

Metallosupramolecular silver complexes of bis- and tetrakis-(2-pyridylsulfanylmethyl)benzenes

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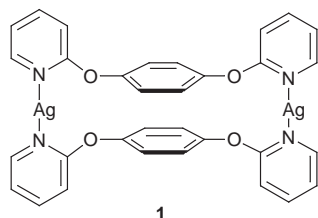
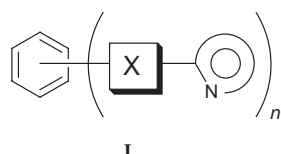
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The three isomeric bis(2-pyridylsulfanylmethyl)benzenes and 1,2,4,5-tetrakis(2-pyridylsulfanylmethyl)benzene have been prepared by reactions of pyridine-2-thiol with the appropriate poly(bromomethyl)benzene, in the presence of triethylamine, in good yields. Each of these new ligands reacts with silver nitrate, in excellent yield, to give co-ordination complexes in which the ligands bridge two or more metal centres. The crystal structures of these complexes have been determined. The *para*-disubstituted isomer self-assembles into a M_2L_2 macrocyclic dimer. The other ligands form one-dimensional metallopolymers containing complex networks of interconnected macrocyclic rings. In the crystal packings π - π stacking interactions between aromatic rings are observed.

Introduction

We are currently involved in the synthesis and study of a large range of ligands represented by the generalised structure **I**, in which various numbers of heterocyclic donors are attached *via* spacer groups, X to a central arene core. For example, we have reported the ability of polypyrazolylmethylbenzenes to encapsulate metal ions,¹ to form large metallosupramolecular cages,² to bridge metal-metal bonded species³ and to undergo double cyclometallation reactions.⁴ We have also shown that 1,4-bis(2-pyridyloxy)benzene self-assembles in the presence of silver nitrate into a M_2L_2 dimetalloparacyclophane **1** with intimate π - π stacking of the central benzene rings.⁵ In the accompanying paper we described experiments designed to assess the factors controlling this self-assembly process.⁶ One such factor that was considered was the possible role of the aryl ether oxygen atoms.



We reasoned that incorporation of sulfur atoms in related ligands would lead to greater chalcogen-metal interactions, as a result of the high thiophilicity of the silver(I) ion. In contrast to the extensive literature on the co-ordination chemistry of heterocyclic thiolates,⁷ less attention has been paid to pyridyl thioethers,⁸ even though thioethers are well established ligands in co-ordination⁹ and metallosupramolecular chemistry.¹⁰ Ligands containing pyridyl substituents directly linked to sulfide spacer groups might be expected to form interesting complexes with silver(I) ions. For example, a thiomethylterpyridine has

recently been shown to self-assemble into aggregated metallosupramolecular boxes in the presence of silver(I) ions, with co-ordination by all N and S donors.¹¹ Furthermore, we have recently shown that reaction of silver nitrate with di-2-pyridyl sulfide, a ligand that normally acts as a N,N-bidentate chelating ligand, results in the formation of a novel binuclear complex in which the ligand co-ordinates in an N,N,S-tridentate bridging mode to form a structure with the same topology as those of the well studied organic photodimers of anthracene.¹² The study of such assembly processes can provide useful information for use in the rapidly expanding area of crystal engineering.¹³ We now report the preparation of four new bridging ligands that contain 2-pyridylsulfanyl groups attached to xylylene cores, and the synthesis and crystal structures of their respective complexes with silver(I) nitrate.

Results and discussion

The three isomeric bis(2-pyridylsulfanylmethyl)benzenes (**II-IV**) were prepared by adaptation of a literature procedure for the preparation of benzyl 2-pyridyl sulfide.¹⁴ Reaction of pyridine-2-thiol with the appropriate bis(bromomethyl)benzene, in the presence of triethylamine, gave **II-IV** in good yields, and the products were fully characterised by ¹H and ¹³C NMR, using a combination of 1-D and 2-D NMR techniques. Each of these ligands reacted smoothly with one equivalent of silver nitrate, in aqueous methanol, to give good yields of the corresponding complexes **2-4**. Crystals suitable for structure determination were obtained by slow evaporation of acetonitrile solutions of these complexes.

The complex **2** crystallises in the triclinic space group $P\bar{1}$ and is a centrosymmetric M_2L_2 dimetalloparacyclophane. Fig. 1 shows a perspective view of the structure, with atom labelling of the asymmetric unit. Selected interatomic distances and angles are also listed. Each silver atom is co-ordinated to two pyridine nitrogens and an oxygen atom of the nitrate anion, with all three silver-donor bond distances within the range expected for such co-ordination.¹⁵ The distances between the silver and the sulfur atoms of the ligand are greater than >3.16 Å, which in structurally related structures has been considered non-interacting.¹⁶ The co-ordination geometry of the silver is distorted T-shaped with the co-ordinated oxygen slightly displaced towards one of the pyridines. The mean planes of the pyridine rings are inclined at angles of $91.9(2)$ and $125.2(2)^\circ$ to

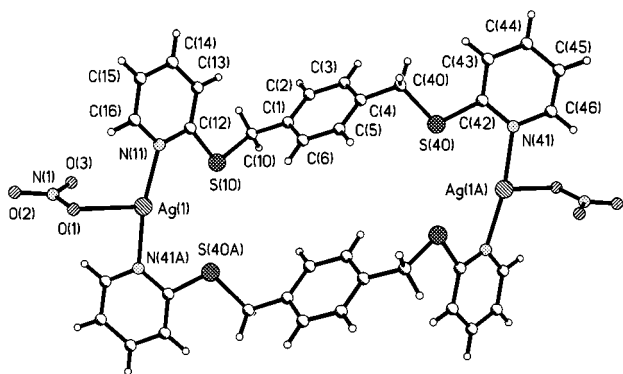
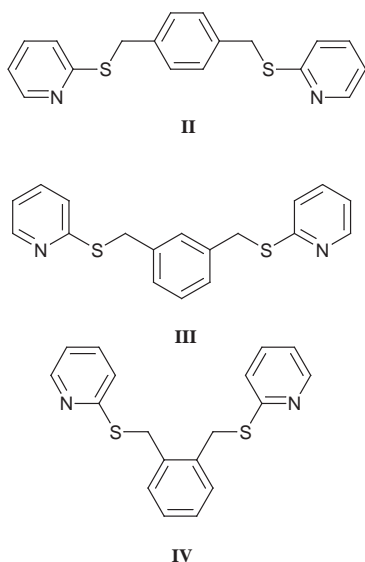


Fig. 1 Perspective view and atom labelling of the crystal structure of complex **2**. Selected interatomic distances (Å) and angles (°): Ag(1)–N(11) 2.166(2), Ag(1)–N(41A) 2.165(2), Ag(1)–O(1) 2.592(2), Ag(1)⋯S(10) 3.160(1), Ag(1)⋯S(40A) 3.164(1); N(11)–Ag(1)–N(41A) 169.70(8), N(11)–Ag(1)–O(1) 98.36(8), N(41A)–Ag(1)–O(1) 91.60(8).



that of the linking benzene ring, while the two pyridine ring mean planes at each silver atom are inclined to one another at an angle of 57.0(2)°.

An important feature of this macrocycle is the absence of an intramolecular π – π stacking interaction, as the two benzene rings are significantly displaced from one another, in contrast to the situation in complexes such as **1**.^{5,6} Thus, such π – π stacking is not a necessary feature for the formation of these M_2L_2 macrocycles. Within the 26-membered macrocycle the Ag⋯Ag separation is 12.196(2) Å, which is considerably greater than the corresponding value [11.269(2) Å] in the structure of a concave dipalladium complex of the same ring size.⁶

Whilst there is an absence of intramolecular π – π stacking, the packing of the macrocycles is controlled, in part, by such interactions. As shown in Fig. 2, the dimetallomacrocycles self-assemble into a two-dimensional array within which there is π – π stacking between pyridine rings of adjacent macrocycles (average plane-to-plane distance = 3.8 Å). As observed in other cases,^{5,6} this stacking occurs with the aromatic rings disposed such that an atom of one ring lies approximately over the centroid of another ring.

The silver complex **3** of the *meta*-disubstituted ligand **III** crystallises in the triclinic space group $P\bar{1}$ and is a one dimensional metallopolymer. Fig. 3 shows a perspective view and atom labelling of the asymmetric unit of the structure, along with selected interatomic distances and angles. The silver atom is co-ordinated to two pyridine nitrogens and a sulfur, each

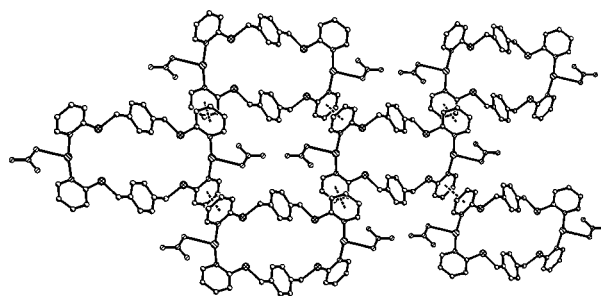


Fig. 2 Packing diagram of complex **2** showing π – π stacking interactions between the pyridine rings of the macrocycles.

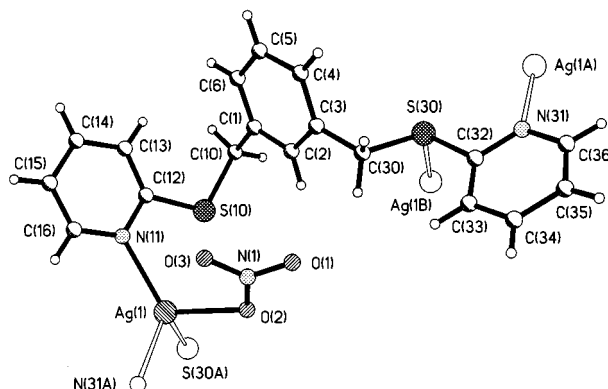


Fig. 3 Perspective view and atom labelling of the crystal structure of complex **3**. Selected interatomic distances (Å) and angles (°): Ag(1)–N(11) 2.285(7), Ag(1)–N(31A) 2.327(6), Ag(1)–S(30A) 2.658(3), Ag(1)–O(2) 2.418(7); N(11)–Ag(1)–N(31A) 119.9(3), N(11)–Ag(1)–S(30A) 118.5(2), N(11)–Ag(1)–O(2) 112.5(3), N(31A)–Ag(1)–S(30A) 106.6(2), N(31A)–Ag(1)–O(2) 88.8(3), S(30A)–Ag(1)–O(2) 105.9(2).

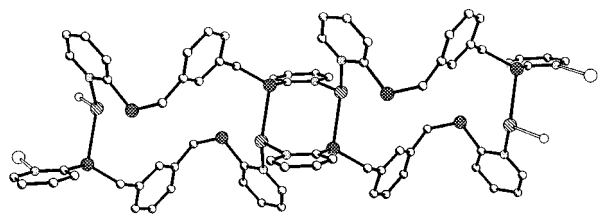


Fig. 4 Perspective view (top), with hydrogens omitted, and schematic representation (bottom) of a section of the extended polymeric structure of complex **3**. Nitrate anions are not shown.

from different ligands, as well as an oxygen from the nitrate counter ion. The geometry of these four donors around the silver is distorted tetrahedral [donor–Ag–donor angles between 88.8(3) and 119.9(3)°]. The distortion from tetrahedral geometry is possibly due to an additional semi-co-ordinative interaction with a second sulfur atom [*viz.* S(10)]. The mean planes of the pyridine rings are inclined at angles of 84.2(9) and 63.3(9)° to that of the linking benzene ring, while the two pyridine ring mean planes are inclined to one another at an angle of 62.1(9)°.

Co-ordination by the silver atom to donors from three different ligands results in the assembly of an intriguing extended polymeric structure. Fig. 4 shows a perspective view and

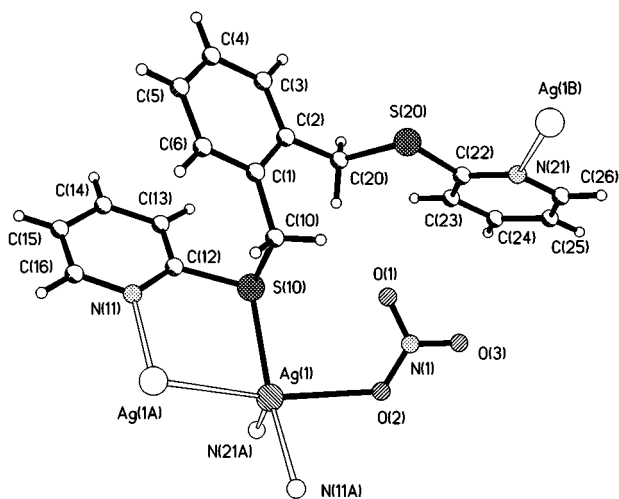


Fig. 5 Perspective view and atom labelling of complex **4**. Selected interatomic distances (Å) and angles ($^{\circ}$): Ag(1)–Ag(1A) 2.9874(5), Ag(1)–N(11A) 2.288(2), Ag(1)–N(21A) 2.377(2), Ag(1)–S(10) 2.4984(8), Ag(1)–O(2) 2.571(2); Ag(1A)–Ag(1)–N(11A) 90.79(6), Ag(1A)–Ag(1)–N(21A) 117.51(6), Ag(1A)–Ag(1)–S(10) 78.35(2), Ag(1A)–Ag(1)–O(2) 155.46(6), N(11A)–Ag(1)–N(21A) 103.82(8), N(11A)–Ag(1)–S(10) 154.44(6), N(11A)–Ag(1)–O(2) 85.09(8), N(21A)–Ag(1)–S(10) 101.71(6), N(21A)–Ag(1)–O(2) 86.91(8), S(10)–Ag(1)–O(2) 95.21(5).

schematic representation of a section of the polymeric chain, which consists of an alternating array of two different sizes of macrocycle fused by a common bond. The smaller of the two is a centrosymmetric eight-membered ring containing two silver atoms [Ag...Ag 4.340(2) Å], bridged by a pair of pyridyl thioether moieties, with the two pyridine rings co-ordinated to different silver atoms. This eight-membered ring adopts a chair conformation with the two pyridine rings *transoid* with respect to the Ag_2S_2 plane, as necessitated by the crystallographic centre of inversion. Such a substructure is also present in the silver nitrate complex of di-2-pyridyl sulfide.¹²

Fused to this macrocycle is a twenty-membered centrosymmetric dinuclear ring. Again, the ring is formed by co-ordination of a pyridine nitrogen and a sulfur atom to each of two silver atoms. However, in this case, instead of the co-ordinating sulfur bonding directly to the co-ordinating pyridine, they are separated by the arene spacer of the ligand. As a result, the macrocycle is enlarged to twenty members with an Ag...Ag interatomic distance of 7.920(2) Å.

While there are no π - π stacking interactions within this polymer chain, inspection of the molecular packing reveals that there does exist a series of such interactions between pyridine rings of adjacent chains. Crystallographically related pyridine rings are parallel stacked with a plane-to-plane separation of only 3.18(1) Å. Once again, the arrangement of this stacking is such that an atom of one ring lies over the centroid of the adjacent ring. Similar intermolecular interactions have recently been shown to exist between molecular squares derived from silver nitrate and pyrimidine.¹⁷

The silver complex **4** of the *ortho*-disubstituted ligand **IV** crystallises in the monoclinic space group $P2_1/n$ and is also a one dimensional metallopolymer. Fig. 5 shows a perspective view of the labelled contents of the asymmetric unit and selected interatomic distances and angles. The silver atom is co-ordinated to two pyridine nitrogens and a sulfur atom, each from different ligands, as well as to an oxygen from the nitrate counter ion. The silver atom further interacts with a silver atom related by a crystallographic centre of inversion [Ag–Ag distance 2.9874(5) Å]. Similar silver–silver interactions have been observed in complexes of other nitrogen-containing heterocyclic ligands.^{3,18} The geometry of the five atoms around the silver is distorted trigonal bipyramidal, with the central silver, sulfur and two nitrogens approximately coplanar and with the

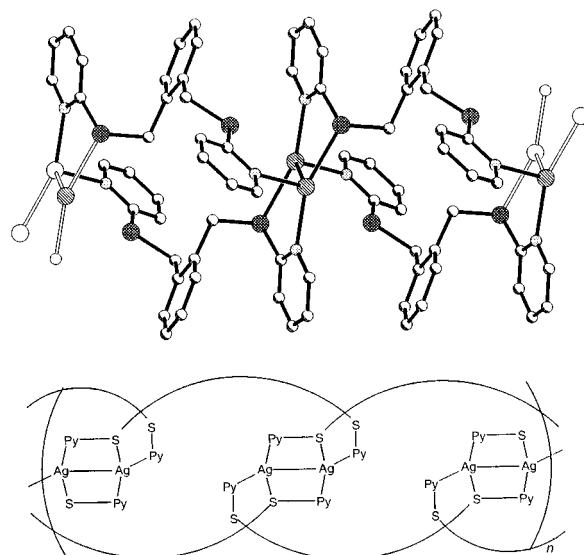


Fig. 6 Perspective view (top), with hydrogens omitted, and schematic representation (bottom) of a section of the extended polymeric structure of complex **4**. The nitrate anions are not shown.

second silver and nitrate oxygen occupying the axial sites. The mean planes of the pyridine rings are inclined at angles of 27.9(2) $^{\circ}$ and 77.9(2) $^{\circ}$ to that of the linking benzene ring, while the two pyridine ring mean planes are inclined to one another at an angle of 62.7(2) $^{\circ}$. The silver atom lies out of the extended planes of the co-ordinated pyridine rings by 0.214(3) and 0.226(3) Å.

Fig. 6 shows a perspective view and a schematic representation of the extended polymeric structure of the complex **4**, which, like that of **3**, consists of a complex system of interconnected rings. In both structures a binuclear bis(pyridyl sulfide) moiety is present, and the pyridyl ring at the opposite end of these ligands co-ordinates to a silver atom of the next binuclear unit. However, there is a difference between the two structures as to which silver of the binuclear pair is bonded to the “bridging” pyridine. In **3** the “bridging” pyridine co-ordinates to the closer silver of the next binuclear pair, while in **4** it co-ordinates to the more distant silver of the next pair. As a result, the twenty-membered macrocycle linking two binuclear units in **4** incorporates four silver atoms, with an Ag...Ag transannular interatomic distance of 8.138(1) Å. Once again, π - π stacking interactions exist between pyridine rings of adjacent chains, although in this case the separation between the rings is somewhat greater (3.55 Å).

The three isomeric bis(2-pyridylsulfanyl)methyl)benzenes **II–IV** react with silver nitrate to form a dimeric structure, for the *para* isomer, and one-dimensional polymeric structures, for the *meta* and *ortho* isomers. A ligand that incorporates all three of these substitution patterns as subunits is the tetrapodal ligand 1,2,4,5-tetrakis(2-pyridylsulfanyl)methyl)benzene **V**, which might also offer the possibility of forming metallopolymers of higher dimensionality. This new ligand was synthesized in excellent yield from pyridine-2-thiol and 1,2,4,5-tetrakis(bromomethyl)benzene (Scheme 1) and treated with two equivalents of silver nitrate to give, in high yield, a complex **5**, the crystal structure of which was determined.

The complex **5** crystallises in the triclinic space group $P\bar{1}$ with the asymmetric unit containing half a ligand, a silver nitrate unit and a water molecule, and is another one-dimensional polymer. Fig. 7 shows a perspective view and atom labelling of the structure. To each silver atom is co-ordinated a chelated pyridyl moiety and a pyridine nitrogen from a different ligand. The nitrate counter ion and the water molecule are disordered, approximately evenly, over two sites. For half of the silver atoms, a water oxygen is also co-ordinated [Ag(1)–O(100)

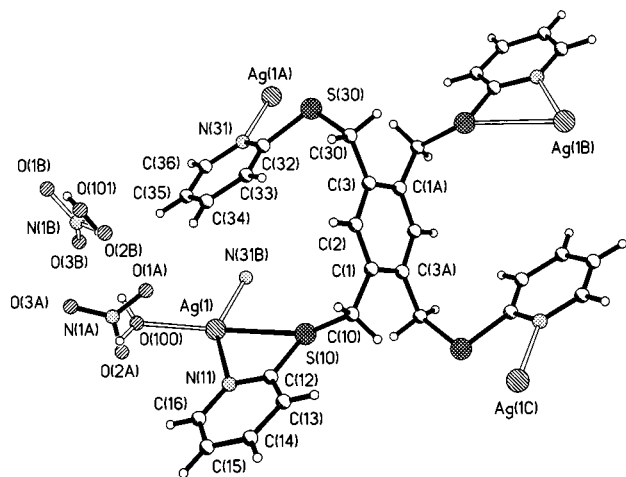
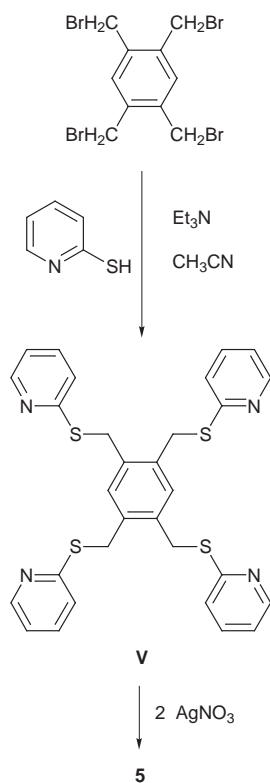


Fig. 7 Perspective view and atom labelling of complex **5**. Selected interatomic distances (Å) and angles (°): Ag(1)–N(11) 2.271(3), Ag(1)–N(31B) 2.227(3), Ag(1)–S(10) 2.956(1), Ag(1)–O(100) 2.360(8), Ag(1)···O(1A) 2.639(8), Ag(1)···O(2A) 2.793(8); N(11)–Ag(1)–N(31B) 145(1), N(11)–Ag(1)–S(10) 57.03(8), N(11)–Ag(1)–O(100) 91.0(2), N(31B)–Ag(1)–S(10) 88.80(8), N(31B)–Ag(1)–O(100) 119.5(2), S(10)–Ag(1)–O(100) 133.4(2).



Scheme 1

2.360(8) Å], and for the other half two nitrate oxygens are weakly co-ordinated to the silver [Ag(1)···O(1A) 2.639(9), Ag(1)···O(2A) 2.793(9) Å]. The mean planes of the pyridine rings are inclined at angles of 87.1(8) and 94.7(8)° to that of the linking benzene ring, and at 7.9(8)° to each other.

Despite the fact that the ligand **V** is co-ordinated to four different silver atoms, the complex is still a one-dimensional polymer, a section of which is shown in Fig. 8. The polymeric structure is a chain of twenty-membered macrocycles joined by benzene rings which are shared by adjacent macrocycles. The Ag···Ag separation [7.447(1) Å] across the macrocycles is shorter than those of the previously described twenty-membered binuclear rings, possibly as a consequence of a

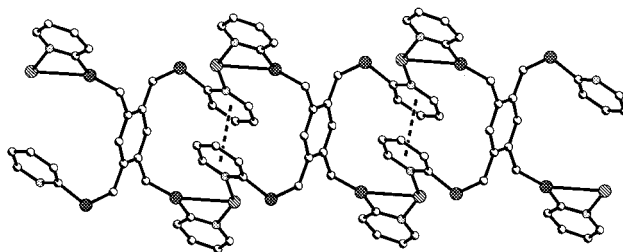


Fig. 8 Perspective view of a section of the extended polymeric structure of complex **5**. The nitrate anions are not shown.

π – π interaction between the two co-ordinated pyridines within the ring, the mean planes of which are separated by 3.34(1) Å. Weak π – π interactions exist between pyridine rings of adjacent polymer chains, which also exhibit short S···S contacts [3.412(2) Å]. Such sulfur–sulfur interactions have recently been shown to exist in other supramolecular silver networks.¹⁹

Conclusion

Reaction of silver nitrate with each of the four new ligands described above results in the assembly of co-ordination complexes within which the ligands bridge two or more metal centres. In general, co-ordination of the ligand nitrogen and sulfur donors results in the formation of extended one-dimensional polymeric structures containing a complex system of interconnected metallomacrocyclic rings. The nature of co-ordination complexes formed from these and related ligands appears to result from a delicate interplay of thermodynamic and kinetic factors, which are now recognised to control the self-assembly of various metallosupramolecular architectures.²⁰

Experimental

General

General experimental details are given in the accompanying paper.⁶ The isomeric bis(bromomethyl)benzenes²¹ and 1,2,4,5-tetrakis(bromomethyl)benzene²² were prepared by literature procedures.

Ligand preparations

1,4-Bis(2-pyridylsulfanylmethyl)benzene II. 1,4-Bis(bromomethyl)benzene (0.59 g, 2.24 mmol) was added, with stirring, to an ice-cooled solution of pyridine-2-thiol (0.50 g, 4.48 mmol) and triethylamine (0.57 g, 5.6 mmol) in acetonitrile (10 ml). The mixture was stirred for 24 h at room temperature, filtered and concentrated to give a yellow residue that was dissolved in chloroform (15 ml). This solution was washed with water (2 × 30 ml), dried (Na₂SO₄), and concentrated to give crude compound **II** as a white solid. Recrystallisation from light petroleum (bp 40–60 °C) gave pure **II** (0.40 g, 55%), mp 76 °C (Found: C, 66.26; H, 4.90; N, 8.71. C₉H₈NS requires C, 66.63; H, 4.97; N, 8.63%). ¹H NMR (CDCl₃): δ 4.41 (4 H, s, CH₂), 6.98 (2 H, t, H5'), 7.15 (2 H, d, H3'), 7.33 (4 H, s, H2,3,5,6), 7.46 (2 H, t, H4'), 8.45 (2 H, d, H6'). ¹³C NMR (CDCl₃): δ 33.92 (CH₂), 119.44 (C3'), 121.92 (C5'), 128.96 (C2,3,5,6), 135.82 (C4'), 136.71 (C1,4), 149.23 (C6'), 158.59 (C2').

1,3-Bis(2-pyridylsulfanylmethyl)benzene III. Reaction of 1,3-bis(bromomethyl)benzene (0.59 g, 2.24 mmol) with pyridine-2-thiol (0.50 g, 4.48 mmol) and triethylamine (0.57 g, 5.6 mmol), as described above for **II**, gave compound **III** as a yellow oil (0.61 g, 84%) (Found: M⁺, 324.0755. C₁₈H₁₆N₂S₂ requires M⁺ 324.0755). ¹H NMR (CDCl₃): δ 4.40 (4 H, s, CH₂), 6.98 (2 H, t, H5'), 7.14 (2 H, d, H3'), 7.22 (1 H, t, H5), 7.28 (2 H, d, H4,6), 7.45 (3 H, H2,4'), 8.44 (2 H, d, H6'). ¹³C NMR (CDCl₃): δ 34.06

Table 1 Crystal data and details of data collections and structure refinements for complexes **2–5**

	2	3	4	5
Formula	C ₃₆ H ₃₂ Ag ₂ N ₆ O ₆ S ₄	C ₁₈ H ₁₆ AgN ₃ O ₃ S ₂	C ₁₈ H ₁₆ AgN ₃ O ₃ S ₂	C ₃₀ H ₃₀ Ag ₂ N ₆ O ₈ S ₄
Formula weight	988.66	494.33	494.33	946.58
Crystal system	Triclinic	Triclinic	Monoclinic	Triclinic
<i>a</i> /Å	7.803(2)	8.281(3)	8.556(1)	9.360(1)
<i>b</i> /Å	10.173(1)	10.011(3)	10.617(1)	9.712(1)
<i>c</i> /Å	13.206(2)	11.488(4)	19.827(2)	10.042(1)
<i>a</i> °	104.39(1)	106.16(2)		92.42(1)
<i>β</i> °	103.84(2)	97.04(3)	97.25(1)	100.10(1)
<i>γ</i> °	104.66(1)	91.75(3)		109.98(1)
<i>V</i> /Å ³	929.9(3)	905.8(5)	1786.7(3)	839.5(2)
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> $\bar{1}$
<i>Z</i>	1	2	4	1
<i>D</i> _c /Mg m ⁻³	1.77	1.81	1.84	1.87
<i>F</i> (000)	496	496	992	474
<i>T</i> /K	168(2)	158(2)	169(2)	169(2)
Crystal form	Colourless block	Colourless plate	Colourless block	Colourless block
Crystal size/mm	0.26 × 0.21 × 0.13	0.54 × 0.52 × 0.12	0.64 × 0.46 × 0.27	0.42 × 0.31 × 0.21
<i>μ</i> /mm ⁻¹	1.33	1.37	1.39	1.48
2 θ range/°	4–55	4–50	4–50	4–50
Reflections collected	4509	3393	3384	3148
Unique reflections (<i>R</i> _{int})	4194 (0.018)	3152 (0.242)	3153 (0.022)	2944 (0.022)
Parameters	244	244	244	272
Difference peaks/e Å ⁻³	0.553	2.901	1.836	0.696
Goodness of fit	0.903	0.966	1.027	0.876
<i>R</i> ^a [<i>I</i> > 2 σ (<i>I</i>)]	0.0301	0.0795	0.0253	0.0320
<i>wR</i> ^b (all data)	0.0598	0.2145	0.0643	0.0658

$$^a R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|, \quad ^b wR = [\Sigma w(F_o^2 - F_c^2)^2]/\Sigma w(F_o^2)^2$$

(CH₂), 119.36 (C3'), 121.74 (C5'), 127.46 (C4,6), 128.36 (C5), 129.29 (C2), 135.77 (C4'), 137.81 (C1,3), 149.04 (C6'), 158.36 (C2').

1,2-Bis(2-pyridylsulfanylmethyl)benzene IV. Reaction of 1,2-bis(bromomethyl)benzene (0.59 g, 2.24 mmol) with pyridine-2-thiol (0.50 g, 4.48 mmol) and triethylamine (0.57 g, 5.6 mmol), as described above for **II**, gave compound **IV** as a yellow solid that was recrystallised from light petroleum (0.61 g, 84%), mp 82 °C (Found: C, 66.42; H, 5.27; N, 8.61%). ¹H NMR (CDCl₃): δ 4.61 (4 H, s, CH₂), 6.96 (2 H, t, H5'), 7.15 (2 H, d, H3'), 7.19 (2 H, dd, H4,5), 7.43 (2 H, dd, H3,6), 7.45 (2 H, t, H4'), 8.42 (2 H, d, H6'). ¹³C NMR (CDCl₃): δ 31.71 (CH₂), 119.41 (C3'), 121.93 (C5'), 127.53 (C3,6), 130.46 (C4,5), 135.80 (C4'), 136.18 (C1,2), 149.24 (C6'), 158.70 (C2').

1,2,4,5-Tetrakis(2-pyridylsulfanylmethyl)benzene V. Reaction of 1,2,4,5-tetra(bromomethyl)benzene (0.50 g, 1.11 mmol) with pyridine-2-thiol (0.50 g, 4.44 mmol) and triethylamine (0.57 g, 5.6 mmol), as described above for **II**, gave a precipitate of compound **V** directly from the reaction mixture. This was filtered off, washed with water (3 × 10 ml) and recrystallised from acetonitrile to give pure **V** (0.52 g, 82%), mp 114 °C (Found: C, 62.84; H, 4.79; N, 9.98. C₁₅H₁₃N₂S₂ requires C, 63.12; H, 4.59; N, 9.82%). ¹H NMR (CDCl₃): δ 4.52 (8 H, s, CH₂), 6.95, (4 H, t, H5'), 7.12 (4 H, d, H3'), 7.44 (4 H, t, H4'), 7.48 (2 H, s, H3,6), 8.38 (4 H, d, H6'). ¹³C NMR (CDCl₃): δ 31.38 (CH₂), 119.40 (C3'), 121.95 (C5'), 132.75 (C3,6), 135.41 (C1,2,4,5), 135.79 (C4'), 149.23 (C6'), 158.62 (C2').

Silver nitrate complexes

[Ag(II)(NO₃)₂]2.** Reaction of compound **II** (71 mg, 0.22 mmol), dissolved in hot methanol (12 ml), with silver nitrate (37 mg, 0.22 mmol), dissolved in water (3 ml), gave complex **2** as a white precipitate (73 mg, 68%), mp >162 °C (decomp.) (Found: C, 43.60; H, 3.42; N, 8.37. C₁₈H₁₆AgN₃O₃S₂ requires C, 43.73; H, 3.26; N, 8.50%).**

[Ag(III)(NO₃)₃]3.** Reaction of compound **III** (79 mg, 0.24 mmol), dissolved in methanol (10 ml), with silver nitrate (41 mg, 0.24 mmol), dissolved in water (3 ml), gave complex **3** as a**

white precipitate (98 mg, 83%), mp 151–152 °C (Found: C, 43.64; H, 3.26; N, 8.57. C₁₈H₁₆AgN₃O₃S₂ requires C, 43.73; H, 3.26; N, 8.50%).

[Ag(IV)(NO₃)₄]4.** Reaction of compound **IV** (82 mg, 0.25 mmol), dissolved in hot methanol (10 ml), with silver nitrate (43 mg, 0.25 mmol), dissolved in hot methanol (5 ml), gave a colourless solution that was filtered. Diethyl ether was diffused into this solution to give complex **4** as a white solid (86 mg, 71%), mp 152–153 °C (Found: C, 43.51; H, 3.33; N, 8.59. C₁₈H₁₆AgN₃O₃S₂ requires C, 43.73; H, 3.26; N, 8.50%).**

[Ag(NO₃)₂(V)·2H₂O]5.** Reaction of compound **V** (70 mg, 0.12 mmol), dissolved in hot acetone (10 ml), with silver nitrate (42 mg, 0.24 mmol), dissolved in water (4 ml), gave complex **5** as a white precipitate (98 mg, 86%), mp 153–154 °C (Found: C, 38.24; H, 3.18; N, 8.94. C₃₀H₂₆Ag₂N₆O₈S₄·2H₂O requires C, 38.07; H, 3.19; N, 8.88%).**

X-Ray crystallography

The crystal data and details of the data collections and refinements for the four structures are listed in Table 1. All measurements were made with a Nicolet P4s diffractometer using graphite-monochromatized Mo-K α (λ = 0.71073 Å) radiation. Cell parameters were determined by least-squares refinement on diffractometer angles for at least 20 accurately centred reflections. Throughout data collections (ω scan mode) the intensities of three standard reflections were monitored at regular intervals and in no case showed variations of >5%. Intensities were corrected for Lorentz-polarisation effects and for minor absorption using a technique based on azimuthal ψ scans.

The structures were solved by direct methods using SHELXS²³ and refined on *F*² using all data by full-matrix least-squares procedures with SHELXL 93.²⁴ All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in calculated positions with isotropic displacement parameters 1.3 times the isotropic equivalent of their carrier atoms. The functions minimised were $\Sigma w(F_o^2 - F_c^2)$, with $w = [\sigma^2(F_o^2) + aP^2 + bP]^{-1}$, where $P = [\max(F_o^2) + 2F_c^2]/3$.

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