Unique Structural Features in Silver(I) Dithioether Complexes: the Single-crystal Structures of $[Ag_n(PhSCH_2CH_2CH_2SPh)_{2n}](BF_4)_n{\cdot}0.5nH_2O$ and $[Ag_n(MeSCH_2CH_2CH_2SMe)_n](BF_4)_n$

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The X-ray structure of $[Ag_n(PhSCH_2CH_2CH_2SPh)_{2n}]^{n+}$ shows an infinite array of tetrahedral Ag^I atoms coordinated *via* one S-donor of four distinct $PhSCH_2CH_2CH_2SPh$ ligands, whereas $[Ag_n(MeSCH_2CH_2CH_2SMe)_n]^{n+}$ is a chain polymer involving trigonal $(\mu_2\text{-}S)_2,S$ ligation with one S-donor bridging two adjacent Ag^I centres while the other S-donor of the dithioether ligand is non-bridging.

Fully characterised examples of coordination complexes of thioether ligands with d^{10} Ag^I ions are mainly restricted to macrocyclic thioethers[1,2] and a small number of examples with monodentate thioethers.[3] As part of a systematic investigation of the interaction of acyclic thioether, selenoether and telluroether ligands with Ag^I centres, aimed at identifying trends in X-ray structural, solution ^{109}Ag, ^{77}Se and ^{125}Te NMR spectroscopic and redox data, we have synthesised and structurally characterised two distinct and highly unusual polymeric silver(I) complexes of the dithioether ligands $RSCH_2CH_2CH_2SR$ (R = Ph, Me); one of which (R = Me) displays an unprecedented coordination mode for the non-chelating dithioether in which one thioether S coordinates *via* both lone pairs while the other uses only one.

Reaction of $AgBF_4$, with 2 molar equivalents of $RSCH_2CH_2CH_2SR$ in acetone solution, affords colourless solutions from which air-stable but moderately light-sensitive white solids can be isolated following addition of diethyl ether. Microanalyses are consistent with the 1 : 2 Ag : ligand species $[Ag(RSCH_2CH_2CH_2SR)_2]BF_4$ for R = Ph and Me, and FAB-MS (3-noba matrix) for these products reveal $[^{107/109}Ag(RSCH_2CH_2CH_2SR)_2]^+$ (R = Ph, m/z = 627/629; R = Me, m/z = 379/381) and $[^{107/109}Ag(RSCH_2CH_2CH_2SR)]^+$ (R = Ph, m/z = 367/369; R = Me, m/z = 243/245) as the only silver-containing species present.† Given the propensity for these dithioether ligands to form six-membered chelate rings upon coordination to other metal ions, we were very surprised when a single-crystal X-ray analysis of $[Ag(PhSCH_2CH_2CH_2SPh)_2]BF_4$‡ revealed (Fig. 1) an unexpected three-dimensional infinite lattice of formula $[Ag_n(PhSCH_2CH_2CH_2SPh)_{2n}]^{n+}$, involving monodentate S-ligation of four distinct dithioether ligands to Ag^I giving an approximately tetrahedral geometry at the metal ion, with the second S-donor of each ligand linking to four other Ag^I ions, hence generating the infinite three-dimensional array, Ag–S(1) 2.588(2), Ag–S(2) 2.623(3), Ag–S(3) 2.572(2), Ag–S(4) 2.573(3) Å. Discrete BF_4^- anions maintain electroneutrality.

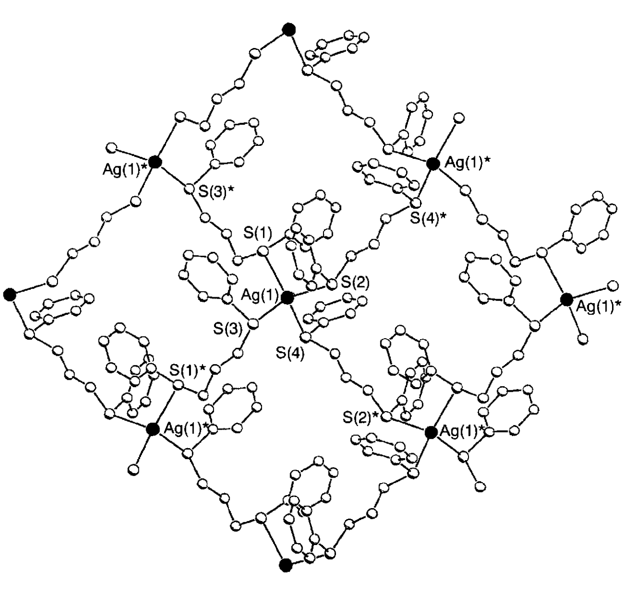

Fig. 1 View of the structure of a portion of the cationic three-dimensional polymer $[Ag_n(PhSCH_2CH_2CH_2SPh)_{2n}]^{n+}$ with numbering scheme adopted (H atoms are omitted for clarity and atoms marked with an asterisk are related by symmetry to those with no asterisks)

In contrast, a single-crystal X-ray analysis on the silver(I) complex of $MeSCH_2CH_2CH_2SMe$§ shows (Fig. 2) that despite the 1 : 2 Ag : dithioether ratio established for the original solid precipitated, in the crystals this compound comprises an infinite chain polymer, $[Ag_n(MeSCH_2CH_2CH_2SMe)_n]^{n+}$, involving approximately trigonal planar Ag^I centres coordinated to two almost symmetrically bridging thioether donors, and one non-bridging thioether, giving a 1 : 1 Ag : dithioether ratio. Thus, S(1) uses both of its lone pairs to coordinate to adjacent silver ions (related by a crystallographic 2_1 screw axis). Contrary to expectation, this bridging results in a small elongation of the Ag–S bond lengths, Ag–S(1) 2.520(2), Ag–S(1)* 2.560(3) Å, relative to the non-bridging thioether–Ag bond, Ag–S(2) 2.475(3) Å. The $S,\mu_2\text{-}S$ bonding mode for $MeSCH_2CH_2CH_2SMe$ observed in this complex is, to our knowledge, unprecedented in acyclic thioether chemistry. A small number of thioether macrocyclic complexes of Ag^I

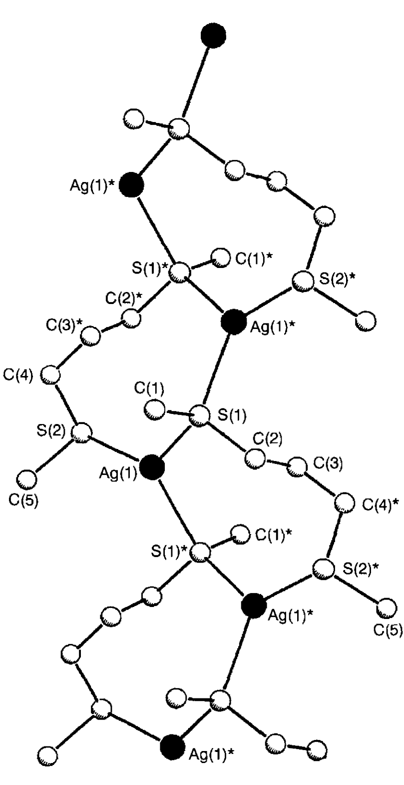

Fig. 2 View of the structure of a portion of the chain polymer $[Ag_n(MeSCH_2CH_2CH_2SMe)_n]^{n+}$ with numbering scheme adopted (H atoms are omitted for clarity and the atoms marked with an asterisk are related by symmetry to those with no asterisks)

incorporating bridging thioether donor atoms have been reported, for example $[Ag_2([15]aneS_5)_2]^{2+}$ in which the Ag^I centres are linked by two asymmetrically bridging thioether donors.[2] Similar Ag–S bond lengths are observed in these complexes. The bridging mode has also been observed with monodentate thioethers, R_2S, most of which bridge metal–metal bonded systems, although this is a quite different scenario from that described for the silver complex in this paper.[4,5] The $MeSCH_2CH_2CH_2SMe$ ligands in the new complex are not chelating, but link adjacent, non-interacting Ag^I centres, Ag(1)···Ag(1)* 4.33 Å. The angles around Ag(1), 115.97(5) [S(1)–Ag(1)–S(1)*], 126.60(9) [S(1)–Ag(1)–S(2)] and 115.42(8)° [S(1)*–Ag(1)–S(2)], give a distorted trigonal arrangement.

Efforts are currently underway to establish the factors controlling formation of polymeric *vs.* monomeric Ag^I cations in these dithioether and related diselenoether and ditelluroether ligand complexes; for example the nature of the R group, and the length of the methylene backbone linking the donor atoms. In this context, we have shown that the crystal structure of the C_2-linked diselenoether complex $[Ag(MeSeCH_2CH_2SeMe)_2]BF_4$ involves discrete, mononuclear bis-chelate $[Ag(MeSeCH_2CH_2SeMe)_2]^+$ cations.[6]

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Footnotes

† Satisfactory spectroscopic and analytical data were obtained for these compounds.

‡ *Crystal data* for $C_{30}H_{32}AgBF_4S_4{\cdot}0.5H_2O$: M = 723.5, monoclinic, space group $P2_1/c$, a = 13.276(7), b = 12.909(3), c = 20.627(4) Å, β = 94.53(2)°, V = 3524 Å^3, Z = 4, D_c = 1.364 g cm^{-3}, μ(Mo-Kα) = 0.849 mm^{-1}. A colourless crystal (0.55 × 0.40 × 0.30 mm) was grown from nitromethane–diethyl ether, and mounted on a Rigaku AFC7S four-circle diffractometer. Data collection at 295 K using Mo-Kα X-radiation (λ = 0.71073 Å), ω–2θ scans gave 6062 unique reflections (R_{int} = 0.04) of which 3858 with $F > 4\sigma(F)$ were used in all calculations. The data were corrected for absorption using ψ-scans (max. and min. transmission factors = 1.00 and 0.92, respectively). The structure was solved using Patterson methods[7] and developed by iterative cycles of least-squares refinement and difference Fourier synthesis which revealed the cationic $[Ag(PhSCH_2CH_2CH_2SPh)_2]^+$ fragment and BF_4^- anion in the asymmetric unit.[8] One 50% occupied water solvent molecule was found to be associated per Ag^I ion. The disordered BF_4^- anion was modelled using partial F atom occupancies. The phenyl rings were refined as rigid groups, and the structure was refined by full-matrix least squares with anisotropic thermal parameters for all non-H atoms. H atoms were included in fixed, calculated positions. At final convergence, R_1 = 0.088, wR_2 = 0.245, S = 1.05 for 314 parameters and the final ΔF synthesis showed only one peak greater than 1.34 e Å^{-3}.

§ *Crystal data* for $C_5H_{12}AgBF_4S_2$: M = 330.94, monoclinic, space group $P2_1/c$, a = 7.882(3), b = 7.059(4), c = 18.964(3) Å, β = 96.11(2)°, V = 1049.2(6) Å^3, Z = 4, D_c = 2.095 g cm^{-3}, μ(Mo-Kα) = 2.321 mm^{-1}. A colourless crystal (0.25 × 0.20 × 0.10 mm) was grown from dissolution of the pure 1:2 Ag:$MeSCH_2CH_2CH_2SMe$ compound in CH_2Cl_2–diethyl ether. The selected crystal was coated with mineral oil on a glass fibre and mounted on a Rigaku AFC7S four-circle diffractometer. Data collection at 150 K using Mo-Kα X-radiation (λ = 0.71073 Å), ω–2θ scans gave 2018 unique reflections (R_{int} = 0.05) of which 1046 with $F > 6\sigma(F)$ were used in all calculations. The structure was solved by direct methods[7] and developed by iterative cycles of least-squares refinement and difference Fourier syntheses which revealed the cationic $[Ag(MeSCH_2CH_2CH_2SMe)]^+$ repeating fragment and discrete BF_4^- anion in the asymmetric unit.[9] The structure was refined by full-matrix least-squares, with anisotropic thermal parameters for all non-H atoms: H atoms were included in fixed, calculated positions. At final convergence, R = 0.035, R_w = 0.032, S = 1.50 for 118 parameters and the final ΔF synthesis showed no $\Delta\rho$ outside the range +0.58 to −0.81 e Å^{-3}. A unit cell measurement on another crystal from the batch gave the same cell parameters for both compounds and space group absences, indicating that the structure obtained is representative of the whole batch of crystalline material. Atomic coordinates, bond lengths and angles, and thermal parameters for both compounds have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

References

1 For examples see: J. Clarkson, R. Yagbasan, P. J. Blower and S. C. Rawle, *J. Chem. Soc., Chem. Commun.*, 1987, 950; H.-J. Kuppers, K. Wieghardt, Y.-H. Tsay, C. Kruger, B. Nuber and J. Weiss, *Angew. Chem., Int. Ed. Engl.*, 1987, **26**, 575; A. J. Blake, R. O. Gould, A. J. Holder, T. I. Hyde and M. Schröder, *Polyhedron*, 1989, **8**, 513; B. de Groot and S. J. Loeb, *Inorg. Chem.*, 1991, **30**, 3103.

2 A. J. Blake, R. O. Gould, G. Reid and M. Schröder, *J. Chem. Soc., Chem. Commun.*, 1990, 974; A. J. Blake, D. Collison, R. O. Gould, G. Reid and M. Schröder, *J. Chem. Soc., Dalton Trans.*, 1993, 521; A. J. Blake, G. Reid and M. Schröder, *J. Chem. Soc., Chem. Commun.*, 1992, 1074.

3 B. Noren and A. Oskarsson, *Acta Chem. Scand., Ser. A*, 1984, **38**, 479; J. C. Barnes and J. D. Paton, *Acta Crystallogr., Sect. C*, 1984, **40**, 72.

4 For examples see: F. A. Cotton and R. C. Najjar, *Inorg. Chem.*, 1981, **20**, 2716; P. M. Boorman, K. J. Moynihan and R. T. Oakley, *J. Chem. Soc., Chem. Commun.*, 1982, 899; P. M. Boorman, K. J. Moynihan and K. A. Kerr, *J. Chem. Soc., Chem. Commun.*, 1981, 1286.

5 D. L. Sales, J. Stokes and P. Woodward, *J. Chem. Soc. A*, 1968, 1852.

6 J. R. Black, N. R. Champness, W. Levason and G. Reid, unpublished work.

7 SHELXS-86, Program for Crystal Structure Solution, G. M. Sheldrick, University of Cambridge, 1986.

8 SHELXL-93, Program for Crystal Structure Refinement, G. M. Sheldrick, University of Göttingen, 1993.

9 TeXsan: Crystal Structure Analysis Package, Molecular Structure Corporation, The Woodlands, TX, 1992.