Homoleptic Silver(I) Complexes with Dithio-, Diseleno- and Ditelluro-ethers: Synthesis, Structures and Multinuclear Nuclear Magnetic Resonance Studies†

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Homoleptic silver(I) complexes $[Ag(L\text{–}L)_2]BF_4$ {L–L = $RE(CH_2)_nER$ [R = Ph or Me, n = 2 or 3 (E = S or Se), n = 3 (E = Te)]} have been prepared and characterised by analysis, FAB mass spectrometry, and multinuclear NMR spectroscopy (^1H, ^{77}Se, ^{125}Te and ^{109}Ag). Variable-temperature NMR studies have been used to probe various exchange processes occurring in solution. The crystal structure of the tetrafluoroborate salt of $[Ag(MeSeCH_2CH_2SeMe)_2]^+$ shows the diselenoether ligands co-ordinated in a bidentate manner to the Ag^I ion forming distorted tetrahedral 1+ cations. In contrast, in the crystal structure of the tetrafluoroborate salt of $[Ag_n(PhSeCH_2CH_2CH_2SePh)_{2n}]^{n+}$ the cation is an infinite network comprising Ag atoms linked tetrahedrally *via* one of the Se atoms of four different diselenoether ligands, which are in turn linked to adjacent Ag atoms.

In marked contrast to the extensive studies of silver complexes with phosphine and arsine ligands, the only detailed work with neutral Group 16 ligands is with thiamacrocycles[1–3] and related S_2O_3[4] and S_4N_2[5] donor ligands. Here we report a systematic study of homoleptic silver(I) complexes with dithio-, diseleno- and ditelluro-ethers, including examples of the main structural types and the use of ^{109}Ag NMR spectroscopy to probe solution behaviour. A preliminary account of aspects of this work has been communicated.[6] We have also reported similar studies of copper(I) analogues,[7] and the synthesis of homoleptic copper(II) dithio- and diselenoether complexes.[8]

Experimental

Physical measurements were made as described elsewhere.[7] Silver-109 NMR spectra were recorded on a Bruker AM360 spectrometer at 16.75 MHz. Spectra were obtained from solutions in CH_2Cl_2, Me_2CO or $MeNO_2$ containing 5% of the deuteriated analogue to provide the lock, in 10 mm outside-diameter tubes. Spectra were recorded by direct observation from solutions containing the free radical relaxation agent 4-hydroxy-2,2,6,6-tetramethylpiperidine *N*-oxyl (htempo) (TANOL)[9] and with a 2 s pulse delay, typically 20 000 scans being accumulated. A 9.1 mol dm^{-3} solution of $AgNO_3$ in D_2O containing Fe^{3+} as relaxation agent was used as zero reference.[10] This 'zero' is +47 ppm from the Ag^+ resonance at 'infinite dilution'.[10]

Synthesis.—The complexes were prepared by the same general method described below, along with the minor modifications used in certain cases. Complexes were made under a nitrogen atmosphere, and samples were stored in sealed containers wrapped in aluminium foil in a freezer. Most are light sensitive to some degree and some including $[Ag(MeSeCH_2CH_2SeMe)_2]BF_4$ and $[Ag_n(MeSCH_2CH_2CH_2SMe)_n][BF_4]_n$ darken rapidly in solution in diffuse daylight.

$[Ag(L\text{–}L)_2]BF_4$. The ligand (2 mmol) was added to a solution of dry powdered $AgBF_4$ (1 mmol) in acetone (10 cm^3). The solution was concentrated to *ca.* 2 cm^3 *in vacuo* and the solvent decanted from the solid formed. The solid was rinsed with diethyl ether (3 × 10 cm^3) and dried *in vacuo* in the dark. Yields are typically 75%. For complexes of $PhSeCH_2CH_2SePh$, $PhSeCH_2CH_2CH_2SePh$ and $PhSCH_2CH_2SPh$, the reaction mixture was evaporated to an oil which was triturated with ice-cold pentane. The resulting solid was washed with pentane, then diethyl ether and dried *in vacuo*.

$[Ag(MeSeCH_2CH_2SeMe)_2]BF_4$. A solution of $AgBF_4$ (1 mmol) in acetone (5 cm^3) was added to a solution of $MeSeCH_2CH_2SeMe$ (2 mmol) in dichloromethane (5 cm^3). The solvent was removed *in vacuo* and the residue redissolved in CH_2Cl_2. The solution was filtered and the filtrate evaporated to dryness. The resulting solid was rinsed with pentane (10 cm^3), diethyl ether (10 cm^3) and dried *in vacuo*.

Single-crystal Structure Determination of $[Ag(MeSeCH_2CH_2SeMe)_2]BF_4{\cdot}CH_2Cl_2$.—Colourless needles were obtained by layering a solution of the complex in CH_2Cl_2 with diethyl ether at −15 °C. The selected crystal (0.60 × 0.10 × 0.10 mm) was coated with mineral oil and mounted on a glass fibre.

Crystal data. $C_8H_{20}AgBF_4Se_4{\cdot}CH_2Cl_2$, M = 711.7, orthorhombic, space group $P2_12_12_1$, a = 11.224(3), b = 17.715(3), c = 10.339(3) Å, U = 2075.7(7) Å^3 [from 2θ values of 25 reflections measured at ±ω ($26.3 \leqslant 2\theta \leqslant 35.5°$, λ = 0.710 73 Å)], Z = 4, D_c = 2.299 g cm^{-3}, T = 140 K, μ = 8.343 mm^{-1}, F(000) = 1336.

Data collection and processing. Rigaku AFC7S four-circle diffractometer equipped with an Oxford Systems low-temperature attachment, using graphite-monochromated Mo-Kα X-radiation, T = 140 K, ω scans with ω scan width = (1.00 + 0.35 tan θ)°, 2086 unique data collected ($2\theta_{max}$ 50°, h 0–13, k 0–21, l 0–12) giving 1635 reflections with $F \geqslant 6\sigma(F)$ for use in all calculations. No significant crystal decay or movement was observed. As there were no identifiable faces, the data were corrected for absorption using ψ scans (maximum and minimum transmission factors = 1.000 and 0.641 respectively).

Structure solution and refinement. The structure was solved by heavy-atom Patterson methods[11] and developed by using iterative cycles of full-matrix least-squares refinement and Fourier-difference syntheses which located all non-H atoms for the discrete, ordered $[Ag(MeSeCH_2CH_2SeMe)_2]^+$ cation and BF_4^- anion in the asymmetric unit.[12] During refinement one fully occupied CH_2Cl_2 solvent molecule was identified per

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

Table 1 Fractional atomic coordinates for $[Ag(MeSeCH_2CH_2SeMe)_2]BF_4{\cdot}CH_2Cl_2$

Atom	x	y	z
Ag	−0.257 77(10)	−0.007 96(5)	−0.228 6(1)
Se(1)	−0.437 1(1)	0.053 82(7)	−0.104 4(1)
Se(2)	−0.239 7(1)	0.114 36(6)	−0.372 9(1)
Se(3)	−0.060 3(1)	−0.047 92(7)	−0.109 2(1)
Se(4)	−0.269 3(1)	−0.140 68(6)	−0.337 6(1)
Cl(1)	−0.805 6(3)	−0.179 8(2)	−0.467 1(4)
Cl(2)	−0.556 3(3)	−0.137 0(2)	−0.474 6(4)
F(1)	−0.730 6(9)	−0.056 7(4)	−0.976 6(8)
F(2)	−0.586(2)	−0.124 6(9)	−1.052(2)
F(3)	−0.671 9(9)	−0.164 7(5)	−0.885(1)
F(4)	−0.764(2)	−0.165 6(6)	−1.067(2)
C(1)	−0.575(1)	0.036 9(8)	−0.215(1)
C(2)	−0.403(1)	0.156 4(6)	−0.161(1)
C(3)	−0.382(1)	0.166 0(7)	−0.306(1)
C(4)	−0.119(1)	0.173 9(8)	−0.284(2)
C(5)	0.068(1)	−0.017 8(8)	−0.223(1)
C(6)	−0.068(1)	−0.154 3(7)	−0.158(1)
C(7)	−0.109(1)	−0.172 6(7)	−0.294(1)
C(8)	−0.357(1)	−0.201 9(7)	−0.215(1)
C(9)	−0.696(1)	−0.116 3(7)	−0.413(2)
B(1)	−0.695(2)	−0.130 1(8)	−0.991(2)

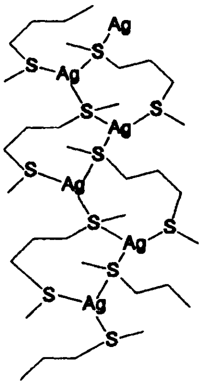
complex cation. All non-H atoms were refined anisotropically, while H atoms were included in fixed, calculated positions. The absolute configuration was checked by inverting the structure; the configuration chosen showed smaller e.s.d.s on the atomic coordinates and slightly smaller R and R' values at convergence. The weighting scheme $w^{-1} = \sigma^2(F)$ gave satisfactory agreement analyses. At final convergence R, R' = 0.035, 0.037 respectively, S = 1.63 for 190 refined parameters. The final ΔF synthesis showed no peaks above 0.87 or below −0.98 e Å^{-3} and the maximum Δ/σ = 0.01. Fractional atomic coordinates are listed in Table 1.

Single-crystal Structure Determination of $[Ag_n(PhSeCH_2CH_2CH_2SePh)_{2n}][BF_4]_n{\cdot}nMeNO_2$.—Colourless prisms were obtained by vapour diffusion of diethyl ether into a solution of the complex in $MeNO_2$. The selected crystal (0.40 × 0.20 × 0.15 mm) was coated with mineral oil and mounted on a glass fibre.

Crystal data. $C_{30}H_{32}AgBF_4Se_4{\cdot}CH_3NO_2$, M = 964.1, monoclinic, space group $P2_1/c$, a = 13.775(2), b = 12.956(2), c = 19.646(2) Å, β = 94.023(8)°, U = 3497.6(7) Å^3 [from 2θ values of 25 reflections measured at ±ω (22.8 ⩽ 2θ ⩽ 33.4°, λ = 0.710 73 Å)], Z = 4, D_c = 1.831 g cm^3, T = 150 K, μ = 4.788 mm^{-1}, F(000) = 1872.

Data collection and processing. Rigaku AFC7S four-circle diffractometer equipped with an Oxford Systems low-temperature attachment, using graphite-monochromated Mo-Kα X-radiation, T = 150 K, ω–2θ scans with ω scan width = (1.05 + 0.35 tan θ)°, 6762 data collected, 6478 unique (R_{int} = 0.05) ($2\theta_{max}$ 50°, h 0–16, k 0–15, l −23 to 23) giving 3906 reflections with $F \geqslant 6\sigma(F)$ for use in all calculations. No significant crystal decay or movement was observed. As there were no identifiable faces, the data were corrected for absorption using ψ scans (maximum and minimum transmission factors = 0.996 and 0.831 respectively).

Structure solution and refinement. The structure was solved by direct methods[12] and developed by using iterative cycles of full-matrix least-squares refinement and Fourier-difference syntheses which located all non-H atoms for the ordered $[Ag(PhSeCH_2CH_2CH_2SePh)_2]^+$ cationic repeating unit and discrete BF_4^- anion in the asymmetric unit.[13] During refinement one fully occupied $MeNO_2$ solvent molecule was identified per repeating unit. All non-H atoms were refined anisotropically, while H atoms were included in fixed, calculated positions. The weighting scheme $w^{-1} = \sigma^2(F)$ gave satisfactory agreement analyses. At final convergence R, R' = 0.036, 0.036 respectively, S = 1.84 for 397 refined parameters. The final ΔF synthesis showed no peaks above 0.81 or below −0.89 e Å^{-3} and the maximum Δ/σ = 0.02. Fractional atomic coordinates are listed in Table 2.



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Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles for both structures.

Results

The silver(I) complexes were prepared by reaction of anhydrous silver fluoroborate with the appropriate ligand in acetone. The complexes of stoichiometry $[Ag(L\text{–}L)_2]BF_4$ (Table 3) are white powders, and appear air-stable although several are light sensitive both in the solid state and in solution in organic solvents, and hence samples were stored in aluminium foil wrapped containers in a freezer. The FAB mass spectra were consistent with the formulations and showed $[Ag(L\text{–}L)]^+$ and $[Ag(L\text{–}L)_2]^+$ as major ions, sometimes with much weaker ions due to ligand fragmentation. Notably in view of the polymeric nature of some complexes (below) no $[Ag_2(L\text{–}L)_n]^+$ ions were observed.

As reported elsewhere[6] crystals of stoichiometry $[Ag(MeSCH_2CH_2CH_2SMe)]BF_4$ were deposited from solutions of the 2:1 complex in CH_2Cl_2–diethyl ether. Several batches of this composition were grown and analytical and ^1H NMR data obtained, but unfortunately insufficient quantities were obtained to record a ^{109}Ag NMR spectrum. The crystals were very unstable to light, darkening rapidly even in diffuse daylight.

X-Ray Crystallographic Studies.—In a preliminary communication[6] we reported the structures of the tetrafluoroborate salts of $[Ag_n(PhSCH_2CH_2CH_2SPh)_{2n}]^{n+}$ and $[Ag_n(MeSCH_2CH_2CH_2SMe)_n]^{n+}$. The former comprises an infinite array of tetrahedral Ag^I atoms co-ordinated to one of the S donors of four distinct $PhSCH_2CH_2CH_2SPh$ ligands which link adjacent Ag^I atoms *via* the second S donor. The latter adopts a highly unusual arrangement comprising an infinite-chain $[Ag_n(MeSCH_2CH_2CH_2SMe)_n]^{n+}$ polymer involving trigonal $(\mu\text{-}S)_2S$ co-ordination at Ag^I from $MeSCH_2CH_2CH_2SMe$ ligands, with one S donor using both lone pairs to bridge two adjacent Ag^I centres while the other S donor of the dithioether ligand co-ordinates *via* only one lone pair (structure **I**). In view of the paucity of structurally characterised examples of silver(I) selenoether complexes and in order to establish whether these are typical of the structures adopted by the silver(I) dithio-, diseleno- and ditelluro-ether complexes being studied, single-crystal X-ray analyses were also undertaken on certain other examples, namely $[Ag(MeSeCH_2CH_2SeMe)_2]BF_4{\cdot}CH_2Cl_2$ and $[Ag_n(PhSeCH_2CH_2CH_2SePh)_{2n}][BF_4]_n{\cdot}nMeNO_2$.

Table 2 Fractional atomic coordinates for $[Ag_n(PhSeCH_2CH_2CH_2SePh)_{2n}][BF_4]_n{\cdot}nMeNO_2$

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ag	0.252 83(4)	0.154 29(5)	0.728 56(3)	C(11)	0.016 6(6)	0.150 5(7)	0.947 0(5)
Se(1)	0.211 57(5)	0.292 88(6)	0.820 90(4)	C(12)	0.053 2(5)	0.199 5(6)	0.892 6(4)
Se(2)	0.361 23(5)	0.261 62(6)	0.644 75(4)	C(13)	0.456 6(5)	0.154 9(6)	0.632 8(4)
Se(3)	0.346 67(6)	−0.024 18(6)	0.743 79(4)	C(14)	0.551 0(6)	0.156 7(7)	0.662 3(4)
Se(4)	0.077 97(5)	0.107 20(6)	0.666 12(5)	C(15)	0.611 5(6)	0.072 8(8)	0.651 7(5)
F(1)	0.765 9(4)	−0.030 6(5)	0.834 2(3)	C(16)	0.580 4(6)	−0.008 7(7)	0.612 8(5)
F(2)	0.681 3(4)	0.119 0(5)	0.821 6(3)	C(17)	0.485 4(7)	−0.009 5(8)	0.583 8(5)
F(3)	0.782 4(4)	0.090 8(5)	0.913 1(3)	C(18)	0.423 5(6)	0.071 9(7)	0.592 8(4)
F(4)	0.844 4(4)	0.117 8(5)	0.811 9(3)	C(19)	0.264 6(5)	−0.092 8(6)	0.805 2(4)
O(1)	0.444 6(6)	0.103 6(7)	0.974 7(4)	C(20)	0.228 8(5)	−0.189 1(6)	0.785 6(4)
O(2)	0.463 4(7)	0.244 7(7)	0.925 0(7)	C(21)	0.164 5(5)	−0.239 1(6)	0.825 7(5)
N(1)	0.496 3(7)	0.176 7(8)	0.962 6(6)	C(22)	0.136 4(6)	−0.194 4(7)	0.885 5(5)
C(1)	0.100 5(5)	0.358 5(6)	0.771 7(4)	C(23)	0.174 6(6)	−0.099 3(7)	0.904 7(4)
C(2)	0.062 8(5)	0.449 4(6)	0.812 8(4)	C(24)	0.237 4(6)	−0.047 2(6)	0.863 5(5)
C(3)	0.436 2(5)	0.365 4(6)	0.700 2(4)	C(25)	0.128 1(5)	0.020 8(7)	0.596 8(4)
C(4)	0.494 8(5)	0.431 0(7)	0.653 2(4)	C(26)	0.153 2(6)	−0.081 1(7)	0.608 3(4)
C(5)	0.451 7(6)	0.020 2(7)	0.809 2(5)	C(27)	0.192 8(7)	−0.136 9(7)	0.556 5(5)
C(6)	0.022 8(6)	0.002 8(6)	0.724 9(4)	C(28)	0.210 3(7)	−0.090 3(8)	0.495 3(5)
C(7)	0.151 8(5)	0.224 5(5)	0.894 9(4)	C(29)	0.185 7(6)	0.013 0(8)	0.485 4(4)
C(8)	0.212 4(5)	0.198 7(6)	0.951 4(4)	C(30)	0.143 0(6)	0.068 6(7)	0.536 1(5)
C(9)	0.176 0(6)	0.145 4(7)	1.004 5(4)	C(31)	0.600 2(7)	0.176(1)	0.985 4(6)
C(10)	0.077 8(6)	0.123 2(7)	1.003 7(4)	B(1)	0.768 3(7)	0.074 6(8)	0.843 9(5)

Table 3 Analytical data * (%)

Compound	C	H
$[Ag\{MeS(CH_2)_2SMe\}_2]BF_4$	22.0 (21.9)	4.7 (4.6)
$[Ag\{MeS(CH_2)_3SMe\}_2]BF_4$	25.5 (25.7)	5.5 (5.2)
$[Ag\{PhS(CH_2)_2SPh\}_2]BF_4$	49.2 (48.9)	4.2 (4.1)
$[Ag\{PhS(CH_2)_3SPh\}_2]BF_4$	49.9 (50.4)	4.8 (4.5)
$[Ag\{MeSe(CH_2)_2SeMe\}_2]BF_4$	15.5 (15.3)	3.3 (3.2)
$[Ag\{MeSe(CH_2)_3SeMe\}_2]BF_4$	18.3 (18.3)	3.4 (3.7)
$[Ag\{PhSe(CH_2)_2SePh\}_2]BF_4$	38.2 (38.4)	3.1 (3.2)
$[Ag\{PhSe(CH_2)_3SePh\}_2]BF_4$	39.7 (39.9)	3.5 (3.6)
$[Ag\{MeTe(CH_2)_3TeMe\}_2]BF_4$	14.2 (14.1)	3.0 (2.9)
$[Ag\{PhTe(CH_2)_3TePh\}_2]BF_4$	33.0 (32.8)	3.1 (2.9)
$[Ag\{MeS(CH_2)_3SMe\}]BF_4$	18.7 (18.2)	3.8 (3.7)

* Calculated value in parentheses.

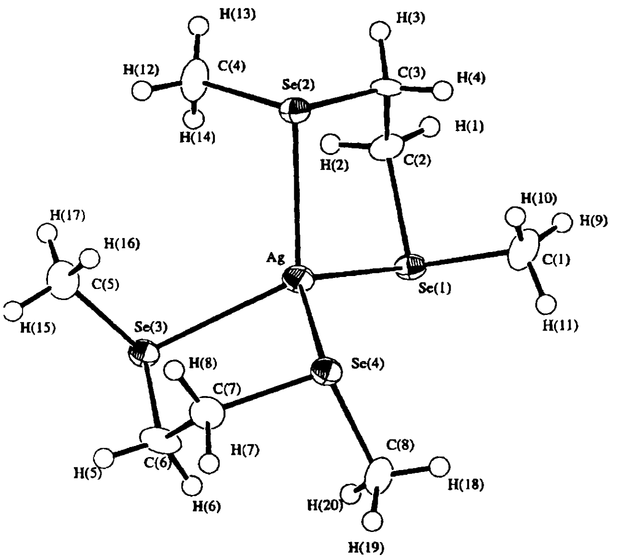

Fig. 1 View of the structure of $[Ag(MeSeCH_2CH_2SeMe)_2]^+$ with numbering scheme adopted. Ellipsoids are drawn at 40% probability

Table 4 Selected bond lengths (Å) and angles (°) for $[Ag(MeSeCH_2CH_2SeMe)_2]BF_4{\cdot}CH_2Cl_2$

Ag–Se(1)	2.626(2)	Ag–Se(2)	2.638(1)
Ag–Se(3)	2.634(2)	Ag–Se(4)	2.610(1)
Se(1)–C(1)	1.95(1)	Se(1)–C(2)	1.95(1)
Se(2)–C(3)	1.96(1)	Se(2)–C(4)	1.94(1)
Se(3)–C(5)	1.93(1)	Se(3)–C(6)	1.95(1)
Se(4)–C(7)	1.94(1)	Se(4)–C(8)	1.94(1)
C(2)–C(3)	1.53(2)	C(6)–C(7)	1.51(2)
Se(1)–Ag–Se(2)	89.61(5)	Se(1)–Ag–Se(3)	121.85(6)
Se(1)–Ag–Se(4)	123.24(6)	Se(2)–Ag–Se(3)	114.89(6)
Se(2)–Ag–Se(4)	119.97(5)	Se(3)–Ag–Se(4)	90.12(5)
Ag–Se(1)–C(1)	104.9(4)	Ag–Se(1)–C(2)	95.3(4)
C(1)–Se(1)–C(2)	96.9(6)	Ag–Se(2)–C(3)	97.0(3)
Ag–Se(2)–C(4)	103.4(5)	C(3)–Se(2)–C(4)	98.3(5)
Ag–Se(3)–C(5)	105.4(4)	Ag–Se(3)–C(6)	95.9(4)
C(5)–Se(3)–C(6)	98.1(5)	Ag–Se(4)–C(7)	96.6(4)
Ag–Se(4)–C(8)	104.3(4)	C(7)–Se(4)–C(8)	98.8(6)
Se(1)–C(2)–C(3)	115.6(8)	Se(2)–C(3)–C(2)	114.9(9)
Se(3)–C(6)–C(7)	117.3(8)	Se(4)–C(7)–C(6)	116.0(9)

The crystal structure of $[Ag(MeSeCH_2CH_2SeMe)_2]^+$ shows (Fig. 1, Table 4) discrete cations involving two bidentate $MeSeCH_2CH_2SeMe$ ligands generating a distorted tetrahedral stereochemistry at Ag^I involving two five-membered chelate rings, Ag–Se(1) 2.626(2), Ag–Se(2) 2.638(1), Ag–Se(3) 2.634(2), Ag–Se(4) 2.610(1)Å. The bond lengths may be compared with those in $[Ag\{(CH_2Se)_3\}_2]AsF_6$ where Ag–Se lies in the range 2.78(1)–3.05(1) Å.[13] The Se–Ag–Se angles involved in the five-membered chelate rings are restricted by the small chelate bite to be very close to 90°, while those which do not correspond to chelate rings are considerably more open, close to 120°.

The crystal structure of the tetrafluoroborate salt of $[Ag_n(PhSeCH_2CH_2CH_2SePh)_{2n}]^{n+}$ shows (Fig. 2, Table 5) tetrahedrally co-ordinated Ag^I ions ligated *via* one Se donor of four distinct diselenoether ligands, with the other Se donor of each ligand linking adjacent Ag^I ions to give an infinite array (Fig. 3), Ag–Se(1) 2.643(1), Ag–Se(2) 2.687(1), Ag–Se(3) 2.656(1), Ag–Se(4) 2.695(1) Å. In this species all of the angles around Ag^I are in the range 103–130°. Discrete, non-co-ordinating BF_4^- anions and $MeNO_2$ solvent molecules occupy voids in the cationic network and neutralise the charge. This is a very similar arrangement to that observed for the dithioether analogue, $[Ag_n(PhSCH_2CH_2CH_2SPh)_{2n}]^{n+}$, described earlier.[6]

These studies show that in the three examples the solid-state

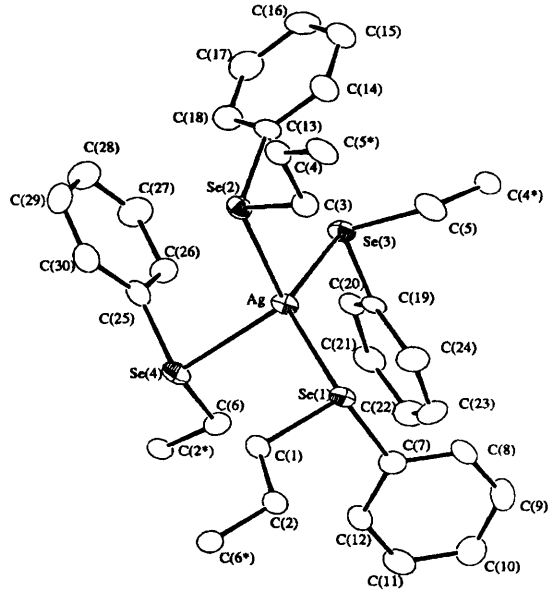

Fig. 2 View of the cationic monomer $[Ag(PhSeCH_2CH_2CH_2SePh)_2]^+$ repeating unit with numbering scheme adopted. Ellipsoids are drawn at 40% probability and asterisked atoms represent the nearest symmetry related neighbours

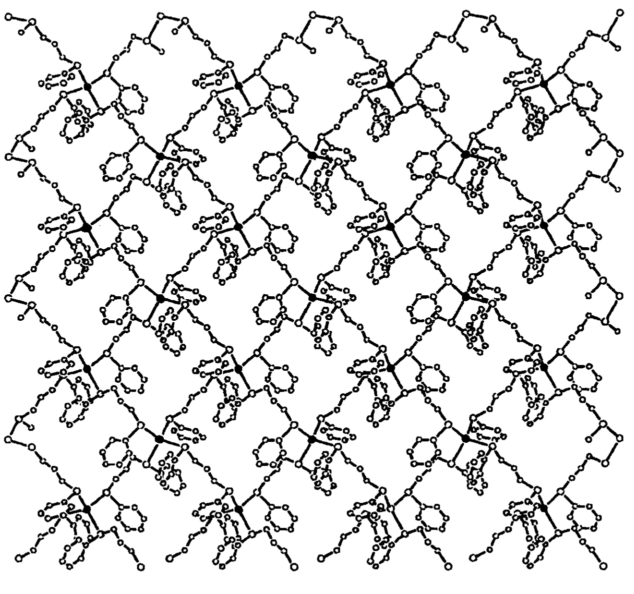

Fig. 3 View of the polymeric structure of $[Ag_n(PhSeCH_2CH_2CH_2SePh)_{2n}]^{n+}$ (H atoms are omitted for clarity)

structures of the silver(I) complexes involving the two C_3-linked L–L ligands adopt extended polymeric structures in which L–L links adjacent Ag^I ions, and similar structures may be present for other trimethylene-linked ligands.* In contrast, with C_2-linked $MeSeCH_2CH_2SeMe$ ligands, a discrete, mononuclear chelated structure is formed. In the absence of any crystal-field stabilisation for d^{10} metal complexes and their lability in solution, the relationship between the structures deduced from X-ray crystallographic studies and the structures in solution is not clear. However, on the basis of their solubilities and the NMR properties described below, it seems likely that those complexes which are polymeric in the solid-state are monomeric $Ag(S/Se/Te)_4{}^+$ cations in solution, while those which are chelates in the solid-state probably remain so in solution.

Table 5 Selected bond lengths (Å) and angles (°) for $[Ag_n(PhSeCH_2CH_2CH_2SePh)_{2n}][BF_4]_n{\cdot}nMeNO_2$

Ag–Se(1)	2.643(1)	Ag–Se(2)	2.687(1)
Ag–Se(3)	2.656(1)	Ag–Se(4)	2.695(1)
Se(1)–C(1)	1.947(8)	Se(1)–C(7)	1.935(8)
Se(2)–C(3)	1.976(7)	Se(2)–C(13)	1.933(8)
Se(3)–C(5)	1.953(8)	Se(3)–C(19)	1.927(8)
Se(4)–C(6)	1.966(8)	Se(4)–C(25)	1.928(9)
C(2)–C(6)	1.514(10)	C(1)–C(2)	1.54(1)
C(4)–C(5)	1.53(1)	C(3)–C(4)	1.53(1)
Se(1)–Ag–Se(2)	102.98(3)	Se(1)–Ag–Se(3)	129.84(4)
Se(1)–Ag–Se(4)	103.76(3)	Se(2)–Ag–Se(3)	103.45(3)
Se(2)–Ag–Se(4)	110.83(3)	Se(3)–Ag–Se(4)	105.46(3)
Ag–Se(1)–C(1)	98.9(2)	Ag–Se(1)–C(7)	109.1(2)
C(1)–Se(1)–C(7)	102.2(3)	Ag–Se(2)–C(3)	107.8(2)
Ag–Se(2)–C(13)	96.6(2)	C(3)–Se(2)–C(13)	102.7(3)
Ag–Se(3)–C(5)	98.6(2)	Ag–Se(3)–C(19)	99.8(2)
C(5)–Se(3)–C(19)	99.5(3)	Ag–Se(4)–C(6)	105.0(2)
Ag–Se(4)–C(25)	95.7(2)	C(6)–Se(4)–C(25)	100.8(3)
C(1)–C(2)–C(6)	112.0(6)	Se(1)–C(1)–C(2)	110.9(5)
C(3)–C(4)–C(5)	112.7(7)	Se(2)–C(3)–C(4)	108.9(5)
Se(4)–C(6)–C(2)	110.3(5)	Se(3)–C(5)–C(4)	113.8(6)
Se(1)–C(7)–C(12)	123.2(6)	Se(1)–C(7)–C(8)	116.7(6)

Multinuclear NMR Studies.—The ^1H NMR spectra (Table 6) are unexceptional, showing resonances little shifted from those of the free ligands, and with no sign of coupling to the silver nuclei. In particular, even at 200 K the spectra observed from $[Ag\{MeS(CH_2)_nSMe\}_2]BF_4$ ($n = 2$ or 3) contained single sharp δ(Me) resonances. Slow pyramidal inversion at the Group 16 atom would be expected to give rise to several closely spaced resonances due to NMR distinguishable invertomers.[15] The absence of such signals could be due to fast inversion even at low temperatures, but is probably due to rapid reversible intramolecular ring opening in these very labile complexes.

The $^{77}Se\text{-}\{^1H\}$ NMR spectra of $[Ag(MeSeCH_2CH_2SeMe)_2]BF_4$ and $[Ag(PhSeCH_2CH_2SePh)_2]BF_4$ in CH_2Cl_2 (Table 7) contain single sharp resonances over the temperature range 300–180 K, the absence of one-bond coupling to $^{107/109}Ag$ being due to the fast reversible ligand dissociation. The co-ordination shifts in most seleno- and telluro-ether complexes of transition metals are to high frequency of the free-ligand resonance, with complexes containing five-membered chelate rings having particularly large shifts.[16] In the present complexes the shifts are to *low* frequency, an effect also observed in the copper(I) complexes and tentatively attributed[7] to the presence of the electron-rich d^{10} metal centre. For a particular ligand the co-ordination shift is larger in the silver(I) than in the copper(I) complex. The complexes $[Ag(RSeCH_2CH_2CH_2SeR)_2]BF_4$ (R = Me or Ph) show smaller low frequency co-ordination shifts. The extreme lability of the complexes $[Ag(RSeCH_2CH_2SeR)_2]BF_4$ was shown by variable-temperature $^{77}Se\text{-}\{^1H\}$ studies in the presence of added free ligand. For R = Ph a single resonance with a chemical shift varying with the relative amount of free ligand was observed at > *ca.* 200 K, consistent with fast ligand exchange. On cooling further this split into two, but even at the lowest temperature obtainable in CH_2Cl_2 (*ca.* 175 K) the lines were still broad and exchange was still evident. For the complex with R = Me in acetone, even at 180 K only a single broad resonance was present showing exchange is fast. The complexes $[Ag(RSeCH_2CH_2CH_2SeR)_2]BF_4$ were poorly soluble in CH_2Cl_2 and spectra were

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* *Note added at proof.* The complex $[Ag(MeTeCH_2CH_2CH_2TeMe)_2]BF_4$ has also been found to possess an infinite polymeric structure.[14]

Table 6 Proton NMR data

Complex	δ(*J*/Hz)
$[Ag\{MeS(CH_2)_2SMe\}_2]BF_4$[a]	2.28 (s, 6 H), 2.98 (s, 4 H)
$[Ag\{MeS(CH_2)_3SMe\}_2]BF_4$[b]	2.16 (q, 2 H), 2.41 (s, 6 H), 2.95 (t, 4 H)
$[Ag\{PhS(CH_2)_2SPh\}_2]BF_4$[a]	3.22 (s, 4 H), 7.2–7.6 (m, 10 H)
$[Ag\{PhS(CH_2)_3SPh\}_2]BF_4$[b]	2.10 (q, 2 H), 3.27 (t, 4 H), 7.2–7.5 (m, 10 H)
$[Ag\{MeSe(CH_2)_2SeMe\}_2]BF_4$[a]	2.22 (s, 6 H, $^2J_{Se-H}$ = 10), 3.13 (s, 4 H, $^2J_{Se-H}$ = 11)
$[Ag\{MeSe(CH_2)_3SeMe\}_2]BF_4$[c]	2.10 (q, 2 H), 2.15 (s, 6 H), 2.80 (t, 4 H)
$[Ag\{PhSe(CH_2)_2SePh)_2]BF_4$[a]	3.28 (s, 4 H, $^2J_{Se-H}$ = 10), 7.2–7.6 (m, 10 H)
$[Ag\{PhSe(CH_2)_3SePh\}_2]BF_4$[c]	2.00 (q, 2 H), 3.00 (t, 4 H), 7.2–7.6 (m, 10 H)
$[Ag\{MeTe(CH_2)_3TeMe\}_2]BF_4$[b]	2.21 (q, 2 H),[d] 2.18 (s, 6 H), 2.95 (t, 4 H)
$[Ag\{PhTe(CH_2)_3TePh\}_2]BF_4$[a]	2.28 (q, 2 H), 3.10 (t, 4 H), 7.1–7.6 (m, 10 H)
$[Ag\{MeS(CH_2)_3SMe\}]BF_4$[b]	2.16 (q, 2 H), 2.40 (s, 6H), 2.94 (t, 4 H)

[a] In CD_2Cl_2. [b] In CD_3NO_2. [c] In CD_3CN. [d] Coupling $^2J_{Te-H}$ not clear due to overlap of Me and CH_2 resonances.

Table 7 Selenium-77 and ^{125}Te NMR data

Complex[a]	δ(^{77}Se or ^{125}Te)[b]	δ(free ligand)	Comment
$[Ag\{MeSe(CH_2)_2SeMe\}_2]^+$	+2	+127	δ −3 at 180 K fast exchange with L–L > *ca.* 180 K
$[Ag\{PhSe(CH_2)_2SePh\}_2]^+$	+226	+336	δ +238 at 190 K fast exchange with L–L > *ca.* 200 K
$[Ag\{MeSe(CH_2)_3SeMe\}_2]^+$[c]	+41	+74	δ +38 at 243 K
$[Ag\{PhSe(CH_2)_3SePh\}_2]^+$[c]	+248	+289	See text
$[Ag\{MeTe(CH_2)_3TeMe\}_2]^+$[c]	+24	+104	δ +30 at 250 K, δ +47 with added L–L at 300 K, fast exchange with added L–L 300–250 K
$[Ag\{PhTe(CH_2)_3TePh\}_2]^+$	+361	+466	δ +381 at 253 K, resonance broadens *ca.* 270 K and then disappears on cooling below *ca.* 250 K

[a] In CH_2Cl_2–CD_2Cl_2 unless indicated otherwise. [b] Relative to external neat $SeMe_2$ or $TeMe_2$ at 300 K. [c] In $MeNO_2$–CD_3NO_2.

Table 8 Silver-109 NMR data

Complex	δ(^{109}Ag)[a]	Comments
$[Ag\{MeS(CH_2)_2SMe\}_2]^+$[b]	+1004	δ +1090 at 180 K, no change with added L–L
$[Ag\{MeS(CH_2)_3SMe\}_2]^+$[c]	+840	δ +901 at 250 K, δ + 926 with excess L–L at 250 K
$[Ag\{PhS(CH_2)_2SPh\}_2]^+$[b]	+944	δ +1030 at 180 K, no change with added ligand
$[Ag\{PhS(CH_2)_3SPh\}_2]^+$[d]		δ +948 at 200 K, see text
$[Ag\{MeSe(CH_2)_2SeMe\}_2]^+$[b]	+1046	δ +1133 at 180 K, no change with added L–L
$[Ag\{MeSe(CH_2)_3SeMe\}_2]^+$[c]	+829	δ +898 at 250 K, δ +924 with excess L–L at 250 K
$[Ag\{PhSe(CH_2)_2SePh\}_2]^+$[b]	+991	δ +1065 at 180 K, no change with added L–L
$[Ag\{PhSe(CH_2)_3SePh\}_2]^+$[c]		No clear resonance, see text
$[Ag\{MeTe(CH_2)_3TeMe\}_2]^+$[c]	+1053	δ +1091 with added L–L at 300 K, δ +1114 with added L–L at 250 K
$[Ag\{PhTe(CH_2)_3TePh\}_2]^+$[b]	+989	δ +1037 with added L–L at 300 K, δ +1072 with added L–L at 180 K

[a] At 300 K relative to 9.1 mol dm^{-3} solution of Ag^+ in H_2O–D_2O.[10] [b] In CH_2Cl_2–CD_2Cl_2. [c] In $MeNO_2$–CD_3NO_2. [d] In Me_2CO–$(CD_3)_2CO$.

obtained from $MeNO_2$ (m.p. 244 K) solutions, fast exchange with added ligand being apparent over the temperature range 245–300 K.

The complex $[Ag(PhTeCH_2CH_2CH_2TePh)_2]BF_4$ dissolved in CH_2Cl_2 showed a low-frequency co-ordination shift at 300 K, but on cooling the resonance broadened rapidly and disappeared completely below *ca.* 250 K. No resonances appeared on further cooling.

Silver-109 *NMR studies.* Silver has two spin $\frac{1}{2}$ isotopes* with ^{109}Ag slightly the more favourable, but the low magnetogyric ratio, low receptivity and long relaxation times have made direct observations difficult.[17] For complexes showing spin–spin coupling of silver to another nucleus such as ^{31}P the insensitive nuclei enhanced by polarisation transfer (INEPT) pulse sequence is preferred.[18] However, for the present complexes which lack any resolved couplings or, for the thioethers, even a suitable second nucleus, direct observation was required, requiring large amounts of instrument time. We used concentrated solutions containing small amounts of the paramagnetic relaxation agent htempo and with a pulse delay of 2 s to observe ^{109}Ag spectra, typically recording *ca.* 20 000 scans. Although the presence of htempo has been shown to cause small chemical shifts in Ag^+ ions in various solvents,[9] in the present complexes where the silver is already ligated by soft donors we did not observe significant differences on varying the relative amount of htempo, and in view of the large chemical shifts observed, any such effects are judged to be negligible.

The ^{109}Ag spectra of $[Ag(RSCH_2CH_2SR)_2]BF_4$ in CH_2Cl_2 at 300 K showed single sharp lines (Table 8) at δ +1004 (R = Me) or δ +944 (R = Ph), which were not significantly shifted by adding an excess of the appropriate free ligand. Hence for these complexes we conclude that the resonances are due to AgS_4 species. On cooling the solutions a significant high frequency shift in δ(^{109}Ag) was observed of approximately +0.7 ppm K^{-1}. Similar results were obtained for the diselenoether analogues (Table 8) and here too the results are consistent with $AgSe_4$ species as established in the solid state by the crystal study. As in the ^{77}Se spectra no coupling to ^{109}Ag was observed.

The spectra of complexes of the trimethylene-backboned ligands were more difficult to obtain due to the poorer solubility, and showed significant differences with the ligand involved. Hence they will be briefly described in turn. In

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* ^{107}Ag, $I = \frac{1}{2}$, 51.8%, Ξ = 4.047, D_c (receptivity compared to ^{13}C) = 0.195; ^{109}Ag, $I = \frac{1}{2}$, 48.2%, Ξ = 4.653, D_c = 0.276.

$MeNO_2$ solution at 250 K $[Ag(MeSCH_2CH_2CH_2SMe)_2]BF_4$ exhibited a sharp resonance at δ +901, and on addition of excess (*ca.* five-fold) of free ligand shifts to δ +926. At 300 K the single resonance is weak and broad at δ +840. In contrast, although reasonably soluble in acetone, the complex $[Ag(PhSCH_2CH_2CH_2SPh)_2]BF_4$ gave only a weak resonance δ +948 (200 K) and no signal was evident at room temperature, even on addition of an excess of ligand. The ^{109}Ag NMR spectra obtained from $[Ag(MeSeCH_2CH_2CH_2SeMe)_2]BF_4$ were qualitatively similar to those of the sulfur analogue, specifically in $MeNO_2$ solution a weak resonance at δ +829 (300 K) which shifted to high frequency on cooling to δ +898 (250 K). Addition of an excess of free ligand also caused a high frequency shift, for example to δ +924 (250 K). Repeated attempts to observe a convincing silver resonance from solutions of $[Ag(PhSeCH_2CH_2CH_2SePh)_2]BF_4$ in non-co-ordinating solvents (Me_2CO or $MeNO_2$) over the temperature range 300–250 K were rather unsuccessful. At 300 K a very weak resonance was observed at δ +729 ($MeNO_2$). At 250 K a sharper resonance appeared in the presence of an excess of ligand at δ +915. In MeCN solution at 300 K, the complex gave a strong, sharp resonance at δ +598, and the solution had a ^{77}Se NMR resonance at δ +272, indicative of a different constitution in this solvent (see below). The behaviour of the two telluroether complexes was more straightforward, in that both showed sharp ^{109}Ag resonances at 300 K in non-co-ordinating solvents, which shifted to high frequency on addition of an excess of ligand and on cooling (Table 8).

Attempted Oxidations to Ag^{II}.—Transient formation of deep blue silver(II) species identified by ESR spectroscopy, has been observed on reaction of several silver(I) thiamacrocycle complexes with concentrated $HClO_4$ or H_2SO_4.[1,3] Cyclic voltammetry studies of the silver(I) complexes of the dithioethers showed only completely irreversible oxidations at highly positive potentials. Treatment of the complexes with 70% perchloric acid did not generate any deeply coloured species, and we conclude that these acyclic ligands do not stabilise Ag^{II}.

Discussion

The X-ray crystallography has demonstrated that for the four cases examined, Group 16 donor bidentate ligand complexes of silver(I) are mononuclear chelates if the ligand has a C_2 backbone, and polymeric with a bridging ligand for those with C_3 backbones. In one case $[Ag_n(MeSCH_2CH_2CH_2SMe)_n][BF_4]_n$ the bonding mode of the dithioether has not been previously observed.[6] From the spectroscopic properties of the other complexes it appears that their structures conform with this pattern, although for d^{10} ions it is always possible that changes in the counter anion or reaction conditions will generate different solid-state structures {*cf.* $[Cu(Me_2PCH_2CH_2PMe_2)_2]^+$ and $[(Me_2PCH_2CH_2PMe_2)Cu(\mu\text{-}Me_2PCH_2CH_2PMe_2)_2Cu(Me_2PCH_2CH_2PMe_2)]^{2+}$ (ref. 7), and for silver(I) macrocycles[1]}.

The other features worthy of more discussion are the solution behaviour of these homoleptic silver(I) cations as probed by ^{109}Ag, supplemented by ^{77}Se and ^{125}Te NMR spectroscopy. It has been observed[17] with various weakly bonded N or O donor ligand complexes of silver AgL_n^+ that as the ratio L:Ag increases, the silver resonance shifts progressively to high frequency. A single ^{109}Ag resonance is observed in these cases, corresponding to the weighted-mean chemical shift of the various species present, which are interconverting rapidly on the NMR time-scale. At the other extreme complexes such as $[Ag(diphosphine)_2]^+$ show sharp resonances with well resolved $^{109}Ag\text{-}^{31}P$ couplings, showing exchange is slow on the NMR time-scale.[18] The present Group 16 complexes seem to be intermediate in behaviour, in that no couplings to ^{77}Se or ^{125}Te were observed even at low temperatures, and the spectra obtained in the presence of added ligand, revealed exchange to be fast down to low temperatures. Nonetheless for the chelated complexes with C_2-backboned ligands, the ^{109}Ag chemical shifts were unchanged in the presence of an excess of the appropriate ligand, showing that despite the fast exchange, the equilibria $[Ag(L\text{–}L)_2]^+ \rightleftharpoons [Ag(L\text{–}L)]^+ + L\text{–}L$ lie well to the left. From the data on the chelated complexes with C_2-backboned ligands, ^{109}Ag chemical shifts δ *ca.* 900–1100 are characteristic of $Ag(S/Se)_4$ species.

The behaviour of the complexes with C_3-backboned ligands is more complicated. The infinite polymer structures found in the solid state must be disrupted in solution. In fact they dissolve, sometimes with difficulty, in weak donor solvents such as acetone or $MeNO_2$ to give solutions which exhibit single ^{109}Ag resonances at somewhat lower frequencies than the C_2-backboned analogues. Moreover addition of an excess of ligand to these solutions results in a high frequency shift of the ^{109}Ag resonance by $\leqslant 50$ ppm (Table 8). The fast exchange and the absence of any resolved couplings even at the lowest temperatures, prevents conclusive identification of the species, but the behaviour is consistent with the presence of a mixture of species $Ag(S/Se/Te)_4$, $Ag(S/Se/Te)_3$ and possibly lower co-ordination numbers, in fast equilibrium. The addition of an excess of ligand shifts the equilibria in favour of the higher co-ordinated species. We have not investigated the behaviour of these complexes in stronger donor solvents in any detail, although we did observe that $[Ag(PhSeCH_2CH_2CH_2SePh)_2]BF_4$ in MeCN solution had $\delta(^{109}Ag)$ at 598. This much lower resonance frequency suggests fewer Se donors around the silver, presumably a mixture of species $[Ag(PhSeCH_2CH_2CH_2SePh)(MeCN)_x]^+$. Consistent with this, the ^{77}Se resonance of this solution (δ +272) was intermediate between that of the bis(diselenoether) complex and free ligand.

As we noted for the corresponding copper(I) complexes,[7] the silver complexes of Group 16 donor ligands are much more labile than their Group 15 analogues, which results in more diverse solution behaviour. More generally this study has shown that despite its low sensitivity, direct observation of ^{109}Ag resonances can yield invaluable information about silver(I) complexes in solution.

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