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Molecular rectangles from metallomacrocycles: development of dibenzofuran ligands

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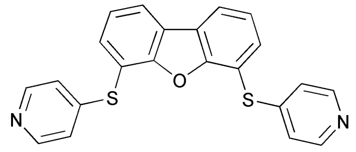
Received 20th January 2003, Accepted 13th March 2003
First published as an Advance Article on the web 28th March 2003

Two new ligands 4,6-bis(4′-pyridylsulfide)dibenzofuran **L**^{1} and 4,6-bis(methylsulfanylmethyl)dibenzofuran **L**^{2}, based on dibenzofuran with exodentate thio-pyridine arms were prepared. The crystal structures of three metallomacrocycles were determined. Reaction of **L**^{1} with $AgClO_4$ in a 1 : 1 metal-to-ligand ratio gave a ClO_4^- clamped metallomacrocycle, **1**. The analogous reaction with $CuCl_2$ gave a metallomacrocycle, **2**, in which bridging chloride ions bisected the macrocycle. Both metallomacrocycles were rectangular in shape but their cavities were occluded by bridging interactions. Reaction of **L**^{2} with CuI in a 1 : 2 metal-to-ligand ratio gave a metallomacrocycle, **3**, in which Cu_2I_2 moieties were incorporated into the edge of the macrocycle. This allowed for clearly defined cavities, which formed channels containing MeCN molecules in the overall three-dimensional honeycomb array.

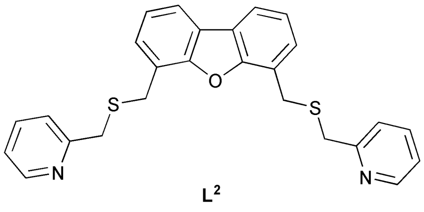
Introduction

The self assembly of ligand spacers and metal connectors has been used in supramolecular chemistry to prepare a wide variety of different structural motifs, ranging from extended coordination polymer arrays[1] to discrete molecular entities.[2] Current interest in discrete polyhedra and polygons, such as the formation of tetrahedral cages, squares and rectangles,[3] has stemmed from their many potential applications including molecular recognition and separation. In particular, molecular rectangles, as lower symmetry hosts, are expected to show enhanced binding and selectivity over the more symmetric molecular squares for certain types of guests.[3e,f] However, molecular rectangles have proven difficult to make because their formation generally requires the self-assembly of a metal precursor with two different types of ligands, which have tended to preferentially form separate discrete complexes.[4] Metallomacrocycles offer a half-way house in that they can provide rectangular shapes without the need for the combination of mixed ligands.[5] However for these metallomacrocycles, the issue of cavity size needs to be addressed through careful ligand design.

We have synthesised two new ligands **L**^{1} and **L**^{2}, based on a dibenzofuran spacer with exodentate thio-pyridine arms, for the exploration of the nature of cavities in metallomacrocycle formation. The ligands have been designed with additional functionality intended for the construction of ordered supramolecular arrays. Furthermore, the furan O and the thioether S donors might aid with the incorporation of small guest molecules into the host metallomacrocycle. Reaction of **L**^{1} with $AgClO_4$ and with $CuCl_2$ gave metallomacrocycles which did not have any appreciable cavities due to bridging of the Ag(I) ions by the ClO_4^- anions in **1** (Fig. 1) and the presence of a Cu_2Cl_2 bridge in **2** (Fig. 3). The ligand **L**^{2} was then developed as an extended-reach ligand to provide a larger cavity. Reaction of **L**^{2} with CuI successfully gave a larger metallomacrocycle with a cavity which resulted in the formation of channels in the overall three-dimensional structure.



L^1

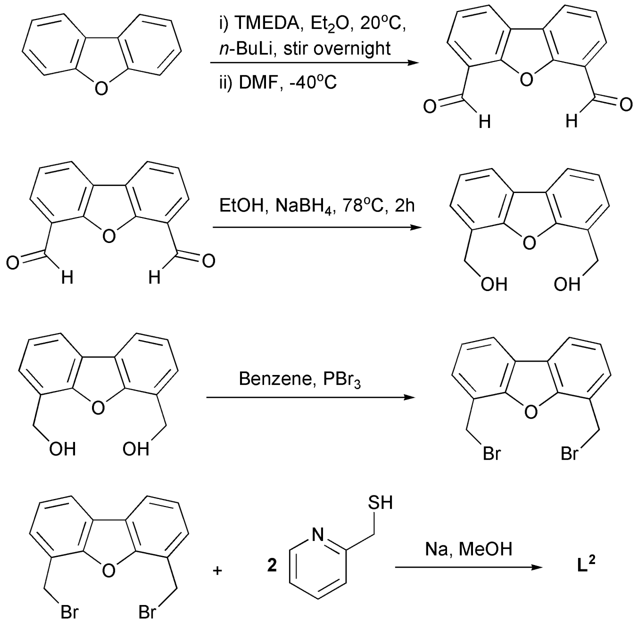


L^2

Results and discussion

Ligand syntheses

Ligand **L**^{1} was prepared in adequate yield by treatment of dilithiated dibenzofuran[6] with two equivalents of bis(4-pyridyl)-disulfide obtained commercially. For the synthesis of the extended-reach ligand **L**^{2}, the precursor, 4,6-bis(bromomethyl)-dibenzofuran was prepared in a three-step process[7] from the starting material dibenzofuran (Scheme 1). The ligand **L**^{2} was then prepared in satisfactory overall yield by treatment of 4,6-bis(bromomethyl)dibenzofuran with two equivalents of 2-(sulfanylmethyl)pyridine[8] in a solution of sodium methoxide (Scheme 1).



Scheme 1

DOI: 10.1039/b300761h

Synthesis and structure of $[Ag_2(\mathbf{L}^1)_2](ClO_4)_2$ 1

Equimolar reaction of $\mathbf{L}^1$ with $AgClO_4$ gave a fawn solid which had an analysis consistent with $Ag(\mathbf{L}^1)ClO_4{\cdot}H_2O$. The ^1H NMR spectrum of the complex was consistent with a symmetrical species in solution. Electrospray mass spectrometry under normal operating conditions showed ions at *m*/*z* 387 $[\mathbf{L}^1H]^+$, 495 $[Ag\mathbf{L}^1]^+$, 881 $[Ag(\mathbf{L}^1)_2]^+$ and 1087 $[Ag_2(\mathbf{L}^1)_2ClO_4]^+$ which were assigned by appropriate isotope patterns. Consideration of the structure of $\mathbf{L}^1$ and the presence of fragments at *m*/*z* 881 and 1087 suggested that the complex might be dimeric.

X-Ray crystal structure analysis confirmed the complex was dimeric and formed a concave centrosymmetric metallomacrocycle $\mathbf{1}{\cdot}3CH_2Cl_2$ (Fig. 1). The pyridine arms of each ligand adopted a *syn* conformation and were bent at S(1) by 101.6° and at S(2) by 103.3°, with respect to the dibenzofuran spacer. This gave the complex an overall *anti* arrangement and approximate C_{2h} symmetry. Intramolecular π stacking between overlaid pyridine rings appeared to be unlikely because of a centroid-to-centroid distance of 4.10 Å and an interplanar angle of 33.6°.[9] The Ag(I) ions were each coordinated to two pyridine N donors in a slightly bent fashion, such that the metal centres pointed in towards each other (Fig. 1). The Ag ··· Ag distance of 3.171(1) Å was in the middle of the range for argentophilic interactions observed in similar two-coordinate Ag–N systems.[5b,10] Two related metallomacrocycles had longer Ag ··· Ag distances despite the presence of intramolecular π stacking.[5b,10b] Although the two Ag(I) ions in **1** were bridged by $\mathbf{L}^1$ and the resulting Ag ··· Ag interaction would be considered "ligand supported", the flexible nature of $\mathbf{L}^1$ and the apparent lack of intramolecular π stacking did not explain the proximity of the Ag(I) ions to each other. However, consideration must be given to the role of the ClO_4^- counter ions. Two diametrically opposite ClO_4^- anions weakly bridged the two Ag(I) ions in a bidentate manner [Ag(1A)–O(14) 2.836(6), Ag(1)–O(13) 2.943(6) Å],[11] possibly acting as clamps squeezing the Ag(I) ions together (Fig. 1). Although the ClO_4^- anions were slightly disordered, the bridging oxygens were not affected. Other structures can also be identified with bridging ClO_4^- or NO_3^- anions which may contribute to shortened Ag ··· Ag contacts depending on the strength of the anion interaction.[10]

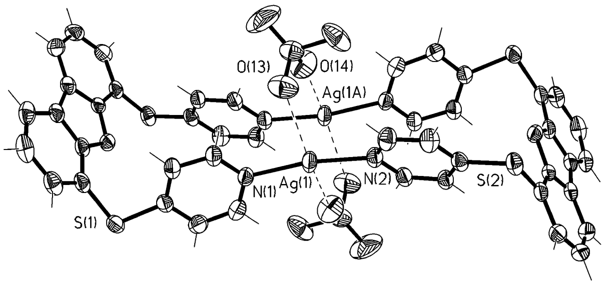


Fig. 1 Metallomacrocycle **1** showing clamping by ClO_4^- anions, solvent molecules are omitted for clarity (50% probability ellipsoids). Selected bond lengths (Å) and angles (°): Ag(1)–N(1) 2.151(4), Ag(1)–N(2) 2.150(4), Ag(1) ··· Ag(1A) 3.171(1); N(1)–Ag(1)–N(2) 169.4(1) (symmetry code: A 1 − *x*, −*y*, 1 − *z*).

The metallomacrocycles formed one-dimensional polymeric chains along the *b* axis through intermolecular π stacking interactions between strictly parallel pyridine rings (centroid-to-centroid distance 3.62 Å)[9] and Ag ··· S interactions [3.301(2) Å] (Fig. 2). Two-dimensional sheets were formed in the (1 0 1) diagonal plane through intermolecular π stacking between dibenzofuran spacers (centroid-to-centroid distance 3.75 Å) of adjacent polymeric chains. While the sheets stacked directly on top of each other, the convex nature of the metallomacrocyclic cavity caused the channels to be essentially closed. The CH_2Cl_2 solvent molecules interacted with the bound ClO_4^- anions (H ··· O–Cl 2.50–2.53 Å) and weakly interacted with protons from adjacent sheets (Cl ··· H–C 2.83–2.87 Å) to generate the overall three-dimensional network. The solvent molecules occupied a total solvent accessible volume of 23.9%.[12]

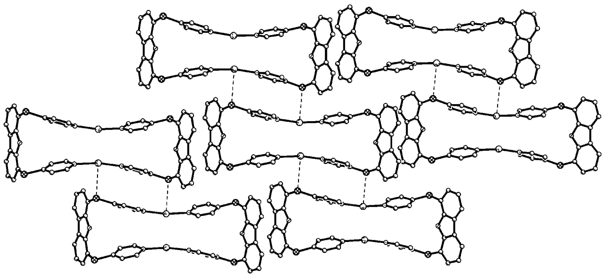


Fig. 2 View of a two-dimensional sheet of **1** in the (1 0 1) diagonal plane showing Ag ··· S and π-stacking interactions. Hydrogens, anions and solvent molecules are omitted for clarity.

Synthesis and structure of $Cu_2(\mathbf{L}^1)_2Cl_4$ 2

Reaction of $\mathbf{L}^1$ and $CuCl_2$ in a 1 : 1 molar ratio gave a green solid which had a microanalysis consistent with $Cu(\mathbf{L}^1)Cl_2{\cdot}H_2O$. Mass spectral data were unable to be obtained due to the low solubility of the complex in all common organic solvents. A solid state UV–vis spectrum of the complex showed a broad asymmetric band at 693 nm (width at half height 475 nm). Similar broad asymmetric features have been observed for other five-coordinate $CuCl_2$ complexes of polypyridyl ligands.[13]

X-Ray crystal structure analysis revealed the dimeric complex $\mathbf{2}{\cdot}6CHCl_3$ was closely related to the previous Ag(I) complex $\mathbf{1}{\cdot}3CH_2Cl_2$. The complex **2** was generated by two $\mathbf{L}^1$ ligands, joined together by an asymmetric Cu_2Cl_2 bridge, related by a centre of inversion at the mid-point between the two Cu(II) ions (Fig. 3). The bridging Cu(II) ions adopted distorted square-pyramidal geometries (τ = 0.18)[14] and were coordinated in the basal plane by a NN′Cl(μ-Cl) donor set, with the elongated axial site occupied by the remaining μ-Cl donor. The Cu ··· Cu distance of 3.464(2) Å was in the middle of the range for similar five-coordinate Cu_2Cl_2 bridged systems.[11] The *syn* ligand conformation found for **1** was also present in **2**, with the two pyridine arms bent at 101.8° and 103.1° for S(1) and S(2), respectively. Again complex **2** had an overall *anti* arrangement with C_i symmetry. While no intramolecular π stacking between the pyridine rings of $\mathbf{L}^1$ was observed (centroid-to-centroid distance = 4.19 Å, interplanar angle = 28.4°),[9] any potential metallomacrocycle cavity was closed by the Cu_2Cl_2 bridge.

Each dimeric unit was involved in six Cu–Cl ··· H–C interactions (μ-Cl ··· H = 2.78 Å and terminal-Cl ··· H = 2.74–2.90 Å) with adjacent dimers, which generated a one-

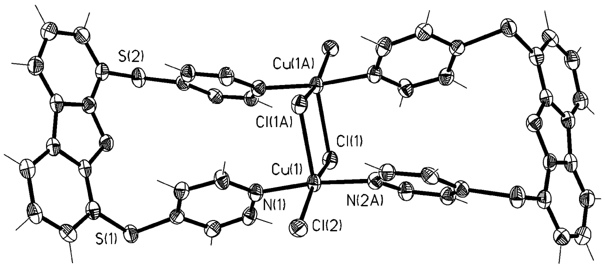


Fig. 3 Metallomacrocycle **2** showing the Cu_2Cl_2 bridge, solvent molecules are omitted for clarity (50% probability ellipsoids). Selected bond lengths (Å) and angles (°): Cu(1)–N(1) 2.016(5), Cu(1)–N(2A) 2.025(5), Cu(1)–Cl(1) 2.331(2), Cu(1)–Cl(1A) 2.647(2) Cu(1)–Cl(2) 2.298(2); Cu(1)–Cl(1)–Cu(1A) 87.95(5), N(1)–Cu(1)–N(2A) 172.8(2), Cl(1)–Cu(1)–N(1) 88.9(1), Cl(2)–Cu(1)–N(1) 87.2(1), Cl(2)–Cu(1)–Cl(1) 162.09(6), N(2A)–Cu(1)–Cl(1) 92.1(1), N(2A)–Cu(1)–Cl(2) 89.7(1), Cl(1A)–Cu(1)–N(1) 94.8(1), Cl(1A)–Cu(1)–N(2A) 92.2(1), Cl(1A)–Cu(1)–Cl(2) 105.70(6), Cl(1)–Cu(1)–Cl(1A) 92.05(5) (symmetry code: A 1 − *x*, 1 − *y*, −*z*).

dimensional polymeric chain running parallel to the *b* axis (Fig. 4). As found in **1**, two-dimensional sheets formed through intermolecular π-stacking interactions between dibenzofuran spacers of adjacent polymeric chains (centroid-to-centroid distance = 3.70 Å), but for **2** these resided in the *ab* plane. The solvent molecules occupied a total solvent accessible volume of 43.8%.[12] This extreme value led to disorder of some of the solvent molecules.

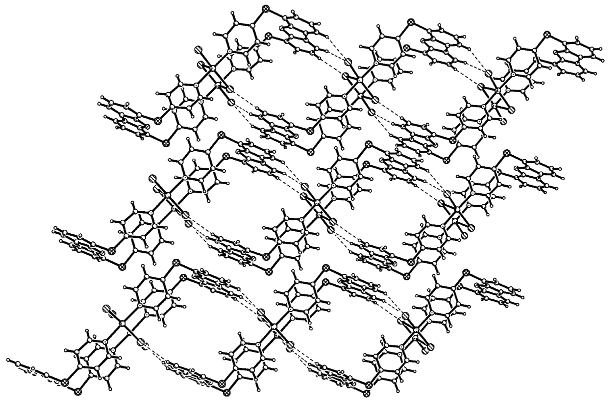


Fig. 4 View of the two-dimensional sheet of **2** in the *ab* plane formed through Cu–Cl ··· H–C and π-stacking interactions.

Synthesis and structure of $Cu_4(L^2)_2I_4$ 3

The reaction of $\mathbf{L}^2$ with CuI was initially carried out in a 1 : 1 molar ratio and gave a pale-yellow solid in low yield. This solid had an analysis consistent with $Cu_2(\mathbf{L}^2)I_2{\cdot}H_2O$. The reaction was subsequently repeated with a 1 : 2 ligand-to-metal ratio and a pale-yellow solid, which analysed in the same way, was obtained in good yield. The complex was not soluble in most organic solvents and therefore no ^{1}H NMR or electrospray mass spectral data were obtained.

X-Ray structural analysis of **3**·2MeCN revealed a centrosymmetric molecular rectangle comprising two ligands, two Cu_2I_2 connectors and a clearly defined cavity with two associated MeCN solvent molecules (Fig. 5). Each of the Cu_2I_2 connectors was chelated by N and S donors from two separate ligands. The Cu(I) ions of each Cu_2I_2 bridge adopted distorted-tetrahedral arrangements and were separated by a very short distance of 2.464(2) Å. Typical values for Cu ··· Cu distances of this type were in the range 2.53–3.58 Å.[11] Each ligand adopted an endo-*anti* arrangement in which one of the thiopyridine arms was above and the other was below the plane of the dibenzofuran spacer. As a result of this ligand conformation the rectangle adopted an overall stepped-*anti* arrangement and had approximate C_{2h} symmetry. All the heteroatoms of the ligand faced inwards towards the rectangle cavity which was 6.8 × 6.2 Å in size, as defined by the distances between the four S atoms.

Rectangles stacked along the *a* axis forming channels in which MeCN molecules resided (Fig. 5). The dibenzofuran spacers of neighbouring rectangles interdigitated (centroid-to-centroid distance 3.97 Å)[9] and C–H ··· π interactions (C–H_{perp} distance 2.74 Å) were present.[15] In addition, the pyridine rings on the opposite sides of the rectangles also interdigitated with adjacent pyridine rings (centroid-to-centroid distance 4.31 Å). These interdigitations gave rise to a three-dimensional pseudo-honeycomb pattern (Fig. 6).

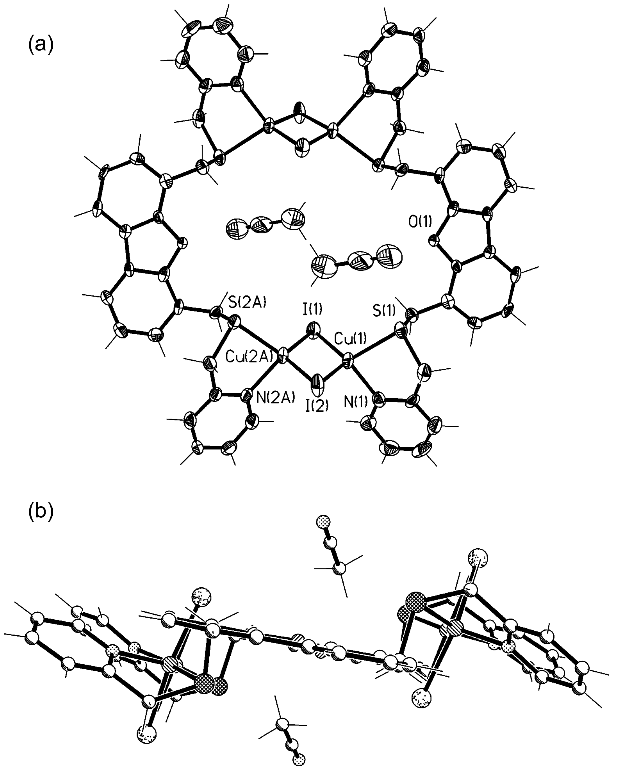


Fig. 5 Views of molecular rectangle **3**. (a) View showing the cavity and solvent molecules (50% probability ellipsoids). Selected bond lengths (Å) and angles (°): Cu(1)–N(1) 2.034(6), Cu(2A)–N(2A) 2.106(6), Cu(1)–S(1) 2.384(2), Cu(2A)–S(2A) 2.299(2), Cu(1)–I(1) 2.698(2), Cu(1)–I(2) 2.604(2), Cu(2A)–I(1) 2.588(2), Cu(2A)–I(2) 2.705(2); N(1)–Cu(1)–S(1) 88.5(2), N(1)–Cu(1)–I(2) 107.3(2), S(1)–Cu(1)–I(2) 105.23(6), N(1)–Cu(1)–I(1) 109.8(2), S(1)–Cu(1)–I(1) 115.51(6), I(2)–Cu(1)–I(1) 124.37(5), N(2A)–Cu(2A)–S(2A) 86.8(2), N(2A)–Cu(2A)–I(1) 112.1(2), I(1)–Cu(2A)–S(2A) 112.81(7), N(2A)–Cu(2A)–I(2) 102.3(2), I(2)–Cu(2A)–S(2A) 110.92(7), I(1)–Cu(2A)–I(2) 124.72(5), Cu(2A)–I(1)–Cu(1) 55.53(4), Cu(1)–I(2)–Cu(2A) 55.27(4) (symmetry code: A −*x*, 1 − *y*, 1 − *z*). (b) Edge on view showing the *anti* ligand arrangement and placement of the MeCN solvent molecules.

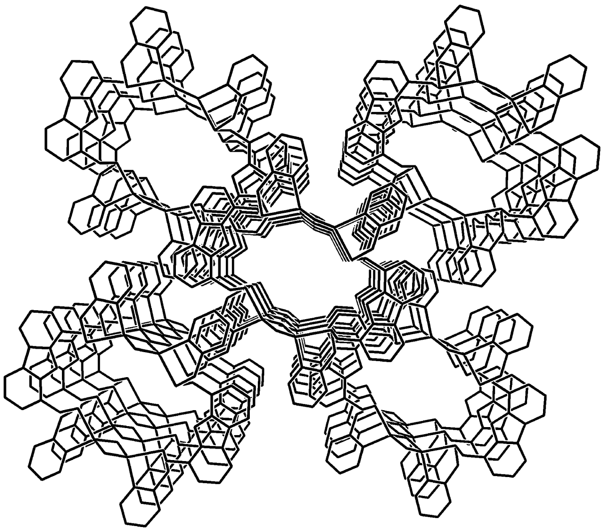


Fig. 6 View down the crystallographic *a* axis showing the channels and interdigitation of the rectangles. Solvent molecules and hydrogen atoms are omitted for clarity.

Conclusion

We have shown that ligands with the correct geometric requirements can be readily synthesised to form metallomacrocycles with rectangular shapes. Our initial ligand design was compromised by the close proximity of the pyridyl N donors which came about as a result of the particular S donor arrangement. This facilitated Ag ··· Ag clamping and Cu_2Cl_2 bridging interactions which bisected the metallomacrocycle. All of these factors contributed to the formation of rectangular cavities which were too small for guest incorporation. Changing the ligand design by extending the thio-pyridine arms and making the S donors available for chelation allowed CuI, which is prone to forming Cu_2I_2 dimers, to be incorporated into an edge of the metallomacrocycle rather than occluding the cavity. In addition, the large dibenzofuran aromatic spacer and thioether linkers have shown promise in generating ordered sheets with channels. In this way we have successfully made a metallomacrocycle with a clearly defined cavity, which has shown that such carefully shaped systems can be used as alternatives to more traditional methods for fabricating discrete rectangular species.

Experimental

General

Bis(4-pyridyl)disulfide was obtained from Aldrich and used as supplied. Elemental analyses were performed by the Campbell Microanalytical laboratory at the University of Otago. ^{1}H and ^{13}C NMR spectra were recorded on either a Varian unity INOVA 300 or 500 MHz spectrometer. The solid-state electronic spectrum was collected as a $BaSO_4$ diluted sample with a Cary-500 Scan UV–vis–NIR spectrophotometer fitted with a 110 mm PTFE coated integrating sphere. The electrospray mass spectrum (ES–MS) was measured on a Shimadazu LCMS-QP800α spectrometer with a mass range *m*/*z* 10–2000. Samples were injected by direct infusion using a Rheodyne manual injector. The mobile phase flow rate was 0.2 mL min^{-1} and consisted of a 90% MeCN–10% H_2O solvent mixture. The high-resolution mass spectrum was collected on a Kratos MS-80 mass spectrometer at the University of Canterbury.

CAUTION: Although no problems were encountered in this work, transition metal perchlorates are potentially explosive. They should be prepared in small amounts and handled with care.

Ligand preparation

4,6-Bis(4′-pyridylsulfide)dibenzofuran (L^1). Under a N_2 atmosphere a solution of dibenzofuran (1.0 g, 5.9 mmol), TMEDA (2.1 g, 18 mmol) and 100 mL dried distilled diethyl ether was cooled to −78 °C. Degassed *n*-BuLi (11 mL of a 1.6 M solution in hexane, 18 mmol) was added to the reaction over 0.5 h and left to stir for a further 1 h before allowing the reaction mixture to warm to room temperature and stir overnight. The mixture was then cooled to −78 °C before slowly adding bis(4-pyridyl)disulfide (2.6 g, 12 mmol) dissolved in 100 mL of degassed dried, distilled diethyl ether. The reaction was stirred for 1 h before warming to room temperature. The resulting mixture was reduced to give a cream solid which was dissolved in 200 mL of CH_2Cl_2 and washed with H_2O (2 × 200 mL). The CH_2Cl_2 layer was dried ($MgSO_4$), filtered and reduced in volume to give a cream-orange solid. The crude product was recrystallised from *i*-PrOH to give cream crystals. Yield: 0.89 g (39%). ^{1}H NMR ($CDCl_3$, 298 K, 300 MHz), δ 8.27 (br d, 4H), 8.09 (dd, 2H, ^3J(HH) 7.8, ^4J(HH) 1.2 Hz), 7.67 (dd, 2H, ^3J(HH) 7.8, ^4J(HH) 1.2 Hz), 7.46 (t, 2H, ^3J(HH) 7.8 Hz), 6.89 (br d, 4H); ^{13}C NMR ($CDCl_3$, 298 K, 75 MHz), δ 156.36, 149.56, 148.32, 134.56, 125.40, 124.71, 123.20, 121.53, 113.27. Anal. Calc. For $C_{22}H_{14}N_2S_2O\cdot H_2O$: C, 65.32; H, 3.99; N, 6.93; S, 15.85. Found: C, 65.39; H, 3.71; N, 7.10; S, 15.74%.

4,6-Bis(methylsulfanylmethyl)dibenzofuran (L^2). 2-(Sulfanylmethyl)pyridine (3.7 g, 29 mmol) was added to dry degassed MeOH (250 mL) containing 0.66 g (29 mmol) of Na metal and was stirred for 0.5 h. 4,6-Bis(bromomethyl)dibenzofuran (5.2 g, 15 mmol) was suspended in dry degassed benzene (100 mL), added to the above solution, refluxed for 2 h, and stirred overnight. The resulting solution was reduced to give a brown oil which was dissolved in $CHCl_3$ (200 mL) and washed with H_2O (2 × 200 mL). The H_2O layers were combined and then washed with $CHCl_3$ (2 × 150 mL). All of the $CHCl_3$ layers were combined, dried ($MgSO_4$), filtered and reduced to give a crude brown oil. Column chromatography [5% hydrated silica gel v/v, eluted with 70 : 30 ethyl acetate–light petroleum (bp 40–60 °C)] of a 2 g sample of the crude oil gave 0.58 g of **L^2** as a yellow oil (overall yield: 37%). (Found: M$^+$ 443.1256, $^{12}C_{26}{}^{1}H_{23}{}^{14}N_2{}^{16}O^{32}S_2$ requires M, 443.1252); ^{1}H NMR ($CDCl_3$, 298 K, 500 MHz), δ 8.52 (br d, 2H), 7.81 (d, 2H, ^3J(HH) 7.8 Hz), 7.58 (dt, 2H, ^3J(HH) 7.5, ^4J(HH) 1.8 Hz), 7.46 (d, 2H, ^3J(HH) 7.5 Hz), 7.29–7.33 (m, 4H), 7.10–7.14 (m, 2H), 4.07 (s, 4H), 3.85 (s, 4H); ^{13}C NMR ($CDCl_3$, 298 K, 125 MHz), δ 158.5, 154.3, 149.4, 136.6, 127.9, 124.5, 123.1, 123.0, 122.5, 121.9, 119.6, 38.0, 29.7. Anal. Calc. For $C_{26}H_{22}N_2S_2O\cdot\frac{3}{4}H_2O$: C, 68.49; H, 5.20; N, 6.15; S, 14.06. Found: C, 68.51; H, 5.18; N, 5.90; S, 14.36%.

Complexes

[Ag$_2$(L^1)$_2$](ClO$_4$)$_2$ 1. $AgClO_4$ (27 mg, 0.13 mmol) was dissolved in degassed MeCN and added *via* cannula to **L^1** (50 mg, 0.13 mmol) dissolved in degassed MeCN and allowed to stir overnight. The resulting pale fawn precipitate was filtered and dried *in vacuo*. Yield: 42 mg (54%). Colourless crystals were grown from the slow diffusion of a $CHCl_3$ solution (2 mL) of **L^1** (20 mg, 0.052 mmol) layered with CH_2Cl_2 (1 mL) and a MeCN solution (5 mL) of $AgClO_4$ (11 mg, 0.052 mmol). Anal. Calc. for $C_{22}H_{14}N_2S_2O_5AgCl\cdot H_2O$: C, 43.18; H, 2.64; N, 4.58; S, 10.48. Found: C, 42.92; H, 2.29; N, 4.53; S, 10.47%. ^{1}H NMR (CD_3CN, 298 K, 300 MHz), δ 8.45 (dd, 2H, ^3J(HH) 7.8, ^4J(HH) 0.9 Hz), 8.17 (d, 4H, ^3J(HH) 6.6 Hz), 7.85 (dd, 2H, ^3J(HH) 7.8, ^4J(HH) 0.9 Hz), 7.68 (t, 2H, ^3J(HH) 7.8 Hz), 7.32 (d, 4H, ^3J(HH) 6.6 Hz). ES MS: *m*/*z* 387 [**L^1**H]$^+$, 495 [Ag**L^1**]$^+$, 881 [Ag(**L^1**)$_2$]$^+$ and 1087 [Ag$_2$(**L^1**)$_2$ClO$_4$]$^+$.

Cu$_2$(L^1)$_2$Cl$_4$ 2. Ligand **L^1** (50 mg, 0.13 mmol) was dissolved in $CHCl_3$ (10 mL) and added dropwise to a solution of $CuCl_2$ (17 mg, 0.13 mmol) in EtOH (10 mL). This immediately gave a green precipitate, which was filtered and dried *in vacuo*. Yield: 55 mg (81%). Green crystals were grown from the slow diffusion of a $CHCl_3$ solution (2 mL) of **L^1** (20 mg, 0.052 mmol) layered with CH_2Cl_2 (1 mL) and a MeOH solution (5 mL) of $CuCl_2$ (7 mg, 0.05 mmol). Anal. Calc. for $C_{22}H_{14}N_2S_2OCuCl_2\cdot H_2O$: C, 49.03; H, 2.99; N, 5.20; S, 11.90. Found: C, 49.41; H, 2.88; N, 5.20; S, 12.11%. UV–vis–NIR ($BaSO_4$)/nm: 693.

Cu$_4$(L^2)$_2$I$_4$ 3. CuI (42 mg, 0.22 mmol) was dissolved in degassed MeCN and added *via* cannula to **L^2** (50 mg, 0.11 mmol) dissolved in degassed $CHCl_3$ and allowed to stir for 3 h. The resulting lemon precipitate was filtered off and dried *in vacuo*. Yield: 55 mg (60%). Colourless crystals were grown from the slow evaporation of a MeCN solution. Anal. Calc. for $C_{26}H_{22}N_2S_2OCu_2I_2\cdot H_2O$: C, 37.12; H, 2.88; N, 3.33; S, 7.62. Found: C, 37.38; H, 2.75; N, 3.62; S, 7.38%

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[16] and a multiscan absorption correction[17] was applied. The structures were solved by direct methods (SHELXS)[18] and refined on F^2 using all data by full-matrix least-squares procedures (SHELXL 97).[19] All calculations were performed using the WinGX interface.[20] One of the unique CH_2Cl_2 molecules in **1**·3CH$_2$Cl$_2$ was disordered across a centre of symmetry. Two of the three unique solvent molecules in **2**·6CHCl$_3$ were modelled as constrained $CHCl_3$ molecules and were each disordered over two sites. Crystallographic data for the three structures are listed in Table 1.

CCDC reference numbers 186275 and 186276.

See http://www.rsc.org/suppdata/dt/b3/b300761h/ for crystallographic files in CIF or other electronic format.

Table 1 Crystallographic data for complexes

	1·3CH$_2$Cl$_2$	**2**·6CHCl$_3$	**3**·2MeCN
Formula	$C_{23.5}H_{17}AgCl_4N_2O_5S_2$	$C_{25}H_{17}CuCl_{11}N_2OS_2$	$C_{56}H_{50}Cu_4I_4N_6O_2S_4$
M	721.18	879.02	1729.02
Crystal system	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)
a/Å	9.666(5)	11.050(4)	9.843(5)
b/Å	10.113(5)	12.715(5)	12.283(5)
c/Å	14.921(5)	13.400(5)	13.537(5)
α/°	81.954(5)	95.549(5)	79.209(5)
β/°	72.710(5)	110.840(4)	88.332(5)
γ/°	81.553(5)	106.598(5)	77.788(5)
U/Å^3	1370(1)	1644(1)	1571(1)
Z	2	2	1
T/K	168(2)	158(2)	168(2)
μ/mm^{-1}	1.316	1.712	3.477
Reflections collected	10 953	20 408	19 251
Unique reflections (R_{int})	5386 (0.0147)	6439 (0.0278)	5985 (0.0852)
$R1$ indices [$I > 2\sigma(I)$]	0.0537	0.0612	0.0583
$wR2$ (all data)	0.1689	0.2004	0.1186

Acknowledgements

We thank Prof. Ward T. Robinson and Dr Jan Wikaira (University of Canterbury) for X-ray data collection and the University of Otago, Otago Research Committee, for financial support.

References

1 A. N. Khlobystov, A. J. Blake, N. R. Champness, D. A. Lemenovskii, A. G. Majouga, N. V. Zyk and M. Schröder, *Coord. Chem. Rev.*, 2001, **222**, 155; A. J. Blake, N. R. Champness, P. Hubberstey, W.-S. Li, M. A. Withersby and M. Schröder, *Coord. Chem. Rev.*, 1999, **183**, 117; S. R. Batten and R. Robson, *Angew. Chem., Int. Ed.*, 1998, **37**, 1460; M. Munakata, L. P. Wu and T. Kuroda-Sowa, *Bull. Chem. Soc. Jpn.*, 1997, **70**, 1727.

2 J. A. R. Navarro and B. Lippert, *Coord. Chem. Rev.*, 2001, **222**, 219; G. F. Swiegers and T. J. Malefetse, *Chem. Rev.*, 2000, **100**, 3483; S. Leininger, B. Olenyuk and P. J. Stang, *Chem. Rev.*, 2000, **100**, 853.

3 *Cages:* (*a*) C. He, L.-Y. Wang, Z.-M. Wang, Y. Liu, C.-S. Liao and C.-H. Yan, *J. Chem. Soc., Dalton Trans.*, 2002, 134; (*b*) D. L. Caulder, C. Brückner, R. E. Powers, S. König, T. N. Parac, J. A. Leary and K. N. Raymond, *J. Am. Chem. Soc.*, 2001, **123**, 8923; *Squares:* (*c*) S.-S. Sun and A. J. Lees, *Inorg. Chem.*, 2001, **40**, 3154; (*d*) L. Carlucci, G. Ciani, D. M. Proserpio and S. Rizzato, *Chem. Commun.*, 2001, 1198; *Rectangles:* (*e*) T. Rajendran, B. Manimaran, F.-Y. Lee, G.-H. Lee, S.-M. Peng, C. M. Wang and K.-L. Lu, *Inorg. Chem.*, 2000, **39**, 2016; (*f*) K. D. Benkstein, J. T. Hupp and C. L. Stern, *Angew. Chem., Int. Ed.*, 2000, **39**, 2891.

4 C. J. Kuehl, S. D. Huang and P. J. Stang, *J. Am. Chem. Soc.*, 2001, **123**, 9634; D. J. Holliday and C. A. Mirkin, *Angew. Chem., Int. Ed.*, 2001, **40**, 2022.

5 (*a*) Y. Cui, H. L. Ngo and W. Lin, *Inorg. Chem.*, 2002, **41**, 1033; (*b*) R. Schneider, M. W. Hosseini, J.-M. Planeix, A. De Cian and J. Fischer, *Chem. Commun.*, 1998, 1625; (*c*) C. M. Hartshorn and P. J. Steel, *Inorg. Chem.*, 1996, **35**, 6902.

6 M. W. Haenel, D. Jakubik, E. Rothenberger and G. Schroth, *Chem. Ber.*, 1991, **124**, 1705.

7 C. Kuehm-Caubère, S. Adach-Becker, Y. Fort and P. Caubère, *Tetrahedron*, 1996, **52**, 9087; M. L. Skar and J. S. Svendsen, *Tetrahedron*, 1997, **53**, 17425; L. V. Dunkerton, B. C. Barot and A. Nigam, *J. Heterocycl. Chem.*, 1987, **24**, 749; T. A. Robbins and D. J. Cram, *J. Chem. Soc., Chem. Commun.*, 1995, 1515.

8 E. C. Constable, A. C. King and P. R. Raithby, *Polyhedron*, 1998, **17**, 4275.

9 C. Janiak, *J. Chem. Soc., Dalton Trans.*, 2000, 3885.

10 (*a*) B.-L. Fei, W.-Y. Sun, T. Okamura, W.-X. Tang and N. Ueyama, *New J. Chem.*, 2001, **25**, 210; (*b*) Y. Zhao, M. Hong, W. Su, R. Cao, Z. Zhou and A. S. C. Chan, *Chem. Lett.*, 2000, 28; (*c*) J. A. R. Navaro, J. M. Salas, M. A. Romero and R. Faure, *J. Chem. Soc., Dalton Trans.*, 1998, 901; (*d*) M.-L. Tong, X.-M. Chen, B.-H. Ye and S. W. Ng, *Inorg. Chem.*, 1998, **37**, 5278.

11 F. H. Allen, J. E. Davies, J. J. Galloy, O. Johnson, O. Kennard, C. F. Macrae, E. M. Mitchell, G. F. Mitchell, J. M. Smith and D. G. Watson, *J. Chem. Inf. Comput. Sci.*, 1987, **31**, 187.

12 A. L. Spek, *Acta Crystallogr., Sect. A*, 1990, **46**, 467.

13 P. L. Caradoc-Davies, D. H. Gregory, L. R. Hanton and J. M. Turnbull, *J. Chem. Soc., Dalton Trans.*, 2002, 1574; L. R. Hanton and K. Lee, *J. Chem. Soc., Dalton Trans.*, 2000, 1161; J. B. Dagdigian, V. McKee and C. A. Reed, *Inorg. Chem.*, 1982, **21**, 1332.

14 A. W. Addison, T. Nageswara Rao, J. Reedijk, J. van Rijn and G. C Verschoor, *J. Chem. Soc., Dalton Trans.*, 1984, 1349.

15 H. Suezawa, T. Yoshida, M. Hirota, H. Takahashi, Y. Umezawa, K. Honda, S. Tsuboyama and M. Nishio, *J. Chem. Soc., Perkin Trans. 2*, 2001, 2053; Y. Umezawa, S. Tsuboyama, K. Honda, J. Uzawa and M. Nishio, *Bull. Chem. Soc. Jpn.*, 1998, **71**, 1207; M. Nishio, Y. Umezawa, M. Hirota and Y. Takeuchi, *Tetrahedron*, 1995, **51**, 8665.

16 SAINT V4, Area Detector Control and Integration Software, Siemens Analytical X-Ray Systems Inc., Madison, WI, 1996.

17 G. M. Sheldrick, SADABS, Program for Absorption Correction, University of Göttingen, 1996.

18 G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 1990, **46**, 467.

19 G. M. Sheldrick, SHELXL 97, University of Göttingen, 1997.

20 L. J. Farrugia, *J. Appl. Crystallogr.*, 1999, **32**, 837.