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Notes

Silver(I) Coordination Polymers Using Thioether Macrocycle Building Blocks

Alexander J. Blake, Neil R. Champness,*,†
Steven M. Howdle,* and Paul B. Webb

School of Chemistry, The University of Nottingham,
University Park, Nottingham NG7 2RD, U.K.

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Introduction

Inorganic crystal engineering has undergone a recent expansion primarily through the development of coordination polymer chemistry.[1] This chemistry has given rise to many remarkable structures through the use of various transition metal junctions and primarily bipyridyl based bridging ligands.[1,2] Ligands with donor atoms other than aromatic nitrogen have received far less attention but have much to offer the coordination polymer chemist. For example, thioether donors are particularly interesting as they coordinate soft transition metals similarly to pyridine donors but, due to the angle at the S-donor and the bridging capacity of thioethers, motifs inaccessible using simpler donor systems become accessible.[3,4] This has been illustrated not only with bidentate thioethers[3] but also with macrocyclic ligands.[4] This may at first seem surprising as macrocyclic ligands, and particularly [9]aneS_3, are often cited as good examples of capping ligands that encourage both the blocking of transition metal coordination sites and the formation of discrete metal complexes.[5] However, the bridging potential of thioether macrocycles is perhaps less surprising when one considers the conformations adopted by the free ligands: all the sulfur lone pairs are oriented in an exo fashion, an arrangement which is perfectly organized for the generation of coordination polymers. The larger thioether macrocycles and those which incorporate propylene backbones, such as [12]aneS_3,[4a] [16]aneS_4,[4b] $(HO)_2$-[16]aneS_4,[4c] [15]aneS_5,[4d] and [24]aneS_8[4b] show an increased tendency to generate polymeric products,[5] and this is particularly noticeable in the products of their reactions with Ag(I).[4] Indeed Ag(I) has a strong tendency to form oligomeric species with thioether macrocycles[4−6] and even thioether cryptands,[7] reflecting its versatile coordination sphere. We now demonstrate that this tendency to form polymers is not limited to the larger thioether macrocycles and that even [9]aneS_3 can be exploited to generate new coordination polymers.

The anion used when constructing Ag(I) coordination polymers has been shown to be extremely influential in affecting, or even determining, the overall structure of the network formed.[2c,8] Bearing this in mind, we are investigating the role of strongly coordinating diketonate anions, which have been shown to limit the number of available coordination sites, allowing controlled formation of one-dimensional polymeric species.[9] We now report the results of our studies investigating coordination polymers constructed from Ag[hfpd] and the macrocycles [14]aneS_4 or [9]aneS_3.

Experimental Section

All manipulations were carried out under an inert atmosphere using standard Schlenk techniques and cannula transfer. Solvents used were purified and dried according to literature methods[10] and stored over 4Å molecular sieves. Silver(I) oxide, 1,4,7,-trithiacyclononane ([9]aneS_3) and 1,4,8,11-tetrathiacyclododecane ([14]aneS_4) were used as received (Aldrich) without further purification. 1,1,1,5,5,5-Hexafluoro-2,4-pentanedione (H-hfpd) (Aldrich) was stored under a nitrogen atmosphere. NMR spectra were recorded on a Bruker Avance DPX300 spectrometer using protio impurities of the deuterated solvent as a reference for ^{1}H and ^{13}C chemical shifts. ^{19}F chemical shifts were referenced against $CFCl_3$. Single-crystal IR spectra were recorded on

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[†] E-mail: Neil.Champness@nottingham.ac.uk.

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Table 1. Crystallographic Summary

	$[Ag_2(hfpd)_2([14]aneS_4)]_\infty$	$[Ag(hfpd)([9]aneS_3)]_\infty$
chemical formula	$C_{20}H_{22}Ag_2F_{12}O_4S_4$	$C_{11}H_{13}AgF_6O_2S_3$
M	898.36	495.26
space group	$P\bar{1}$	$P2_1/n$
a/Å	7.937(3)	14.980(3)
b/Å	8.831(5)	7.228(2)
c/Å	11.031(9)	15.224(4)
α/deg	103.63(5)	90
β/deg	94.55(5)	101.90(2)
γ/deg	100.61(4)	90
V/Å^3	732.4(8)	1613.0(7)
Z	1	4
T/°C	−73(2)	−123(2)
λ/Å	0.71073	0.71073
ρ_{calc}/mg m^{-3}	2.037	2.039
μ/mm^{-1}	1.726	1.702
R^a	0.0362	0.0390
$R_w{}^b$	0.0876	0.0906

$^a R = R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. $^b R_w = \sqrt{\{\sum[w(F_o{}^2 - F_c{}^2)^2]/\sum[w(F_o{}^2)^2]\}}$.

a Perkin-Elmer I-Series microscope coupled with a Perkin-Elmer System 2000 FT-IR spectrometer. Mass spectrometry data were obtained using a Vacuum Generators VG 70E micromass spectrometer in the FAB positive ion mode. Elemental analyses were performed by the Nottingham School of Chemistry microanalytical service.

Synthesis. $[Ag_2(hfpd)_2([14]aneS_4)]_\infty$. A solution of $Ag_2(hfpd)_2(H_2O)$[11] (0.1166, 0.163 mmol) in THF (5 cm^3) was layered onto a solution of $[14]aneS_4$ (0.0485 g, 0.181 mmol) in CH_2Cl_2 (5 cm^3). The solutions were left for 24 h at room temperature to afford $[Ag_2(hfpd)_2([14]aneS_4)]_\infty$ as colorless needle crystals. Found (calcd for $C_{20}H_{22}Ag_2F_{12}O_4S_4$): C 26.52 (26.74), H 2.24 (2.47). IR (single crystal) (ν: cm^{-1}): 3287 (w), 3137 (w), 2978 (w), 2937 (w), 2855 (w), 1627 (m), 1603 (m), 1582 (m), 1558 (s), 1530 (s), 1443 (s), 1418 (s), 1354 (w), 1308 (s), 1239 (s), 1180 (s), 1159 (s), 1122 (s), 1053 (w), 1007 (w), 962 (w), 941 (w), 924 (w), 861 (w), 828 (w), 800 (w), 770 (w). ^{1}H NMR (300.13 MHz, DMSO, 298 K): $\delta = 1.97$ (4H, quin, $SCH_2CH_2CH_2S$), 2.84 (8H, t, $SCH_2CH_2CH_2S$), 2.95 (8H, s, SCH_2CH_2S), 5.27 (2H, s, C*H*). ^{13}C NMR (75.47 MHz, DMSO, 298 K): $\delta = 28.74$ (s, $SCH_2CH_2CH_2S$), 31.24 (s, $SCH_2CH_2CH_2S$), 82.13 (s, *C*H), 117.87 (q, $^1J_{CF}$ 294.11 Hz, CF_3), 170.89 (q, $^2J_{CF}$ 29.05 Hz, *C*O). ^{19}F NMR (282.42 MHz, DMSO, 298 K) $\delta = -75.98$ (s, CF_3).

$[Ag(hfpd)([9]aneS_3)]_\infty$. H-hfpd (0.2 cm^3, 1.413 mmol) was added dropwise by syringe to a rapidly stirred slurry of silver(I) oxide (0.186 g, 0.795 mmol) and $[9]aneS_3$ (0.254 g, 1.408 mmol) in THF (ca. 20 cm^3). After 30 min, when dissolution was complete the solution was filtered to remove any unreacted oxide and the volume of the solvent was reduced in vacuo to ca. 5 cm^3. Slow diffusion of diethyl ether into the solution at room temperature yielded $[Ag(hfpd)([9]aneS_3)]_\infty$ as pale yellow colorless needles. Found (calcd for $C_{11}H_{13}AgF_6O_2S_3$): C 26.68 (26.68), H 2.50 (2.65). IR (single crystal) (ν: cm^{-1}): 3278 (w), 3112 (w), 2995 (w), 2977 (w), 2922 (w), 1644 (m), 1540 (m), 1519 (m), 1450 (m), 1409 (m), 1307 (w), 1287 (m), 1249 (s), 1195 (s), 1139 (s), 1082 (s), 985 (w), 939 (w), 924 (m), 886 (m), 833 (m), 821 (m), 801 (m), 790 (m), 765 (m). ^{1}H NMR (300.13 MHz, DMSO 298 K): $\delta =$ 2.89 (12H, s, SCH_2CH_2S), 5.29 (1H, s, C*H*).^{13}C NMR (75.47 MHz, DMSO, 298 K): $\delta = 29.08$ (s, SCH_2CH_2S), 83.19 (s, *C*H), 117.87 (q $^1J_{CF}$ 292.82 Hz, CF_3), 172.64 (q, $^2J_{CF}$ 29.59 Hz, *C*O). ^{19}F NMR (282.42 MHz, DMSO, 298 K) $\delta = -75.96$ (s, CF_3).

X-ray Data Collection, Solution, and Refinement. Crystal data and summaries of the crystallographic analyses for both complexes are given in Table 1. Diffraction data for both compounds were collected on a Stoë Stadi-4 four-circle diffractometer equipped with an Oxford Cryosystems open-flow cryostat[12] using $\omega-\theta$ scans and graphite-monochromated Mo Kα radiation. In both instances a numerical absorption correction was applied. Both structures were solved by direct methods using SHELXS-97[13] and full-matrix least squares refinement was undertaken using SHELXL-97.[14] All hydrogen atoms were placed in geometrically calculated positions and allowed to ride on their parent atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. For $[Ag(hfpd)([9]aneS_3)]_\infty$ the fluorine atoms of one of the CF_3 groups were found to be disordered and were modeled over three sites, the linked occupancies of which refined to 0.36(1), 0.32(1), and 0.32(1).

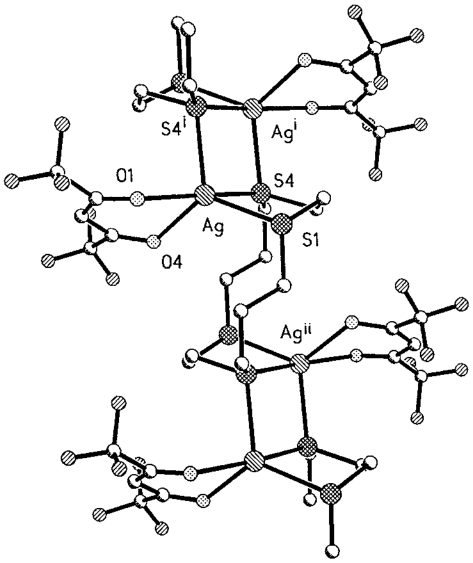

Figure 1. Ribbon polymer formed by $[Ag_2(hfpd)_2([14]aneS_4)]_\infty$ illustrating the bridging nature of the thioethers and the bordering of the hfpd anions (hydrogen atoms are omitted for clarity). Selected bond lengths (Å) and angles (deg); Ag−O(2) = 2.342(3), Ag−O(4) = 2.413(3), Ag−S(1) = 2.477(2), Ag−S(4) = 2.936(2), Ag−S(4)^i = 2.5603(14), S(1)−Ag−S(4) = 77.72(6), S(1)−Ag−S(4)^i = 115.50(6), S(4)−Ag−S(4)^i = 86.67(5), S(1)−Ag−O(2) = 116.72(9), S(1)−Ag−O(4) = 123.47(9), S(4)−Ag−O(2) = 163.87(7), S(4)^i−Ag−O(4) = 118.50(10), O(2)−Ag−O(4) = 76.33(12). Symmetry codes i = −*x*, −*y*, −*z*; ii = 1 − *x*, *y*, *z*.

Results and Discussion

Reaction of "Ag(hfpd)", generated in situ from Ag_2O and H-hfpd in THF, with either $[14]aneS_4$ or $[9]aneS_3$ in a 1:1 (Ag:L ratio) gave colorless solid products, $[Ag_2(hfpd)_2([14]aneS_4)]_\infty$ or $[Ag(hfpd)([9]aneS_3)]_\infty$, respectively. The ratio of silver to thioether macrocycle in the product was found to be independent of metal:ligand ratio used in the reaction mixture. Whereas $[Ag_2(hfpd)_2([14]aneS_4)]_\infty$ was generated as a fine colorless powder which precipitated from solution upon formation, the reaction with $[9]aneS_3$ afforded colorless needle-shaped crystals of $[Ag(hfpd)([9]aneS_3)]_\infty$ suitable for single-crystal X-ray diffraction directly from the reaction solution. Single crystals of $[Ag_2(hfpd)_2([14]aneS_4)]_\infty$ were prepared by slow diffusion of a solution of preformed $Ag_2(hfpd)_2(H_2O)$[11] in THF into a solution of $[14]aneS_4$ in CH_2Cl_2.

Single-crystal X-ray diffraction experiments on $[Ag_2(hfpd)_2([14]aneS_4)]_\infty$ revealed that the Ag(I) center sits in a distorted square-pyramidal coordination sphere in which it is bound by the diketonate anion and by three thioether donors (Figure 1). Of the three thioether donors one acts in a monodentate fashion to the Ag(I) center whereas the other two bridge adjacent silver ions generating a crystallographically centrosymmetric Ag_2S_2

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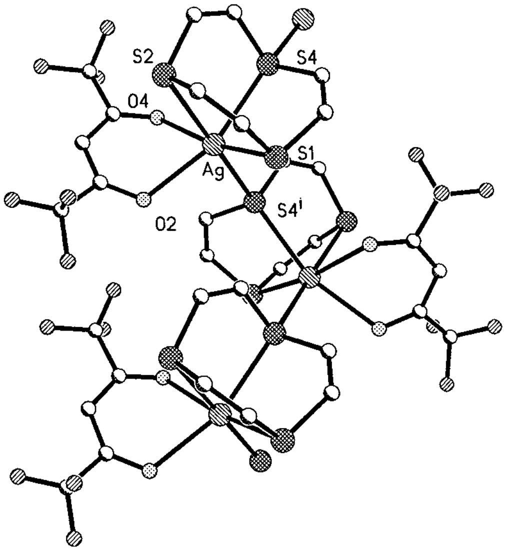

Figure 2. One-dimensional polymer formed by [Ag(hfpd)([9]aneS$_3$)]$_\infty$ showing the octahedral coordination of the Ag(I) center anions (hydrogen atoms are omitted for clarity). Selected bond lengths (Å) and angles (deg); Ag−O(2) = 2.413(4), Ag−O(4) = 2.525(3), Ag−S(1) = 2.6160(15), Ag−S(4) = 2.6299(14), Ag−S(7) = 2.7487(15), Ag−S(4)^i = 2.7516(13), S(1)−Ag−S(4) = 83.51(4), S(1)−Ag−S(7) = 81.99(4), S(4)−Ag−S(7) = 81.21(5), S(1)−Ag−S(4)^i = 103.41(5), S(4)−Ag−S(4)^i = 97.49(3), S(7)−Ag−S(4)^i = 174.30(4), O(2)−Ag−O(4) = 72.62(12), O(2)−Ag−S(1) = 113.06(9), O(2)−Ag−S(4) = 161.00(9), O(2)−Ag−S(7) = 91.63(10), O(2)−Ag−S(4)^i = 87.90(10), O(4)−Ag−S(1) = 169.87(10), O(4)−Ag−S(4) = 89.66(9), O(4)−Ag−S(7) = 89.60(9), O(4)−Ag−S(4)^i = 84.84(9). Symmetry codes $i = {}^3/_2 - x, {}^1/_2 + y, {}^3/_2 - z$.

ring, a bridging motif that has previously been observed in binuclear Ag(I) thioether macrocyclic complexes.[4d,6c] The bridging thioethers generate a one-dimensional {[Ag$_2$([14]aneS$_4$)]$^{2+}$}$_\infty$ polymeric ribbon which is bordered on either side by the coordinated diketonate anions (Figure 1). The coordination sphere of the Ag(I) center is particularly interesting as not only are five-coordinate silver compounds rare but the two S-donors from the same macrocycle adopt very different bond lengths. The bridging thioether forms a significantly longer bond [2.936(2) Å] than the monodentate thioether donor [2.477(2) Å] preferring to engage in a stronger interaction [2.5603(14) Å] with the adjoining Ag(I) along the direction of the polymeric chain. The [Ag$_2$(hfpd)$_2$([14]aneS$_4$)]$_\infty$ chains run parallel to the crystallographic *a*-axis and are packed such that the closest contact is observed between F atoms of hfpd CF$_3$ groups (F···F = ca. 2.87 Å) on adjacent chains.

The role of the anion in this complex is crucial as can be seen by comparison to the structures of [Ag(3-oxo-1,5,8,11-tetrathiacyclotetradecane)(CF$_3$SO$_3$)]$_\infty$[4e] and {Ag[(HO)$_2$-[16]-aneS$_4$]NO$_3$}$_\infty$[4c] in which all four sulfurs of the macrocycles are linked to independent silver ions leading to the generation of infinite three-dimensional networks. The effect of the diketonate anion in the compound reported here is to effectively block two of the Ag(I) coordination sites resulting in the enclosed formation of the {[Ag$_2$([14]aneS$_4$)]$^{2+}$}$_\infty$ ribbon.

The single-crystal X-ray structure of [Ag(hfpd)([9]aneS$_3$)]$_\infty$ indicates that, in contrast to [Ag$_2$(hfpd)$_2$([14]aneS$_4$)]$_\infty$, the silver(I) center adopts a distorted octahedral S$_4$O$_2$ coordination sphere (Figure 2). As with [Ag$_2$(hfpd)$_2$([14]aneS$_4$)]$_\infty$ the polymeric nature of the compound is generated through bridging thioether donors, but in this case neighboring Ag(I) ions are linked through only one S-donor (Figure 2). At the center of the one-dimensional chains sit (Ag−S)$_\infty$ helical chains (Figure 3) which are arranged around a crystallographic 2$_1$ screw-axis, running parallel to the *b*-axis, which gives rise to a zigzag polymer. Again the hfpd anions ligate the silver ions, preventing further propagation of the polymer in the directions perpendicular to the chain. As in [Ag$_2$(hfpd)$_2$([14]aneS$_4$)]$_\infty$ the closest contacts between adjacent chains are observed between F atoms of hfpd CF$_3$ groups (F···F = ca. 2.82 Å).

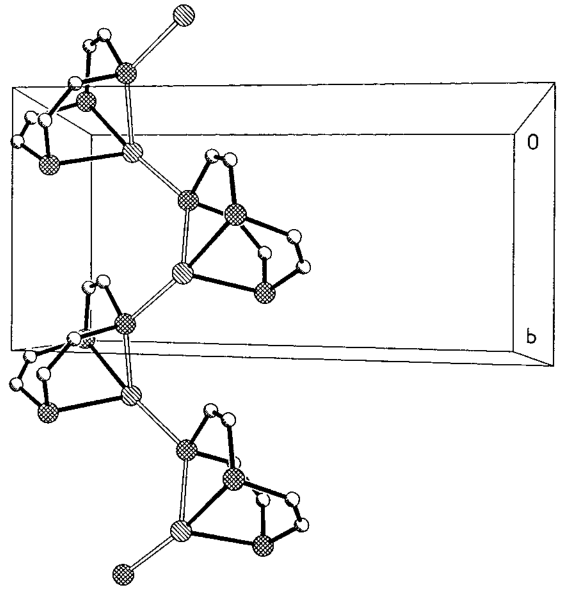

Figure 3. View of the (AgS)$_\infty$ helices, indicated by hollow bonds, formed along the direction of propagation of the [Ag(hfpd)([9]aneS$_3$)]$_\infty$ chains (hfpd ligands and hydrogen atoms are omitted for clarity).

The thioether bridging mode observed in [Ag(hfpd)([9]aneS$_3$)]$_\infty$ is unusual for Ag(I) compounds and has been previously observed only in the discrete trinuclear cationic species {Ag([9]aneS$_3$)}$_3^{3+}$.[6a] Polymeric [9]aneS$_3$ complexes are rare,[15] and in only two cases are the polymers generated via the [9]aneS$_3$ ligand.[15a,b] Interestingly, in both [SbCl$_3$([9]aneS$_3$)]$_\infty$[15a] and {[Hg([9]aneS$_3$)$_2$](HgI$_3$)$_2$}$_\infty$[15b] the same bridging mode is adopted by the macrocycle. Indeed the arrangement of the polymer generated by [SbCl$_3$([9]aneS$_3$)]$_\infty$[15a] is similar to that observed in [Ag(hfpd)([9]aneS$_3$)]$_\infty$ with (Sb−S)$_\infty$ helices running along the direction of polymeric propagation. {[Hg([9]aneS$_3$)$_2$](HgI$_3$)$_2$}$_\infty$[15b] differs in that two [9]aneS$_3$ molecules are coordinated to the same Hg(II) ion but a (Hg−S)$_\infty$ helix is still observed.

Both [Ag$_2$(hfpd)$_2$([14]aneS$_4$)]$_\infty$ and [Ag(hfpd)([9]aneS$_3$)]$_\infty$ are insoluble in common organic solvents except for DMSO and, in the case of [Ag(hfpd)([9]aneS$_3$)]$_\infty$, THF. In DMSO solution the complexes dissociate into smaller fragments as evidenced by mass spectrometry and NMR measurements. Interestingly, whereas the mass spectrum of [Ag$_2$(hfpd)$_2$([14]aneS$_4$)]$_\infty$ in DMSO shows only the Ag([14]aneS$_4$)$^+$ fragment, that of [Ag(hfpd)([9]aneS$_3$)]$_\infty$ in DMSO, or THF, shows the presence of the larger dinuclear Ag$_2$([9]aneS$_3$)$_2$(hfpd)$^+$ fragment in solution. This is surprising if one considers the solid-state structures of the compounds as adjacent silver(I) ions in [Ag(hfpd)([9]aneS$_3$)]$_\infty$ are linked through only one bridging thioether compared to the chelating linkers observed in [Ag$_2$(hfpd)$_2$([14]aneS$_4$)]$_\infty$. However, the structures of the fragments in solution

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are not necessarily simple segments of those observed in the solid state. ^{1}H and ^{13}C NMR spectra of both complexes in DMSO were consistent with dissociation of the polymeric chains and fluxional coordination of the macrocycles to the Ag(I) ions in solution, providing no further insight into the solution structures.

In conclusion we have demonstrated that thioether macrocycles can be used to construct silver(I) coordination polymers and that the hfpd ligand can be usefully employed as a blocking anion which restricts polymer dimensionality. We are further exploring the wider applicability of both the hfpd anion and thioether ligands in the construction of coordination polymers.

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Supporting Information Available: Two X-ray crystallographic files, in CIF format, and thermal ellipsoid plots of both complexes. This material is available free of charge via the Internet at http://pubs.acs.org.

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