdot 2(1b)$, see below} is the first authenticated example of a silver(I) complex of this stoicheiometry in which both olefinic

TABLE 6

Final fractional co-ordinates ($\times 10^4$) for $Ag[O_2CCF_3]\cdot(1a)$ with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c
Ag	163(2)	1 802(1)	941(4)
S	493(7)	3 126(4)	2 814(10)
C(1)	2 281(24)	3 381(18)	2 684(51)
C(2)	2 980(24)	2 524(20)	2 815(58)
C(3)	2 686(33)	1 990(23)	1 056(48)
C(4)	2 300(37)	1 152(24)	1 133(62)
C(5)	2 689(36)	2 084(22)	4 476(41)
C(6)	4 501(32)	2 863(27)	2 676(60)
C(7)	−54(35)	4 101(19)	1 993(53)
C(8)	−2 142(33)	932(23)	2 582(73)
C(9)	−3 452(47)	378(24)	3 051(65)
O(1)	−1 525(26)	757(15)	1 296(44)
O(2)	−1 781(47)	1 455(29)	3 664(59)
F(11)	−3 278(53)	−5(36)	4 625(68)
F(12)	−3 652(57)	−285(37)	2 136(78)
F(13)	−4 340(57)	764(33)	3 373(76)
F(21)	−4 239(62)	410(37)	1 455(72)
F(22)	−4 038(58)	648(35)	4 384(68)
F(23)	−3 299(44)	−402(29)	3 264(64)

TABLE 7

Selected [a] bond lengths (Å) and angles (°) with estimated standard deviations in parentheses

	$Ag[BF_4]\cdot 2(1a)$	$Ag[ClO_4]\cdot(1a)$	$Ag[NO_3]\cdot(1a)$	$Ag[O_2CCF_3]\cdot(1a)$
(*a*) Bond lengths				
Ag–S	2.504(3)	2.545(3)	2.558(2)	2.582(6)
Ag–S′		2.500(3)	2.572(2)	2.632(6)
Ag–C(3)	2.579(10)	2.587(13)	2.522(6)	2.56(3)
Ag–C(4)	2.560(12)	2.493(17)	2.466(7)	2.50(3)
S–C(1)	1.83(1)	1.82(2)	1.808(6)	1.83(2)
S–C(7)	1.82(1)	1.79(1)	1.809(6)	1.81(2)
C(3)–C(4)	1.36(1)	1.33(3)	1.322(12)	1.35(4)
Ag–O(1)			2.537(7)	2.29(2)
Ag–O(2)			2.647(10)	2.99(3)
(*b*) Bond angles				
S–Ag–S′	128.5(2)	149.3(3)	123.0(2)	123.2(4)
S–Ag–C(3)	78.9(3)	78.1(4)	77.5(2)	80.4(5)
S–Ag–C(4)	105.2(3)	101.5(4)	106.2(2)	104.1(7)
C(3)–Ag–C(4)	30.7(3)	30.2(6)	30.7(3)	30.8(8)
Ag–C(3)–C(4)	73.9(7)	70.9(9)	72.3(4)	72.0(20)
Ag–C(4)–C(3)	75.4(7)	79.0(10)	77.0(4)	77.0(20)
Ag–S–Ag′		118.0(3)	121.2(2)	126.4(4)
Ag–S–C(1)	100.2(4)	100.0(5)	101.7(2)	101.2(8)
Ag–S–C(7)	107.0(4)	117.2(8)	109.8(3)	116.3(9)
C(1)–S–C(7)	100.0(5)	99.6(7)	104.6(3)	100.0(10)
S–Ag–O(1)			120.1(2)	122.8(6)
S–Ag–O(2)			91.4(2)	75.2(5)
O(1)–Ag–O(2)			47.2(2)	48.2(7)
(*c*) Torsion angles				
Ag–S–C(1)–C(2)	36.85	45.49	−21.56	−43.06
S–C(1)–C(2)–C(3)	−66.44	−68.77	55.93	71.55
C(1)–C(2)–C(3)–Ag	55.26	50.46	−58.45	−57.86
S–Ag–C(3)–C(2)	−25.37	−17.19	35.00	23.97
C(3)–Ag–S–C(1)	−4.87	−13.67	−7.18	8.09
C(4)–Ag–S–C(1)	−20.91	−32.68	3.98	27.83
C(1)–C(2)–C(3)–C(4)	136.05	128.84	−137.94	−134.15
C(2)–C(3)–C(4)–Ag	−97.38	−97.39	97.12	94.97
S–Ag–C(4)–C(3)	32.03	39.13	−21.71	−40.60
S–Ag–C(3)–C(4)	−148.57	−140.87	158.66	140.20
C(3)–Ag–S–Ag′ [b]		112.43	105.86	103.68
S′–Ag–S–C(1)	−138.38	160.65	−123.61	−95.59
S′–Ag–S–Ag′		−73.25	−10.58	143.04
C(5)–C(2)–C(3)–C(4)	11.95	3.79	−13.64	−5.74
C(6)–C(2)–C(3)–C(4)	−110.72	−116.44	105.18	118.37

[a] Molecular dimensions not given above have been deposited in SUP 22932. [b] The following transformations are required to obtain the co-ordinates of the primed atoms from those given in the co-ordinate tables: $Ag[BF_4]\cdot 2(1a)$ S′ $-x, y, \frac{1}{2} - z$; $Ag[ClO_4]\cdot(1a)$ S′ $-\frac{1}{2} + x, \frac{1}{2} - y, -z$, Ag′ $\frac{1}{2} + x, \frac{1}{2} - y, -z$; $Ag[NO_3]\cdot(1a)$ S′ $-x, -\frac{1}{2} + y, \frac{1}{2} - z$; Ag′ $-x, \frac{1}{2} + y, \frac{1}{2} - z$; $Ag[O_2CCF_3]\cdot(1a)$ S′ $-x, \frac{1}{2} - y, -\frac{1}{2} + z$, Ag′ $-x, \frac{1}{2} - y, \frac{1}{2} + z$.

bonds are complexed. Bis chelated structures of this type have been suggested for *cis*-[Pt(PPh$_3$)$_2$(*o*-SC$_6$H$_4$CH=CH$_2$)$_2$]·Ag[ClO$_4$] [11] and (Ph$_2$PCH=CH$_2$)$_2$·Ag[NO$_3$],[2] but the former was apparently withdrawn [12] subsequently.

The Ag[BF$_4$]·2(1a) structure (Figures 1 and 2) exists as discrete ions [Ag·2(1a)][BF$_4$] with the anion taking no part in the silver co-ordination. In the other three structures, polymeric chains are developed *via* S′–Ag–S–Ag′ linkages about two-fold screw axes. In [Ag·(1a)][ClO$_4$] (Figures 3 and 4) the perchlorate groups play no significant role in the Ag co-ordination (closest Ag · · · O contacts 3.10—3.22 Å) whereas in Ag[NO$_3$]·(1a) (Figures 5 and 6) the nitrato-group chelates in a bidentate manner (Ag–O 2.537 and 2.647 Å); in Ag[O$_2$CCF$_3$]·(1a) (Figures 7 and 8) the carboxyl group co-ordination is predominantly unidentate (Ag–O 2.29 and 2.99 Å).

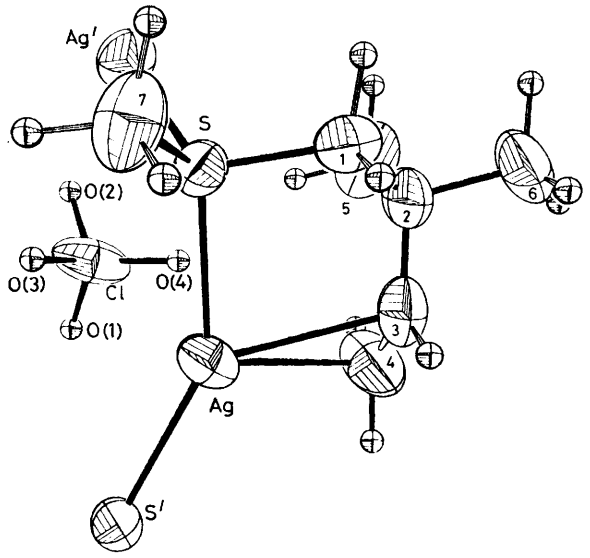


FIGURE 3 View with 50% probability ellipsoids of Ag[ClO$_4$]·(1a) showing ring geometry and details of the numbering scheme. For clarity the perchlorate oxygen atoms and hydrogen atoms are shown as spheres of an arbitrary radius

As was found in the corresponding complexes with palladium and the nitrogen analogue of (1a),[9] the five-membered chelate ring Ag–S–C(1)–C(2)–C(3) in all of the above four structures adopts a C(2) envelope conformation with methyl C(5) axial, methyl C(6) equatorial, and the olefin C(4) *cis* to C(5) [torsion angles C(5)–C(2)–C(3)–C(4) between 4 and 14°]. There, the overall similarity ends. In [Ag·(1a)][ClO$_4$] (Figure 3) the S–Me(7) group is equatorial {as it is in [Ag·2(1a)][BF$_4$]}, *trans* to axial methyl C(5), and the polymeric chain (Figure 4) may be described relative to the five-membered ring as S′(eq.)–Ag–S–Ag′(ax.). In Ag[NO$_3$]·(1a) (Figure 5) the S–Me(7) group is axial, *cis* to axial methyl C(5), with a different polymeric chain geometry, namely S′(ax.)–Ag–S–Ag′(eq.) (Figure 6). The Ag[O$_2$CCF$_3$]·(1a) (Figure 7) structure has the S–Me(7) group equatorial and *trans* to axial methyl C(5) {as in [Ag·(1a)][ClO$_4$]}, but yet another polymeric chain geometry, S′(ax.)–Ag–S–Ag′(ax.) (Figure 8), is found.

Silver–sulphur bond lengths in previous structures have covered a wide range of values, *e.g.* 2.36—2.87 Å in silver(I) cyclohexane thiolate [13] and 2.54—2.69 Å in trithian silver(I) salts.[14] The Ag–S bond lengths found here fall within these ranges. In the monomeric complex [Ag·2(1a)][BF$_4$], the cation has two-fold crystallographic symmetry and a Ag–S bond length of 2.504(3) Å. The Ag–S′ bond [2.500(3) Å] linking the complex cations in [Ag·(1a)][ClO$_4$], is shorter than the intra-ring bond [2.545(3) Å], whereas in Ag[NO$_3$]·(1a) and Ag[O$_2$CCF$_3$]·(1a), with the NO$_3$ and O$_2$CCF$_3$ moieties strongly bound to Ag, the polymer-building Ag–S′ bonds are longer [2.572(2) and 2.632(6) Å] than the intra-ring bonds [2.558(2) and 2.582(6) Å].

The Ag–olefin distances follow a consistent pattern with terminal carbon C(4) closer to the Ag atoms than C(3) (Table 7). The Ag–C distances (2.47—2.59 Å) are in accord with bond lengths reported in other silver(I) complexes, *e.g.* 2.34—2.45 Å in the 1 : 2 adduct of (*o*-allylphenyl)dimethylarsine and silver nitrate [15] and 2.48—2.52 Å in dicyclo-octa-1,5-dienesilver tetrafluoro-

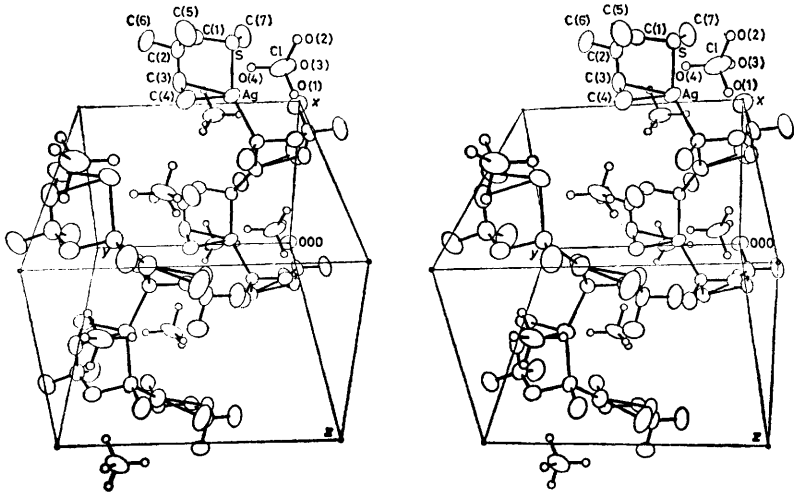


FIGURE 4 Stereoview of the molecular packing for Ag[ClO$_4$]·(1a)

borate.[16] The orientation of the olefin bond with respect to the Ag–S bond is defined by the S–Ag–C(3)=C(4) torsion angles which lie in the range 140—159° (Table 7).

The S–Ag–S′ angles are in the range 123—128° except for [Ag·(1a)][ClO_4] where, with only two sulphur atoms

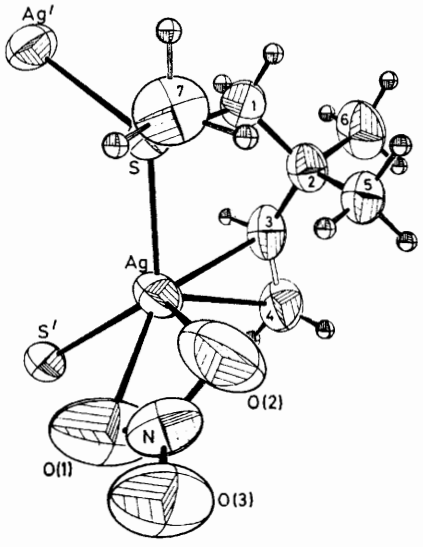


FIGURE 5 View with 50% probability ellipsoids of Ag[NO_3]·(1a) showing ring geometry and details of the numbering scheme. For clarity the hydrogen atoms are shown as spheres of an arbitrary radius

and an olefin co-ordinating to Ag, a much larger angle [149.3(3)°] is observed.

In [Ag·2(1a)][BF_4], the BF_4^- ions lie on inversion centres and are disordered, the mean B–F distance being 1.30 Å. It is probable that disorder also affects the perchlorate oxygen atoms in [Ag·(1a)][ClO_4]; the $U_{iso.}$ values for the oxygen atoms are in the range 0.15—0.22 Å^2 but no more than four distinct maxima were located around the chlorine. The mean Cl–O distance is 1.39 Å. In Ag[NO_3]·(1a), no disorder is found and N–O distances are in the range 1.18—1.23 Å. The fluorines of the CF_3 group in Ag[O_2CCF_3]·(1a) are disordered over two sites with equal populations and it is possible that the carbon and oxygen atoms of this ligand are also slightly disordered (see for example ORTEP plot Figure 7). Mean dimensions in the O_2CCF_3 ligand [C–F, 1.33(5); C–C, 1.57(4); C–O, 1.25(4) Å] are in accord with values found in *e.g.* bis(pyridine)mercury(II) bis(trifluoroacetate).[17] All other bond lengths in ligand (1a) are unexceptional; some mean dimensions are: S–C 1.81, C(sp^3)–C(sp^3) 1.54, C(sp^3)–C(sp^2) 1.50, C=C 1.34 Å.

The i.r. data in Table 1 are consistent with co-ordination of the double bond in all of these complexes in the solid state. The Δν values listed are smaller than those reported for the few known [1-4] chelated olefin complexes of Ag[I] of this type, only approaching comparable values for the (Ag[NO_3])$_2$·L [L = (1a) or (1b)] complexes. If the magnitude of Δν may be taken as an approximate indicator of the strength of metal–olefin bonding, then it appears that this interaction is stronger in the complexes of (1a) than in the analogous complexes of (1b). When the i.r. spectrum of Ag[BF_4]·2(1a) was run in chloroform solution it showed both a sharp peak at 1 641 cm^{-1}, corresponding to free olefin, and a very broad, shallow band at *ca.* 1 600 cm^{-1} which perhaps arises from co-ordinated olefin. This observation is consistent with the expected [4,18] lability of the silver–olefin bond in solution. Complexation of the olefinic moiety of (1b) appears to result in the replacement of a band at 515 cm^{-1} (ms, unassigned) in the ligand by one at 570—575 cm^{-1} in the complexes. The conclusion that this band stems from the vinyl group in (1b) rests on two observations. First, a band of similar intensity is found at this frequency in $N(CH_3)_2CH_2Si(CH_3)_2CH=CH_2$. Second, a re-examination of the i.r. spectra [9] of $PdCl_2$·(1b) and $PdBr_2$·(1b) shows no comparable band within 100 wavenumbers of 515 cm^{-1} while in PdI_2·2(1b), where the olefin is free, this band is again present at 515 cm^{-1}.

Bands assignable to the counter ions (see Table 1) are, in general, not very informative.[19] The tetrafluoroborates of 1 : 1 and 1 : 2 stoicheiometry differ in that the former display a very broad composite band at *ca.* 1 080 cm^{-1} and a fairly intense band at 520 cm^{-1} while the latter show a marked splitting of the 1 080 cm^{-1} band and a weak band at 520 cm^{-1}. Nevertheless, the similarities in band patterns displayed by the analogous complexes of (1a) and (1b) suggest that they have similar structures.

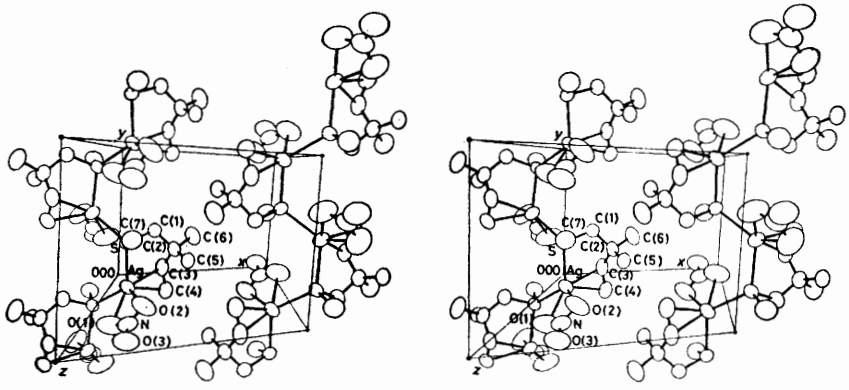


FIGURE 6 Stereoview of the molecular packing for Ag[NO_3]·(1a)

Comparable conclusions may be drawn from the data for the perchlorate complexes. In comparison with the 1 : 2 complexes, the 1 : 1 complexes show a significantly

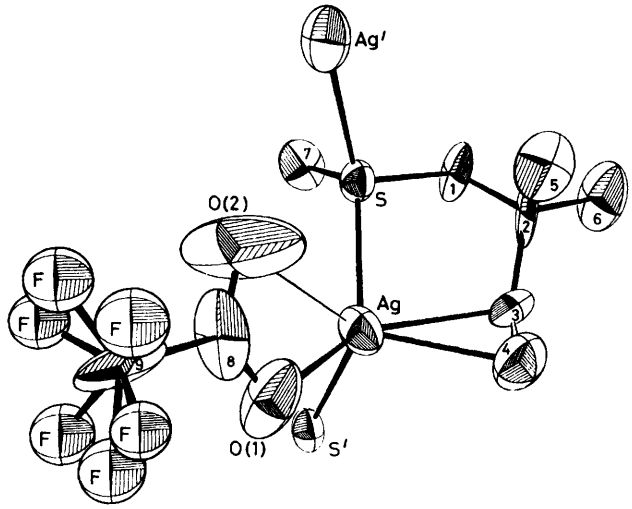


FIGURE 7 View with 50% probability ellipsoids of $Ag[O_2CCF_3]$·(1a) showing ring geometry and details of the numbering scheme. The F atoms of the CF_3 moiety are disordered over two sites

broader, composite band at *ca.* 1 100 cm^{-1} and a relatively more intense band at 928 cm^{-1}. The separations between the symmetric and asymmetric $\nu(CO_2)$ modes in the trifluoroacetates are consistent [19] with the observed unsymmetrical bidentate mode of co-ordination of the anion.

In the ^1H n.m.r. spectra of the complexes all resonances are downfield of their free-ligand positions. In $(CD_3)_2CO$, the magnitudes of these downfield shifts are generally greater for the 1 : 1 than for the 1 : 2 complexes and decrease in the sequence $BF_4^- \geqslant ClO_4^- > CF_3CO_2^- \approx NO_3^-$, while the pairs of 1 : 1 and (acetone insoluble) 2 : 1 nitrates have virtually identical chemical shifts in CD_3OD. The last observation may indicate that, in methanol, dissociation in the sense $Ag_2L^{2+} \longrightarrow AgL^+ + Ag^+$ is taking place. However, there is no evidence of magnetic non-equivalence of the geminal methyl groups suggesting that if chelates are formed in solution they are labile on the n.m.r. time scale. The lability of the metal–olefin bond is indicated by the observation that the olefinic proton resonances undergo significant additional downfield shifts upon cooling in either acetone or chloroform. The observation of downfield shifts for the olefinic resonances of *both* (1a) and (1b) upon complexation to silver(I) contrasts to the finding [9] that on complexation with palladium(II) these resonances shift upfield for (1b) and downfield for (1a). If, as suggested,[9] this difference for palladium reflects an enhanced ability of the silyl olefin to accept back-bonding from the metal, the present observation is consistent with the expectation [10] that silver should display less tendency to back-bond.

Interestingly, the S–CH and olefinic resonances show very similar responses to cooling in both direction and magnitude of shift (see examples in Table 2). The free-ligand resonances undergo much smaller changes in chemical shift upon cooling through the same temperature range. This seems to imply that the metal–sulphur bond is also labile and that exchange processes, such as those outlined in Figure 9, are taking place, the chelate form being favoured at lower temperatures. The chelate, rather than a bridging mode of complexation, is suggested * by the observation that dilution produces relatively small changes in chemical shifts {see *e.g.* sixteen-fold dilution of $Ag[ClO_4]$·(1a) in Table 2}. At the lowest temperatures for which ^1H n.m.r. spectra were obtained, exchange processes were still taking place. Indeed, when two molar equivalents of (1b) were added to $Ag[ClO_4]$·(1b) only a single set of resonances was

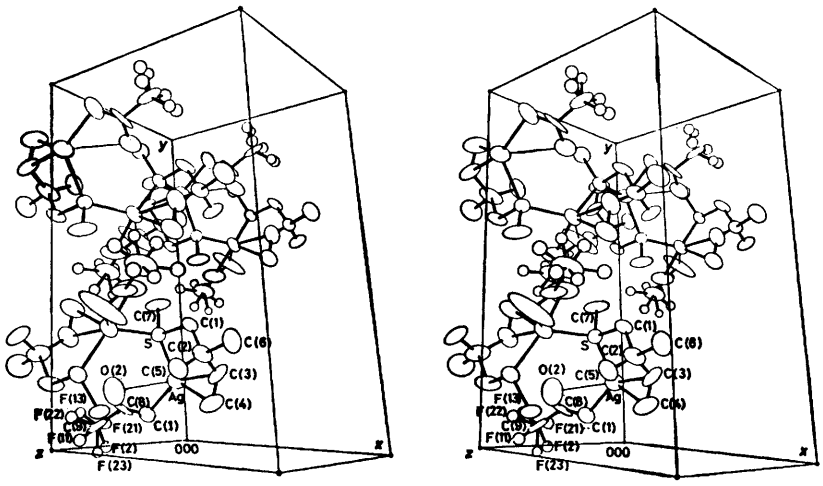


FIGURE 8 Stereoview of the molecular packing for $Ag[O_2CCF_3]$·(1a)

* Relative molecular masses for the complexes were determined by osmometry. However, the results obtained appear to be of no diagnostic value since the magnitudes *increase* upon dilution *e.g.* $Ag[ClO_4]$·(1b) gave 261, 294, 485, and 687 at concentrations of 11.7 × 10^{-3}, 5.83 × 10^{-3}, 2.91 × 10^{-3}, and 1.46 × 10^{-3} mol dm^{-3} respectively in acetone.

observed even at −80 °C, the shift values being intermediate between those of the free ligand and those of the complex at that temperature. In an attempt to find limiting values for the extent of downfield shifts due to complexation, excess of $Ag[ClO_4]$ was added to $Ag[ClO_4]$·(1a). At ambient temperature, additional, moderate

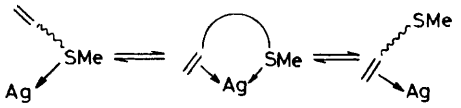


FIGURE 9 Suggested exchange processes occurring in solutions of the silver(I) chelate complexes

downfield shifts of all the proton resonances are observed (see Table 2) with increasing Ag : ligand ratios. These changes are somewhat more marked for the S–CH resonances, a difference which is amplified by cooling. At −80 °C, the chemical shifts of the olefinic protons in $Ag[ClO_4]$·(1a) and $Ag[ClO_4]$·(1a) + $Ag[ClO_4]$ [see for example Ag : (1a), 4 : 1 in Table 2] are almost identical while the S–CH resonances for the latter are markedly downfield of those for the former. Thus, it would appear that in $Ag[ClO_4]$·(1a) at −80 °C the olefin is essentially completely co-ordinated while either the silver–sulphur bond is more labile, or the sulphur atom is able to bridge two silver atoms (*cf.* the solid-state structures), such bridging being favoured by the presence of excess of silver.

In the silver complexes of (1a) and (1b) the magnitudes of the *cis* and *trans* olefinic proton coupling constants are slightly smaller than in the free ligand, the changes upon complexation being similar to those reported [20] for the interaction of simple olefins with $Ag[BF_4]$. On cooling, additional small decreases are observed. These changes constitute further evidence for the complexation of the double bond in solution (contrast refs. 1 and 4 but see ref. 15).

EXPERIMENTAL

Elemental analyses (see Table 8) were performed by M-H-W Laboratories, Phoenix, Arizona, U.S.A., or by Mr. H. S. McKinnon in this department. Infrared spectra were obtained as Nujol mulls sandwiched between thin Polythene sheets and supported on caesium iodide plates using a Beckman IR–12 spectrophotometer. Hydrogen-1 n.m.r. spectra were recorded on Bruker WP60 and WH 400 and Varian Associates A–60A spectrometers with tetramethylsilane as internal standard. Molecular weights were determined using a Hitachi–Perkin-Elmer 115 osmometer. Melting points (see Table 8) were measured in glass capillaries and are uncorrected. Solvents were reagent grade and were used without purification. Ligands were synthesised as indicated previously.[9]

Complexes of Silver Nitrate.—The complexes $(Ag[NO_3])_2$·(1a) and $(Ag[NO_3])_2$·(1b) were obtained as lustrous leaflets by adding the stoicheiometric quantity of ligand to a solution of $Ag[NO_3]$ in methanol and evaporation to small volume. Addition of excess of ligand to a suspension of finely powdered $Ag[NO_3]$ in acetone gave a clear solution on warming. Addition of hexane and cooling gave prisms of $Ag[NO_3]$·(1a) and needles of $Ag[NO_3]$·(1b).

Complexes of Silver Trifluoroacetate.—Fine needles of $Ag[O_2CCF_3]$·(1a) and $Ag[O_2CCF_3]$·(1b) were obtained from acetone–hexane using either the stoicheiometric quantity of ligand or an excess.

Complexes of Silver Perchlorate.—Prisms of $Ag[ClO_4]$·(1a) and needles of $Ag[ClO_4]$·(1b) were obtained from acetone–hexane using the stoicheiometric quantities of reagents. The complexes $Ag[ClO_4]$·2(1a) and $Ag[ClO_4]$·2(1b) crystallised as fine needles when hexane was added to an acetone solution of the salt and 2.2 molar equivalents of the appropriate ligand.

Complexes of Silver Tetrafluoroborate.—Needles of $Ag[BF_4]$·(1a), $Ag[BF_4]$·(1b), and $Ag[BF_4]$·2(1a) and prisms of $Ag[BF_4]$·2(1b) were obtained in an analogous fashion to the corresponding perchlorates.

X-*Ray Analysis.*—*Crystal data for* $Ag[BF_4]$·2(1a). $C_{14}H_{28}AgBF_4S_2$, $M = 455.2$, Monoclinic, $a = 10.838(2)$, $b = 11.720(2)$, $c = 16.355(2)$ Å, $\beta = 105.02(1)°$, $U = 2\,006.5$ Å^3, $Z = 4$, $F(000) = 928$, $D_c = 1.506$ g cm^{-3}, μ(Mo-K_α) = 11.26 cm^{-1}. Space group $C2/c$ (C_{2h}^6, no. 15) from systematic absences: hkl, $h + k = 2n + 1$; $h0l$, $l = 2n + 1$.

Crystal data for $Ag[ClO_4]$·(1a). $C_7H_{14}AgClO_4S$, $M = 337.6$, Orthorhombic, $a = 8.229(3)$, $b = 10.645(3)$, $c = 13.917(3)$ Å, $U = 1\,219.10$ Å^3, $Z = 4$, $F(000) = 672$, $D_c = 1.839$ g cm^{-3}, μ(Mo-K_α) = 18.63 cm^{-1}. Space group $P2_12_12_1$ (D_2^4, no. 19) from systematic absences: $h00$, $h = 2n + 1$; $0k0$, $k = 2n + 1$; $00l$, $l = 2n + 1$.

Crystal data for $Ag[NO_3]$·(1a). $C_7H_{14}AgNO_3S$, $M = 300.1$, Monoclinic, $a = 11.049(1)$, $b = 7.823(1)$, $c = 14.352(3)$ Å, $\beta = 118.392(7)°$, $U = 1\,091.4$ Å^3, $Z = 4$, $F(000) = 576$, $D_c = 1.826$ g cm^{-3}, μ(Mo-K_α) = 18.41 cm^{-1}. Space group $P2_1/c$ (C_{2h}^5, no. 14) from systematic absences: $h0l$, $l = 2n + 1$; $0k0$, $k = 2n + 1$.

Crystal data for $Ag[O_2CCF_3]$·(1a). $C_9H_{14}AgF_3O_2S$, $M = 351.2$, Monoclinic, $a = 10.194(3)$, $b = 15.784(5)$, $c = 8.125(4)$ Å, $\gamma = 95.49(2)°$, $U = 1\,301.33$ Å^3, $Z = 4$, $F(000) = 692$, $D_c = 1.792$ g cm^{-3}, μ(Mo-K_α) = 15.77 cm^{-1}. Space group $P2_1/b$ (C_{2h}^5, no. 14) from systematic absences: $hk0$, $k = 2n + 1$; $00l$, $l = 2n + 1$.

On the basis of precession and Weissenberg photographs taken with Mo-K_α and Cu-K_α radiation respectively, space groups and preliminary unit-cell dimensions were determined. For $Ag[BF_4]$·2(1a) the systematic absences allow the space groups to be $C2/c$ or Cc; $C2/c$ was chosen and confirmed by the analysis. Lattice parameters were obtained from a least-squares analysis of the setting angles of reflections with θ(Mo-K_α) in the range of 10—15° measured on a Hilger and Watts Y290 diffractometer.

Intensity data were collected using graphite monochromatised Mo-K_α radiation and processed in our usual way. The stability of the crystals was checked by measurement of two reflections every 100 measurements. There were small decreases in the intensities of the reference reflections and these changes were allowed for by appropriate scaling; absorption corrections were applied to the various data sets. The number of reflections measured, those with $I > 3\sigma(I)$, and $\theta_{max.}$ were respectively 943, 645, 20° for $Ag[BF_4]$·2(1a), 2 035, 1 259, 30° for $Ag[ClO_4]$·(1a), 1 914, 1 653, 20° for $Ag[NO_3]$·(1a), and 1 212, 846, 20° for $Ag[O_2CCF_3]$·(1a).

Determination of the Structures.—All four structures were solved by the heavy-atom method. The positions of the

TABLE 8

Analytical and m.p. data for the complexes

Complex	M.p. (θ_c/°C)	Analysis (%) Found C	Found H	Found N	Calc. C	Calc. H	Calc. N
$(Ag[NO_3])_2$·(1a)	103—104	17.7	3.55	5.8	17.9	3.0	5.95
$Ag[NO_3]$·(1a)	76—78	27.9	4.65	4.65	28.0	4.7	4.65
$Ag[O_2CCF_3]$·(1a)	93—94	30.85	3.8		30.8	4.05	
$Ag[ClO_4]$·(1a)	155 (decomp.)	24.7	4.8		24.9	4.2	
$Ag[BF_4]$·(1a)	>190 (decomp.)	25.55	4.4		25.85	4.35	
$Ag[ClO_4]$·2(1a)	115—116	35.75	5.9		35.95	6.05	
$Ag[BF_4]$·2(1a)	118—119	36.8	6.2		36.95	6.2	
$(Ag[NO_3])_2$·(1b)	88—90	14.85	3.35	5.85	14.8	2.9	5.75
$Ag[NO_3]$·(1b)	56—58	22.95	4.55	4.8	22.8	4.45	4.45
$Ag[O_2CCF_3]$·(1b)	86—87	26.35	3.85		26.15	3.85	
$Ag[ClO_4]$·(1b)	184 (decomp.)	20.4	3.85		20.4	4.0	
$Ag[BF_4]$·(1b)	215—217 (decomp.)	20.95	4.1		21.15	4.15	
$Ag[ClO_4]$·2(1b)	69—70	29.0	5.55		28.85	5.65	
$Ag[BF_4]$·2(1b)	56—58	29.4	5.85		29.6	5.8	

heavy atoms were determined by Patterson syntheses and Fourier syntheses based on the heavy-atom phases revealed the positions of the non-hydrogen atoms.

Refinement of the Structures.—The four structures were refined by full-matrix least-squares calculations employing the data classified as ' observed ' [$I > 3\sigma(I)$]. In $Ag[BF_4]$·2(1a) the cation lies on a two-fold axis and the BF_4^- ion lies at a centre of symmetry with the fluorine atoms disordered. In $Ag[ClO_4]$·(1a) the ClO_4^- ion showed evidence of large thermal motion of the oxygen atoms. Because $Ag[ClO_4]$·(1a) crystallises in an optically active space group, there must be spontaneous resolution on crystallisation. Attempts to identify which of the two enantiomorphic forms had been selected for data collection, by means of Bijvoet anomalous dispersion calculations, were inconclusive. In the structure of $Ag[O_2CCF_3]$·(1a) the fluorines of the CF_3 group were disordered over two sites and from the large thermal motion of the oxygen atoms it is possible that the entire $COCF_3$ moiety is disordered somewhat. There was no disorder problem with $Ag[NO_3]$·(1a). Difference-Fourier syntheses calculated at various stages of the refinements located all hydrogen atoms in $Ag[BF_4]$·2(1a), $Ag[ClO_4]$·(1a), and $Ag[NO_3]$·(1a); the analysis of $Ag[O_2CCF_3]$·(1a) is not as accurate as the other structures because of the disorder problem, and no hydrogen atoms were included in the calculations for that structure. In $Ag[BF_4]$·2(1a), $Ag[ClO_4]$·(1a), and $Ag[NO_3]$·(1a) the hydrogen atoms were fixed with appropriate idealised geometry at 1.08 Å from the atom to which they were bonded. The hydrogen atoms were allowed for in all subsequent refinement cycles but in each case only an overall isotropic temperature factor was refined. Atomic scattering factors were taken from refs. 21 and 22. At the conclusion of the refinements, difference electron-density syntheses showed no chemically significant maxima for structures $Ag[BF_4]$·2(1a), $Ag[ClO_4]$·(1a), or $Ag[NO_3]$·(1a). There were a number of small peaks around the O_2CCF_3 region in the structure of $Ag[O_2CCF_3]$·(1a), probably arising from small errors in the disordered model. During the refinements a weighting scheme of the form $w^{\frac{1}{2}} = 1/[\sigma^2(F) + (P)F^2]^{\frac{1}{2}}$ was employed. The values of P are 0.001 for $Ag[BF_4]$·2(1a), 0.011 for $Ag[ClO_4]$·(1a), 0.009 for $Ag[NO_3]$·(1a), and 0.003 for $Ag[O_2CCF_3]$·(1a). At termination of refinement the values of R and $R' = (\Sigma w\Delta^2/\Sigma wF_o^2)^{\frac{1}{2}}$ were 0.049 and 0.042 respectively for $Ag[BF_4]$·2(1a), 0.066 and 0.078 respectively for $Ag[ClO_4]$·(1a), 0.049 and 0.063 respectively for $Ag[NO_3]$·(1a), and 0.099 and 0.105 respectively for $Ag[O_2CCF_3]$·(1a). The final atomic fractional co-ordinates and standard deviations for $Ag[BF_4]$·2(1a), $Ag[ClO_4]$·(1a), $Ag[NO_3]$·(1a), and $Ag[O_2CCF_3]$·(1a) are in Tables 3—6. Selected bond lengths and angles are in Table 7. Other bond lengths and angles, tables of hydrogen co-ordinates, temperature factors {anisotropic for non-hydrogen atoms except for the perchlorate oxygen of $Ag[ClO_4]$·(1a)}, and observed and calculated structure factors have been deposited as Supplementary Publication No. SUP 22932 (39 pp.).*

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* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1979, Index issue.

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