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The role of the metal connectors $AgNO_3$, Cu_2I_2 and $CuCl_2$ in co-ordination-polymer formation using the N_2S_2 ditopic ligand 1,4-bis(2-pyridylmethylsulfanylmethyl)benzene †

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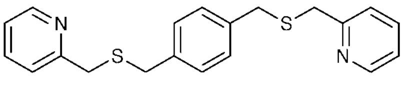
The extended-reach ligand 1,4-bis(2-pyridylmethylsulfanylmethyl)benzene (L) was prepared by base coupling of 2-(chloromethyl)pyridinehydrochloride and 1,4-bis(sulfanylmethyl)benzene. This new ligand was treated with metal connectors $AgNO_3$, CuX (X = Cl, Br or I) and $CuCl_2$ to give co-ordination polymers. The crystal structures of $[Ag_2(L)(NO_3)_2]_\infty$, $[Cu_2(L)I_2]_\infty$ and $[Cu(L)Cl_2]_\infty$ were determined. Comparison of the structures showed that the anion influenced the mode of metal binding with chelating or bridging modes being observed. The anion also influenced the nature of the packing, with the silver polymer forming a three-dimensional array containing clathrated water ladders while the copper polymers existed as related one-dimensional polymers. The remarkable feature of these structures is that while the silver polymer showed extensive intermolecular interactions, the copper polymers, despite the prevalence of aromatic rings, each displayed only one type of CH/π interaction.

Introduction

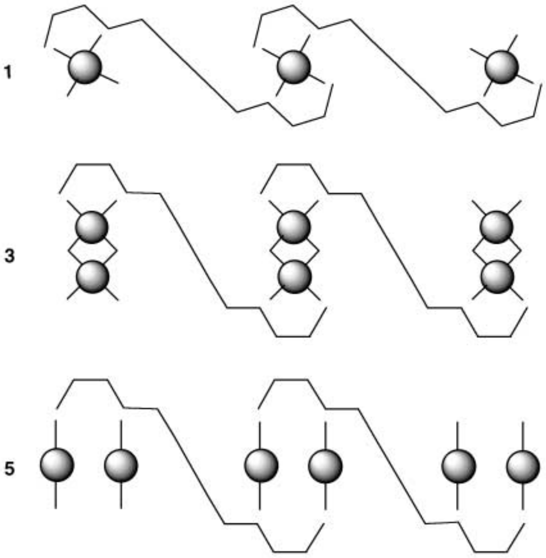
Recently the use of thioether–pyridine moieties in the preparation of new extended-reach ligands has been investigated for the construction of metallosupramolecular arrays.[1–3] The co-ordinating abilities of these donors are ideally suited to forming complexes with the metals most often used in such networks.[4] A number of complexation studies has investigated the influence of systematic variations of ligand structure on the overall molecular architecture.[1,2,5] For example, the three isomeric bis(2-pyridylsulfanylmethyl)benzenes have been shown to bridge two or more silver(I) centres.[2] The *ortho* and *meta* isomers form one-dimensional co-ordination polymers while the *para* isomer forms a metallocyclic dimer.

We decided to investigate the effect of the variation of metal connector on co-ordination-polymer formation using a related but conformationally more flexible ligand based on a *para*-substituted benzene linker with two thioether–pyridine arms. The ligand provides two separate donor regions and this arrangement may allow for the unconstrained formation of dimeric or polymeric complexes upon reaction with metal connectors. The co-ordination preference of the metal connector has an enormous influence in controlling the nature of the co-ordination polymer. For example, the major factor determining the mode of co-ordination for 2,2′-dimethyl-4,4′-bipyrimidine was found to be the type of metal ion used.[6] Copper(II) was found only in a bidentate bridging mode while more than one co-ordination mode was identified for Cu^I and Ag^I. When $AgNO_3$ was used as a connector, NO_3^- played a dominant role in network connectivity. Further, other studies have shown that more subtle effects such as the nature of the anion[7] or intermolecular π–π stacking[8] or M–X···H[9] interactions can also have a significant influence on the co-ordination polymer formed.

We now report the synthesis of a new extended-reach ligand 1,4-bis(2-pyridylmethylsulfanylmethyl)benzene (L) and reactions with the neutral metal connectors $AgNO_3$, Cu_2X_2 (X = Br or I) and $CuCl_2$. The crystal structures of three co-ordination polymers are described and compared. Two different types of metal binding modes, chelating and bridging, are observed (Scheme 1).



L



Scheme 1 Schematic diagram of the bonding modes for the metal connectors in complexes **1**, **3** and **5**.

Results and discussion

Ligand and complex synthesis

The ligand 1,4-bis(2-pyridylmethylsulfanylmethyl)benzene (L) was prepared by the base coupling of 2-(chloromethyl)pyridine-

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† Dedicated to Dr Malcolm Gerloch on the occasion of his retirement from the University of Cambridge, with best wishes for life in Australia.

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hydrochloride[10] and 1,4-bis(sulfanylmethyl)benzene[11] in a 2 : 1 molar ratio. Purification was accomplished by recrystallisation from CH_2Cl_2–light petroleum (bp 40–60 °C) to give a fawn air-stable crystalline solid in moderate yield. The ligand L reacts readily with the metal salts $AgNO_3$, CuX (X = Cl, Br or I) and $CuCl_2$ to give complexes in good yield. A 1 : 2 molar ratio of L and $AgNO_3$ or CuX (X = Br or I) gave the products **1**, **2** and **3** as analytically pure white or cream powders, respectively. The products were insoluble in most common solvents suggesting the formation of co-ordination polymers. In contrast, the product from the analogous reaction with CuCl did not precipitate from solution and appeared unstable. Microanalytical results for the product isolated from this reaction were erratic and inconclusive. Reaction of L and $CuCl_2$ in a 1 : 2 molar ratio produced **4** as a green solid which analysed with a 1 : 2 ligand : metal ratio. This product was also insoluble in most common solvents suggesting the formation of a co-ordination polymer with formula $[Cu_2(L)Cl_4]_\infty$. However crystallisation by slow diffusion of the two precursors over a week consistently produced strongly dichroic green/orange crystals which analysed with a 1 : 1 metal : ligand ratio (**5**). These crystals were suitable for a structure analysis. Bulk reaction of L and $CuCl_2$ in a 1 : 1 molar ratio also produced **5** as a microanalytically pure green powder in good yield.

The solid-state electronic spectra of complexes **2**, **3** and **5** are all very similar in the near-infrared region suggesting an isostructural arrangement of the ligand. The two copper(II) complexes **4** and **5** show different broad d–d features ($\nu_{\frac{1}{2}} \approx 10\,000$ cm^{-1}) in the region 20 000 to 6 250 cm^{-1}. The spectrum of the 1 : 1 compound **5** shows two bands of similar intensity at 13 000 and 9 260 cm^{-1} consistent with an asymmetric co-ordination environment about the copper(II) connector.[12] However, the 1 : 2 compound **4** displays only a single symmetric band at 10 500 cm^{-1} suggesting a more regular environment about the Cu^{II}. All the polymers show a number of broad charge-transfer bands in the UV region.[13] Comparisons of the IR spectra show the same trends as above with **2**, **3** and **5** having almost identical spectra while **1** and, in particular, **4** display a number of differences.

Structure of $[Ag_2(L)(NO_3)_2 \cdot 4H_2O]_\infty$ 1

Colourless rectangular crystals suitable for structure analysis were grown by slow evaporation over a number of weeks from a dilute MeCN solution of complex **1**. In the structure of complex **1** the asymmetric unit consists of a silver(I) ion, half a ligand L, a nitrate anion and two water molecules (Fig. 1). The silver(I) ion adopts a distorted tetrahedral arrangement. It is bound to one pyridine donor of a ligand L and one thioether donor of a second symmetry related ligand, thus forming the basis of a polymeric link between two ligands (Fig. 2). There are no interactions between the Ag^I and the adjacent potentially chelating thioether donor [Ag···S 3.1652(9) Å].[2] Two O atoms of the nitrate anion bind symmetrically to complete the co-ordination sphere about the Ag^I. A second symmetry generated silver ion binds the remaining donors of each arm to form a puckered 10-membered metallocyclic ring [–Ag(1)–S–C–C–N–Ag(2)–S–C–C–N–]. Within the 10-membered ring the donors of each arm bridge two silver(I) centres [Ag···Ag 4.541(1) Å]. The arms of the ligand lie in a *trans* configuration as a result of a centrosymmetric relationship with respect to the central arene ring. The ligand is folded such that the three rings lie in a stepped fashion, essentially parallel to each other [angle between the planes: 9.0°]. All silver-donor bond distances are within accepted values.[2,14] The co-ordination of the Ag to two O atoms of the nitrate anion causes the tetrahedral bond angles about Ag to be severely distorted [O(1)–Ag–O(2) 50.52(6), N(1)–Ag–S(1^I) 132.36(5)°]. The 10-membered rings, formed by two silver connectors and two different ligand arms, are joined by the central arene ring of the ligand to form a one-dimensional polymeric chain approximately along the *b* axis. Surprisingly, the related ligand 1,4-bis(2-pyridylsulfanylmethyl)benzene forms a metallocyclic dimer albeit with a 1 : 1 ligand to Ag ratio.[2]

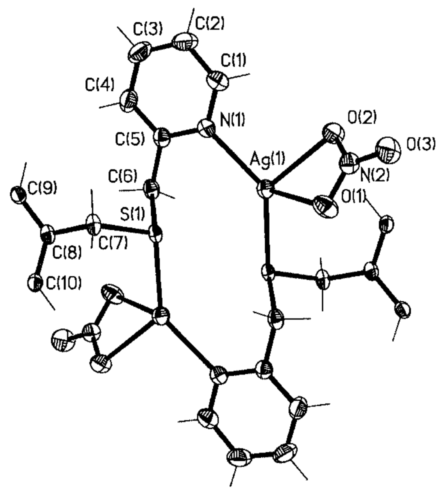

Fig. 1 Perspective view (crystallographic numbering) of the co-ordination environment of complex **1**. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (°): Ag(1)–N(1) 2.277(2), Ag(1)–O(2) 2.500(2), Ag(1)–S(1^I) 2.5048(9) and Ag(1)–O(1) 2.567(2); N(1)–Ag(1)–O(2) 94.42(7), N(1)–Ag(1)–S(1^I) 132.36(5), O(2)–Ag(1)–S(1^I) 132.46(5), N(1)–Ag(1)–O(1) 123.92(7), O(2)–Ag(1)–O(1) 50.52(6) and S(1^I)–Ag(1)–O(1) 97.30(5) (symmetry code: I $-x$, $-y-1$, $-z$).

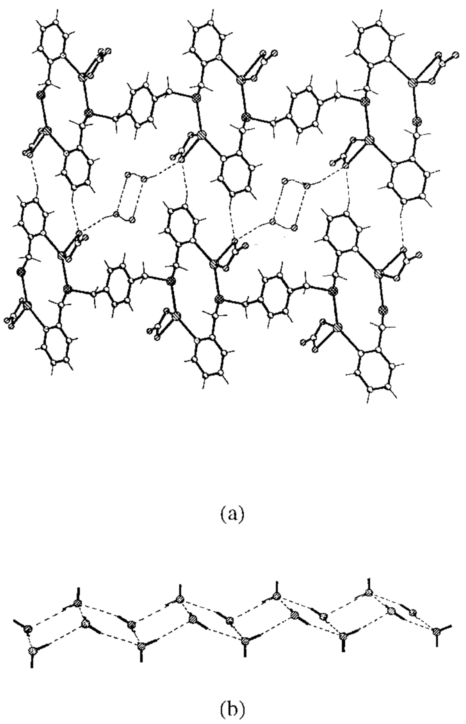

Fig. 2 (a) A view of two adjacent chains of complex **1** showing weak C(pyridine)–H···ONO_2^- and strong HO–H···ONO_2^- interactions and the corrugated ladders of water molecules running into the page. (b) View along a corrugated ladder of water molecules.

The chains stack directly on top of each other and are held together by strong intermolecular interactions {Ag···NO_3^- [Ag···N 3.222(2); Ag···O 2.833(2), 2.996(3) Å], S···NO_3^- [S···O 3.166(2) Å] and Ag···H 3.3447(7) Å} to form a two-dimensional sheet. In addition, weak C–H···arene [H···arene(centroid) 2.84 Å] interactions are also present due to the methylene hydrogens of xylyl moieties being slightly positively charged.[15]

These sheets form a three-dimensional polymer *via* two types of intermolecular interactions. First, there are weak

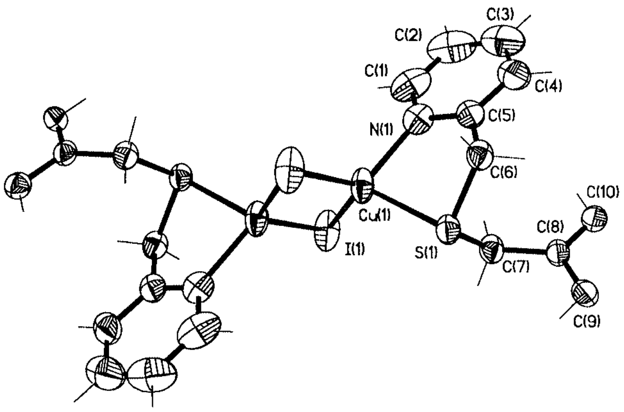

Fig. 3 Perspective view (crystallographic numbering) of the co-ordination environment of complex **3**. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (°): I(1)–Cu(1) 2.5839(7), Cu(1)–I(1$^{\text{I}}$) 2.6406(8), Cu(1)–N(1) 2.073(5), Cu(1)–S(1) 2.374(2) and Cu(1) ··· Cu(1$^{\text{I}}$) 2.531(1); Cu(1)–I(1)–Cu(1$^{\text{I}}$) 57.93(3), N(1)–Cu(1)–S(1) 85.3(1), N(1)–Cu(1)–I(1) 109.9(1), S(1)–Cu(1)–I(1) 117.82(4), N(1)–Cu(1)–I(1$^{\text{I}}$) 116.6(1), S(1)–Cu(1)–I(1$^{\text{I}}$) 98.97(4) and I(1)–Cu(1)–I(1$^{\text{I}}$) 122.07(3) (symmetry code: I $-x + 1$, $-y + 1$, $-z + 1$).

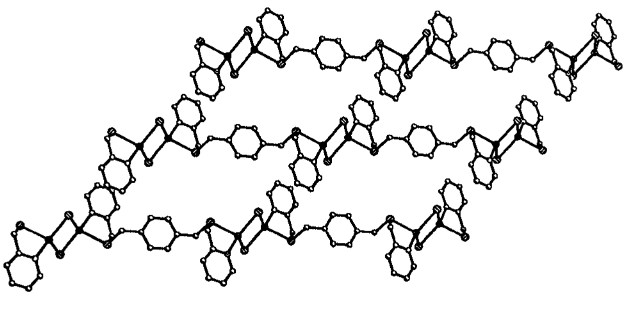

Fig. 4 View of complex **3**, with hydrogens omitted, showing the layer-like arrangement of adjacent polymeric chains and the one ring offset between chains.

C(pyridine)–H ··· NO_3^- [H ··· O 2.577(2) Å] interactions between adjacent sheets (Fig. 2a). Secondly, corrugated ladders of strongly hydrogen-bound water molecules $(H_2O)_\infty$ (Fig. 2b) lie between the sheets, clathrated within channels provided by the central *para*-substituted ring of L. The O–H ··· O distances are comparable to those found in ice[16] [O–H ··· O distances and angles 2.00(3) Å, 167(3)°; 2.21(2) Å, 159(2)° and 2.03(2) Å, 173(2)°]. These ladders are strongly hydrogen-bound to nitrate anions on adjacent sheets [H ··· O 2.04(3) Å] (Fig. 2a).

Structure of $[Cu_2(L)I_2]_\infty$ 3

Yellow rhombic crystals suitable for structure analysis were grown by the slow diffusion over several weeks of MeCN solutions of the two reactants. In the structure of complex **3** the asymmetric unit consists of a copper(I) ion, half a ligand and an iodide counter ion. The Cu$^{\text{I}}$ adopts a distorted tetrahedral co-ordination sphere and is chelated by a pyridine and a thioether donor from a ligand arm and is bound to a bridging iodide counter ion (Fig. 3). A symmetry related iodide completes the co-ordination sphere about the Cu$^{\text{I}}$. Both of these iodides are bound to a symmetry related Cu$^{\text{I}}$ thus forming a CuI_2Cu connector between two ligands as the basis of a polymeric chain (Fig. 4). The formation of CuI_2Cu connections, rather than ones based on more complex CuI motifs, is consistent with the use of a more sterically demanding ligand.[17]

The ligand L is folded in a manner similar to that in complex **1** such that the three rings lie in a stepped fashion [angle between the planes: 19.1°]. The copper(I)–donor bond distances are all within normal values.[18] Within the CuI_2Cu connectors the copper(I) centres are separated by a relatively short distance of 2.531(1) Å, which is significantly shorter than most other reported values.[19] The tetrahedral geometry about each Cu$^{\text{I}}$ is distorted and is most likely due to the NS bite angle constraint imposed by the chelating mode of the ligand [N(1)–Cu(1)–S(1) 85.3(1), N(1)–Cu(1)–I(1) 109.9(1), S(1)–Cu(1)–I(1$^{\text{I}}$) 98.97(4)°].

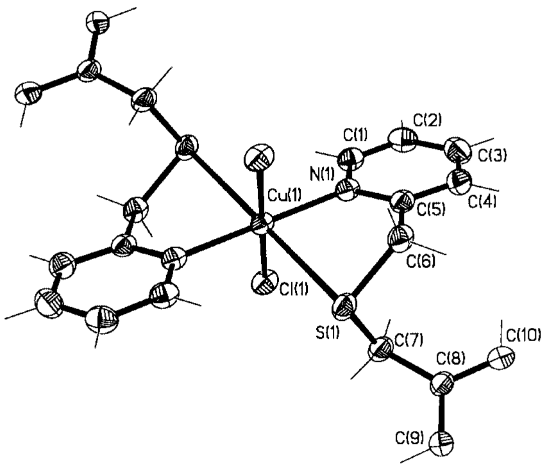

Fig. 5 Perspective view (crystallographic numbering) of the co-ordination environment of complex **5**. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (°): Cu(1)–N(1) 2.043(2), Cu(1)–Cl(1) 2.3273(5) and Cu(1)–S(1) 2.7624(6); N(1)–Cu(1)–Cl(1$^{\text{I}}$) 91.05(4), N(1)–Cu(1)–Cl(1) 88.95(4), N(1)–Cu(1)–S(1$^{\text{I}}$) 101.51(4), N(1)–Cu(1)–S(1) 78.49(4), Cl(1)–Cu(1)–S(1) 92.47(2) and Cl(1)–Cu(1)–S(1$^{\text{I}}$) 87.53(2), (symmetry code: I $-x + 1$, $-y + 1$, $-z + 1$).

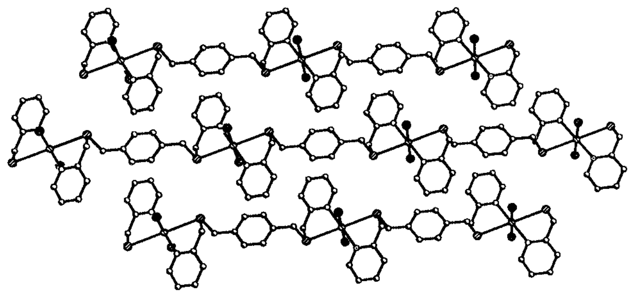

Fig. 6 View of complex **5**, with hydrogens omitted, showing the layer-like arrangement of adjacent polymeric chains and the two rings offset between chains.

These CuI_2Cu moieties connect the ligands to form a one-dimensional zigzag polymeric chain which propagates along the 1 1 0 diagonal axis. The bridging iodides lie above and below the planes of the pyridine rings. The zigzag chains lie side-by-side in a layer-like arrangement, diagonally offset by one ring so that pyridine rings from adjacent chains appear to be overlaid. However, inter-ring distances are too large (5.25 Å) to permit π–π interactions (Fig. 4). These layers lie on top of each other such that the directions of the chains within each layer are orthogonal to those in adjacent layers. While no significant interactions exist between the chains in the layer-like arrangement, there are C(methylene)–H ··· pyridine interactions between orthogonally arranged chains in adjacent layers. The distance of 2.75 Å is within the mean distance of 2.77 ± 0.10 Å for this type of CH/π interaction.[20] There are no other significant interactions within or between the layers suggesting that **3** can be considered a one-dimensional polymer.

Structure of $[Cu(L)Cl_2]_\infty$ 5

The asymmetric unit consists of half a copper(II) ion, half a ligand L and a bound chloride counter ion (Fig. 5). The Cu$^{\text{II}}$ lies on a centre of symmetry and adopts a distorted octahedral co-ordination sphere containing a pyridine and a thioether donor from a chelated ligand arm, a chloride counter ion and the three symmetry-related donors. Thus, it forms a connector between two ligands giving a one-dimensional co-ordination polymer (Fig. 6).

The ligand L is again folded in a stepped configuration [angle between the planes: 24.9°]. The Cu–N and Cu–Cl distances are all within normal values.[18] Interestingly, it is the Cu–S distances [Cu(1)–S(1) 2.7624(6) Å] rather than the Cu–Cl distances that are slightly longer than normal values for the Jahn–Teller distorted copper(II) centre.[12,21] These longer Cu–S distances are made possible by the non-ideal NS chelate-bite angle [N(1)–Cu(1)–S(1) 78.49(4)°] enforced by the ligand. The other bond angles about the Cu^{II} are within normal values [N(1)–Cu(1)–Cl(1) 88.95(4), S(1)–Cu(1)–Cl(1) 92.47(2)]. This asymmetrical co-ordination environment is consistent with the two d–d broad bands observed in the electronic spectrum of **5**. In a similar fashion to that in **3**, the metal centre links two ligands together to form a one-dimensional zigzag polymeric chain which propagates along the 1 1 0 diagonal axis. The zigzag chains lie side-by-side to form a layer and are diagonally offset by two rings so that pyridine rings overlay with arene rings from adjacent chains through very weak edge-to-face π interactions. The C(pyridine)–H···*para*-ring distance of 2.94 Å is at the conventional van der Waals limit (*ca.* 2.9 Å) and considerably longer than the average C(arene)–H···arene distance of 2.76 ± 0.10 Å.[20] However, it has been suggested that the CH/π interaction may be effective at distances beyond the van der Waals limit.[20] The two rings are inclined at 24.9° to each other. These layers are overlaid such that alternate layers are orthogonal to each other with respect to the direction of the chains within the layers. There are no significant interactions between the chains of the adjacent layers and **5** can be considered as a one-dimensional polymer.

Comparison

Despite the flexibility of the $-CH_2-S-CH_2-$ arms, the ligand adopts a very similar *trans*-stepped conformation in all three structures. Upon co-ordination two different binding modes are found. In the case of the silver polymer **1** each polymeric link is formed by a double $AgNO_3$ connection in which the ligand arms bridge rather than chelate the metal centres. Chelation of the ligand, which itself has a small bite angle, is probably disfavoured in **1** by the symmetrical binding of the chelated NO_3^- anion as this would lead to an unfavourably distorted geometry about the Ag^I. The NO_3^- anion has a major role in controlling the stacking of the chains to form sheets and the connectivity between the sheets.[6] Throughout the structure of **1** all the chains are aligned in the same direction. The NO_3^- anion and its extensive interactions are largely responsible for the difference in the structure of **1** compared with **3** and **5**. In contrast, both copper polymers **3** and **5** have chelating polymeric links. While the conformation of the ligands remains almost identical [weighted RMS deviation: 0.275 Å] (Fig. 7a) in the two copper polymers, the use of a longer CuI_2Cu connector allows the construction of a polymer with larger separation between the linking ligands (Fig. 7b). The intra-chain *para*-ring distance increases from 12.84 Å in **5** to 14.20 Å in **3**. This results in an offset of adjacent chains (Figs. 3 and 5) but the overall orthogonal stacking of the sheets remains very similar. As a result of this offset, the weak C(pyridine)–H···*para*-ring interactions which exist between adjacent chains of the same layer in **5** are no longer present in **3** [C(pyridine)–H···*para*-ring 4.61 Å]. Instead the small changes in chain positions make C(methylene)–H···pyridine interactions between orthogonal chains in adjacent layers possible in **3** but not in **5** [C(methylene)–H···pyridine 3.12 Å]. Despite these changes in the CH/π interactions, which are the most significant intermolecular interactions between chains of the two copper polymers, the overall packing does not alter dramatically. This suggests that other weaker nondescript van der Waals interactions rather than the easily identifiable CH/π interactions may be important in controlling the overall packing. Indeed, the surprising feature of the copper polymers is that despite the prevalence of aromatic rings and Cu–X moieties there are no significant π–π or Cu–X···H interactions. These structures, therefore, can be regarded as one-dimensional polymers. By comparison **1** can be considered to be a three-dimensional polymer as a result of extensive intermolecular interactions involving the NO_3^- anion.

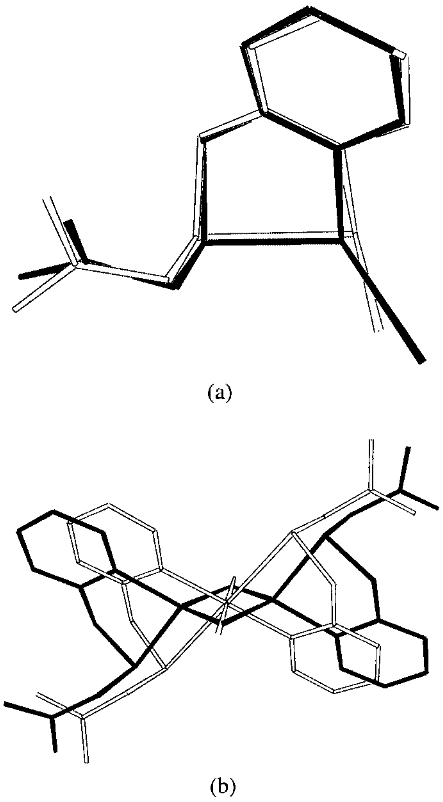

Fig. 7 (a) View of the overlaid asymmetric units of complexes **3** (solid lines) and **5** (open lines). (b) View of the overlaid metal connectors of **3** (solid lines) and **5** (open lines) showing the displacement caused by the different metal connectors.

Experimental

General

The precursors 2-(chloromethyl)pyridine hydrochloride[10] and 1,4-bis(sulfanylmethyl)benzene[11] were prepared by literature methods. The ^1H and ^{13}C NMR spectra were recorded on a Gemini 200 spectrometer operating at 200 and 50 MHz respectively, UV/vis/nir spectra on a Perkin-Elmer Lambda-9 UV/vis/nir spectrophotometer with a 60 mm MgO coated integrating sphere diffuse reflectance attachment on samples diluted with $BaSO_4$ and infrared spectra on a Perkin-Elmer Spectrum BX FT-IR System (samples in KBr disks). Elemental analyses were performed by the Campbell Microanalytical laboratory at the University of Otago.

Ligand preparation: 1,4-bis(2-pyridylmethylsulfanylmethyl)-benzene (L)

2-Chloromethylpyridine hydrochloride (8.55 g, 0.0521 mol) in EtOH (100 mL) was added, with stirring, to a solution of 1,4-bis(sulfanylmethyl)benzene (4.44 g, 0.0261 mol) in CH_2Cl_2 (150 mL) and NaOH (8 g) in EtOH–water (80:20 v/v, 100 mL). The reaction mixture was stirred for 24 h, filtered and reduced in volume to give a brown residue which was dissolved in CH_2Cl_2 (50 mL). This solution was washed with water (2 × 50 mL), dried ($MgSO_4$) and concentrated to give crude product as a brown solid. Recrystallisation from CH_2Cl_2–light petroleum (bp 40–60 °C) gave pure L as fawn crystals (yield 5.80 g, 63.1%), mp 75 °C (Found: C, 67.90; H, 5.85; N, 7.74; S, 18.37. Calc for

Table 1 Crystallographic data for complexes **1**, **3** and **5**

	1	**3**	**5**
Empirical formula	$C_{10}H_{14}AgN_2O_5S$	$C_{10}H_{10}CuINS$	$C_{20}H_{20}Cl_2CuN_2S_2$
M	382.16	366.71	486.94
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/n$	$P2_1/n$
a/Å	5.187(2)	10.282(1)	8.017(2)
b/Å	10.722(3)	9.793(1)	10.026(2)
c/Å	12.636(4)	12.188(1)	13.063(3)
α/°	82.315(4)		
β/°	78.712(4)	105.482(2)	90.816(3)
γ/°	79.952(4)		
U/Å^3	674.9(3)	1182.7(2)	1049.9(4)
Z	2	4	2
T/K	168(2)	158(2)	163(2)
μ/mm^{-1}	1.665	4.594	1.501
Reflections collected	8633	7964	4727
Unique reflections (R_{int})	2734 (0.0283)	2265 (0.0184)	2124 (0.0159)
$R1$ indices [$I > 2\sigma(I)$]	0.0231	0.0397	0.0233
$wR2$ (all data)	0.0575	0.0906	0.0651

$C_{10}H_{10}NS$: C, 68.14; H, 5.72; N, 7.95; S, 18.19%). ^{1}H NMR ($CDCl_3$): δ 8.55 [2H, d, ^3J(HH) 4.9, H6′], 7.64 [2H, dt, ^3J(HH) 7.7, ^4J(HH) 1.8, H4′], 7.30 [2H, d, ^3J(HH) 7.7, H3′], 7.25 (4H, s, H2,3,5,6), 7.16 [2H, dd, ^3J(HH) 4.9, 7.7 Hz, H5′], 3.76 (4H, s, CH_2) and 3.67 (4H, s, CH_2). ^{13}C NMR ($CDCl_3$): δ 158.6, 149.3, 136.9, 136.8, 129.2 (C2,3,5,6), 123.2, 122.0, 37.6 and 35.7.

Complexes

[$Ag_2(L)(NO_3)_2$·$4H_2O$]$_\infty$ 1. Reaction of ligand L (50 mg, 0.14 mmol) dissolved in MeOH (10 mL) with $AgNO_3$ (48 mg, 0.28 mmol) dissolved in water (5 mL) immediately gave complex **1** as a white precipitate (yield 70 mg, 72%) (Found: C, 33.32; H, 2.90; N, 7.77; S, 8.21. Calc. for $C_{10}H_{10}AgN_2SO_3$·H_2O: C, 33.00; H, 3.05; N, 7.69; S, 8.79%). IR (KBr)/cm^{-1}: 1637m, 1594m, 1570w, 1514w, 1473m, 1384vs (br), 1301vs (br), 1156m, 853m, 753m, 706m, 670m and 520w. UV/vis/nir ($BaSO_4$)/cm^{-1}: 4110m, 4350w, 4650w, 5100m, 5720w, 6000w, 6920w (br) and 39 200vs.

[$Cu_2(L)Br_2$]$_\infty$ 2. Reaction of ligand L (50 mg, 0.14 mmol) dissolved in MeCN (15 mL) with CuBr (41 mg, 0.28 mmol) dissolved in MeCN (5 mL) immediately gave complex **2** as a yellow powder (yield 70 mg, 77%) (Found: C, 37.83; H, 3.21; N, 4.57; S, 9.88. Calc. for $C_{10}H_{10}BrCuN$: C, 37.57; H, 3.15; N, 4.38; S, 10.03%). IR (KBr)/cm^{-1}: 1594s, 1566w, 1513w, 1476s, 1436s, 1391w, 1156w, 876w, 763s, 716m and 523w. UV/vis/nir ($BaSO_4$)/cm^{-1}: 4060m, 4300m, 4390m, 4590w, 5090w, 5710w (br), 5980w, 25 400 (sh) and 37 900s.

[$Cu_2(L)I_2$]$_\infty$ 3. Reaction of ligand L (20 mg, 0.057 mmol) dissolved in MeCN (5 mL) with CuI (22 mg, 0.11 mmol) dissolved in MeCN (5 mL) immediately gave the product as a yellow solid (yield 40 mg, 95%) (Found: C, 32.84; H, 2.68; N, 3.79; S, 8.72. Calc. for $C_{10}H_{10}CuINS$: C, 32.75; H, 2.75; N, 3.82; S, 8.74%). IR (KBr)/cm^{-1}: 1593s, 1567m, 1508m, 1472s, 1437s, 1399m, 1152m, 1013m, 852m, 766s, 751s, 711s, 686w, 512w and 416w. UV/vis/nir ($BaSO_4$)/cm^{-1}: 4050m, 4300m, 4340w, 4610w, 5090w, 5710w, 5980w, 26 000 (sh) and 36 400s.

[$Cu_2(L)Cl_4$]$_\infty$ 4. Reaction of ligand L (53 mg, 0.15 mmol) in MeOH (10 mL) and $CuCl_2$ (40 mg, 0.30 mmol) in MeOH (10 mL) immediately precipitated complex **4** as a green solid (yield 85 mg, 91%) (Found: C, 38.99; H, 3.37; N, 4.51; S, 10.66. Calc. for $C_{10}H_{10}Cl_2CuNS$: 38.66; H, 3.24; N, 4.51; S, 10.32%). IR (KBr)/cm^{-1}: 1602s, 1473m, 1438m, 1389m, 1163m, 1110w, 1018m, 850m, 787m, 770m, 713w and 526w. UV/vis/nir ($BaSO_4$)/cm^{-1}: 4130m, 4380m, 4580w, 4650w, 5170w, 5800w, 6060w, 10 500s (br), 23 000s and 27 000s.

[$Cu(L)Cl_2$]$_\infty$ 5. Crystallisation by slow diffusion of the two reactants L and $CuCl_2$ in MeOH consistently produced strongly dichroic green/orange crystals that analysed as a 1 : 1 complex (Found: C, 49.17; H, 4.40; N, 5.77. Calc. for $C_{20}H_{20}Cl_2CuN_2S_2$: C, 49.32; H, 4.14; N, 5.75%).

Bulk preparation. The reaction of ligand L (50 mg, 0.14 mmol) in MeOH (10 mL) with $CuCl_2$ (19 mg, 0.14 mmol) in MeOH (10 mL) immediately gave complex **5** as a light green powder (yield 55 mg, 80%) (Found: C, 48.98; H, 4.32; N, 5.60; S, 12.82. Calc. for $C_{20}H_{20}Cl_2CuN_2S_2$: C, 49.32; H, 4.14; N, 5.75; S, 13.17%). IR (KBr)/cm^{-1}: 1598s, 1566m, 1510w, 1480s, 1431s, 1398m, 1314m, 841m, 769s, 710m, 676w and 523w. UV/vis/nir ($BaSO_4$)/cm^{-1}: 4060m, 4110m, 4300m, 4350m, 4590w, 5080w, 5720w, 5960w, 9260s (br), 13 000s (br), 22 200 (sh), 26 300s and 33 300 (sh).

X-Ray crystallography

Diffraction data were collected on a Bruker SMART CCD diffractometer with graphite monochromated Mo-Kα (λ = 0.71073 Å) radiation. Intensities were corrected for Lorentz-polarisation effects[22] and a multiscan absorption correction[23] was applied. The structures were solved by direct methods (SHELXS)[24] and refined on F^2 using all data by full-matrix least-squares procedures (SHELXL 97).[25] The hydrogen atoms of the two water molecules of complex **1** were located by Fourier difference and restrained to be 0.82 Å from the corresponding oxygen atom. Detailed analyses of interactions within the structures were carried out using PLATON[26] or PARST.[27] Crystallographic data for the three structures are listed in Table 1.

CCDC reference number 186/1864.

See http://www.rsc.org/suppdata/dt/a9/a909601i/ for crystallographic files in .cif format.

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