Thioether macrocycles as spacers for crystal engineering: synthesis and crystal structures of $[Ag_2([24]aneS_8)(CF_3SO_3)_2(MeCN)_2]_\infty$ and $[Ag([16]aneS_4)(BF_4)]_\infty$ ([24]aneS$_8$ = 1,4,7,10,13,16,19,22-octathiacyclotetracosane; [16]aneS$_4$ = 1,5,9,13-tetrathiacyclohexadecane)

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The polymeric complexes $[Ag_2([24]aneS_8)(CF_3SO_3)_2(MeCN)_2]_\infty$ and $[Ag([16]aneS_4)(BF_4)]_\infty$ show infinite ladder and layered structures respectively, with the thioether crown controlling the multi-dimensional architecture.

The coordination chemistry of crown thioethers has been of great interest over the past decade.[1] Most studies have been focused on the coordination chemistry of these ligands to transition metal ions,[1–4] although very little information is available on Ag^I complexes with crown thioethers containing four or eight S-donor atoms.[5] Parallel to this, the design of solid-state architectures has become an area of increasing interest,[6–9] with attention focused predominantly upon the use of supramolecular contacts (particularly hydrogen bonding) between suitable organic molecules to generate multi-dimensional arrays and networks.[6–9] In comparison, the design of inorganic networks,[10–12] particularly polymeric metal complexes, is less well developed[13] with most of the examples being based upon linear bridging ligands bound to tetrahedral metal ions such as Cu^I and Ag^I.[11,12,14] Few polymeric structures for thioether crown complexes have been reported, dimensional control being achieved mainly by variation of the counter-anion.[2,5] We report herein two new polymeric thioether crown complexes of Ag^I whose multi-dimensional architecture is controlled by the thioether crowns building blocks.

Reaction of [24]aneS$_8$ with 2 equiv. of $AgCF_3SO_3$ in CH_2Cl_2–CH_3CN affords a white solid which can be recrystallised from CH_3CN–Et_2O.† A single crystal X-ray structure determination‡ confirms the product to be a one-dimensional polymer, $[Ag_2([24]aneS_8)(CF_3SO_3)_2(MeCN)_2]_\infty$, in which each Ag^I ion is coordinated to four S-donors in a distorted tetrahedral geometry with S–Ag–S angles ranging from 85.83(5) to 127.36(5)° and Ag–S bond distances from 2.5400(14) to 2.627(2) Å. The four S-donors come from two different ligand molecules to generate an infinite ladder polymer along the *b* axis (Fig. 1). Within the ladder, pairs of symmetry-related Ag^I ions are coordinated between two macrocyclic ligands, so that all eight S-donors of each [24]aneS$_8$ molecule are engaged in coordination. Each metal ion is also a spiro centre, being the common atom of two almost perpendicular AgS_2C_2 rings. The macrocycle adopts a unique pattern of alternate *endo*- and *exo*-orientated S-donors, with 9 out of 12 torsion angles less than 90° and all the S–C–C–S torsion angles having a *gauche* arrangement. Stacks of $CF_3SO_3^-$ ions and acetonitrile molecules are observed between the polymeric chains. Significantly, the use of NO_3^- as counter-anion leaves the structure of the polymeric Ag^I complex unchanged in $[Ag_2([24]aneS_8)(NO_3)_2(H_2O)]_\infty$.

Reaction of [16]aneS$_4$ with $AgBF_4$ in 1 : 1 molar ratio in CH_3CN–CH_2Cl_2 affords a white powder which can be recrystallised from hot dmf.† A single crystal X-ray structure determination‡ confirms the product to be a three-dimensional polymer, $[Ag([16]aneS_4)(BF_4)]_\infty$. Each Ag^I ion occupies a crystallographic $\bar{4}$ (S_4) site and is coordinated by four symmetry-equivalent S-donor atoms in a tetrahedral geometry with S–Ag–S angles of 119.44(2) and 90.98(3)° and Ag–S bond distances of 2.6121(7) Å. The donor atoms are derived from four symmetry-related [16]aneS$_4$ molecules, each of which is bound to four different Ag^I ions (Fig. 2). The mcrocycle adopts a [4444] conformation with all the sulfur atoms *exo*-oriented. The [16]aneS$_4$ molecules lie in sheets perpendicular to the *c* axis, within which 24-membered rings can be recognised: these comprise four Ag^I ions and one S–C–C–C–S edge from four different thioether ligands (Fig. 2). Successive layers are stacked offset along *c* so that the [16]aneS$_4$ molecules and the 24-membered rings alternate, giving rise to channels within which the BF_4^- anions lie at the centres of the larger rings. This compound represents the first structurally characterized complex of Ag^I with an unfunctionalised tetradentate thioether

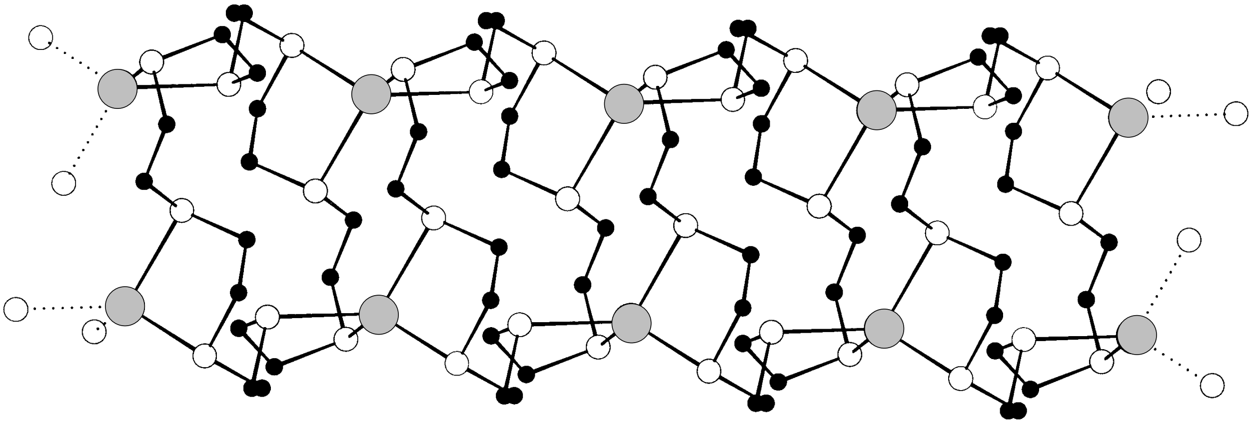

Fig. 1 Packing diagram for the $\{[Ag_2([24]aneS_8)]^{2+}\}_\infty$ polymeric chain. Counter-anion omitted for clarity. Carbon, small black circles, sulfur, white circles; silver, large grey circles.

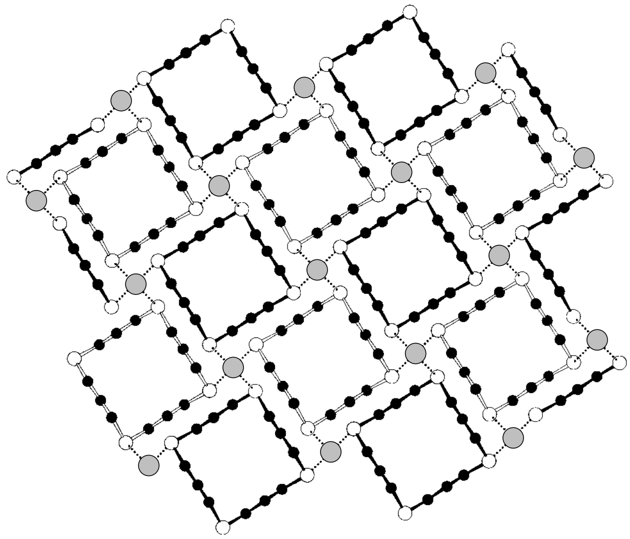

Fig. 2 View of the packing diagram for the $\{[Ag([16]aneS_4)]^+\}_\infty$ polymeric complex along the *c* axis. Counter-anion omitted for clarity. Atoms shaded as in Fig. 1.

crown, although a polymeric structure has been reported with the ligand $(OH)_2$-[16]aneS_4[5] in which the OH groups play a major role in the crystal packing through extensive hydrogen bonding.

This work illustrates the potential of thioether crowns as building blocks for the synthesis of inorganic architectures using their *exo*-orientated S-donors. We are currently investigating how we may fine-tune the multi-dimensional architectures of polymeric Ag^I complexes with tetradentate thioether crowns.

We thank the EPSRC for financial support.

Footnotes and References

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† $[Ag_2([24]aneS_8)(CF_3SO_3)_2(MeCN)_2]_\infty$. To a well stirred solution of [24]aneS_8 (50 mg, 0.104 mmol) in CH_2Cl_2–CH_3CN (20 ml, 1 : 1 v/v) was added a solution of $AgCF_3SO_3$ (53.44 mg, 0.208 mmol) in CH_3CN (5 ml). The mixture was stirred at room temp. for 1 h. The white solid formed was filtered off and dried under reduced pressure (70 mg, 62.5% yield). Single crystals were obtained by recrystallization from CH_3CN–Et_2O.

$[Ag([16]aneS_4)(BF_4)]_\infty$. To a well stirred solution of [16]aneS_4 (35.44 mg, 0.1195 mmol) in CH_2Cl_2–CH_3CN (15 ml, 1 : 1 v/v) was added a solution of $AgBF_4$ (23.26 mg, 0.1195 mmol) in CH_3CN (5 ml). The mixture was stirred at room temp. for 24 h. The white solid formed was filtered off and dried under reduced pressure (30 mg, 51.0% yield). Single crystals were obtained by recrystallization from hot dmf. Satisfactory elemental analyses were obtained for both compounds.

‡ Stoe Stadi-4 four-circle diffractometer, graphite-monochromated Mo-Kα radiation, ω–θ scans, θ_{max} = 25°. Both structures were solved using direct methods[15] and all non-H atoms were located using subsequent difference Fourier methods.[16] Hydrogen atoms were placed in calculated positions and thereafter allowed to ride on their parent atoms.

Crystal data for $[Ag_2([24]aneS_8)(CF_3SO_3)_2(MeCN)_2]_\infty$: $C_{22}H_{38}Ag_2F_6N_2O_6S_{10}$, M = 1076.88, monoclinic, space group $P2_1/c$ (no. 14), a = 13.285(2), b = 6.3340(10), c = 22.547(3) Å, β = 91.721(14)°, U = 1890.7(3) Å^3, Z = 2, $F(000)$ = 1080, D_c = 1.892 g cm^{-3}, μ(Mo-Kα) = 1.66 mm^{-1}. Colourless plate (0.07 × 0.21 × 0.25 mm), ψ-scan absorption corrections (T_{min} = 0.61, T_{max} = 0.81), 3344 unique reflections, of which 2255 had $I \geqslant 2\sigma(I)$. The weighting scheme $w^{-1} = [\sigma^2(F_o^2) + (0.0252P)^2 + 0.40P]$, $P = [\max(F_o^2, 0) + 2F_c^2]$, was applied. At final convergence R_1 $[I \geqslant 2\sigma(I)]$ = 0.0431, wR_2 (all data) = 0.0874 for 218 refined parameters, S = 1.03, $(\Delta/\sigma)_{max}$ = −0.001, $\Delta\rho_{max}$ = 0.55 e Å^{-3}.

Crystal data for $[Ag([16]aneS_4(BF_4)]_\infty$: $C_{12}H_{24}AgBF_4S_4$, M = 491.23, tetragonal, space group $I\bar{4}$ (no. 82), a = 10.3955(14), c = 8.227(2) Å, U = 889.1(2) Å^3, Z = 2, $F(000)$ = 496, D_c = 1.835 g cm^{-3}, μ(Mo-Kα) = 1.632 mm^{-1}. Colourless tablet (0.15 × 0.27 × 0.29 mm), ψ-scan absorption corrections (T_{min} = 0.614, T_{max} = 0.709), 778 unique reflections (R_{int} = 0.040), of which 767 had $I \geqslant 2\sigma(I)$. The weighting scheme $w^{-1} = [\sigma^2(F_o^2) + (0.0272P)^2 + 0.51P]$, $P = [\max(F_o^2, 0) + 2F_c^2]$ was adopted. At final convergence R_1 $[I \geqslant 2\sigma(I)]$ = 0.0176, wR_2 (all data) = 0.0471 for 51 refined parameters, S = 1.07, $(\Delta/\sigma)_{max}$ = 0.001, $\Delta\rho_{max}$ = 0.38 e Å^{-3}. CCDC 182/573.

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Received in Cambridge, UK, 7th July 1997, 7/04796G