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Probing copper halide supramolecular arrays of a ditopic ligand with complexes of a monotopic analogue†

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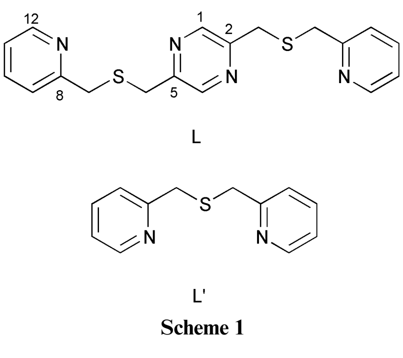
The ligand bis(2-pyridylmethyl)sulfide **L**′ and the complexes it formed were used as simple probes for the complexes of 2,5-bis(2-pyridylmethylsufanylmethyl)pyrazine **L**. **L**′ and **L** were reacted in 1 : 1 and 1 : 2 molar ratios, respectively, with both $CuCl_2$ and CuI. Crystal structures of all four complexes were determined, $CuCl_2L'\cdot H_2O$ (**1**), Cu_2Cl_4L (**2**), $Cu_2I_2L'_2$ (**3**) and $[Cu_2I_2L]_\infty$ (**4**). The Cu(II) ions in **1** and **2** were square pyramidal. For **2** crystal structures of the *anti* (**2a**) and the *syn* (**2b**) isomers were determined and both were found to form proto-polymeric chains. Complex **3** was dimeric and contained Cu_2I_2 bridges. The structure of **4** revealed one-dimensional polymeric chains in which the ligands were joined by Cu_2I_2 bridges. This work demonstrated the successful use of the complexes of **L**′ as probes for **4** and to a lesser extent for **2a** and **2b**.

Introduction

There has been considerable interest in the way in which organic building blocks can be combined with transition metal centres to form ordered supramolecular frameworks.[1–3] The synthetic strategies, which have been used to assemble these arrays, include the use of covalent bonding,[3] hydrogen bonding[4] and other weak intermolecular interactions.[5,6] It was of interest to consider how these interactions were affected, and the supramolecular structure was altered, by symmetric changes in the ligand makeup. The structures of polymers constructed from rigid linear ligands have shown parallels with certain standard inorganic substances such as graphite, diamond, zinc blende, wurtzite or fluorite.[1b,7] However, ligands that are more flexible often give rise to less predictable architectures.[8,9] Paradigms for arrays built from flexible ligands may be modelled from similar but less complicated ligands.

We have specifically designed two ligands, bis(2-pyridylmethyl)sulfide **L**′ and the centrosymmetrically extended 2,5-bis(2-pyridylmethylsufanylmethyl)pyrazine **L**, to investigate whether the supramolecular structure of the copper complexes of **L** are modelled by the simpler **L**′ complexes (Scheme 1).



Scheme 1

Previously we have investigated the differences between Ag(I) complexes of **L**′ and **L** and have found that the π-stacked dimeric arrangement in $[Ag_2(\mathbf{L}')_2]^{2+}$ was often incorporated into the more complicated arrays of **L**.[10–12] Furthermore, a ligand such as **L** is time-consuming to prepare and as such, it would be advantageous to develop a probe for investigating the desirable features of a coordination polymer before construction of the more complicated ligand is undertaken.

We report the synthesis and characterisation of the copper(II) chloride complexes **1** and **2** of **L**′ and **L**, respectively, and the copper(I) iodide complexes **3** and **4** of **L**′ and **L**, respectively. While **1** was a discrete square-pyramidal mononuclear complex, **2** crystallised as proto-polymeric *anti* and *syn* isomers also with square-pyramidal Cu(II) centres. Compound **3** was a discrete Cu_2I_2 bridged dimer, which accurately modelled the one-dimensional chain of **4**, a coordinate-covalently bonded polymer.

Results and discussion

Synthesis and structure of $CuCl_2L'\cdot H_2O$ 1

A 1 : 1 molar ratio of $CuCl_2$ and **L**′ was reacted and a green solid was isolated. The resulting complex gave an analysis consistent with $CuCl_2L'\cdot H_2O$. The solid-state UV-vis spectrum contained a very broad asymmetric band at 1106 nm due to d–d transitions, with a shoulder at 901 nm. Similar broad asymmetric features were observed in the UV-vis spectrum for the related square-pyramidal Cu(II) complex of the tridentate 2,2′-bis(2-(5,6-dimethylbenzimidazoyl))diethylsulfide ligand.[13]

The X-ray structure showed the complex was monomeric and the Cu(II) ion adopted a square-pyramidal geometry with τ = 0.14 (for an ideal square pyramid τ = 0 and for a trigonal bipyramid τ = 1) (Fig. 1).[14] The five-coordinate geometry consisted of N_2S donation from the ligand with two Cl^- ions completing the coordination sphere. The thioether S, two pyridine N donors and one Cl^- ion occupied the basal plane with a second Cl^- ion in an elongated apical site. The ligand adopted a meridional stretched-out conformation with the Cu(II) ion and all non-hydrogen atoms of **L**′, with the exception of sulfur, lying in the same plane (mean deviation from mean plane 0.037 Å). This meridional arrangement of the tridentate ligand has been observed for other copper complexes with similar donor sets although those tridentate ligands tended to

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† Dedicated to Barbara Duncan on the occasion of her retirement as Senior Teaching Fellow in Chemistry at the University of Otago, in acknowledgement of her contribution to our research activities.

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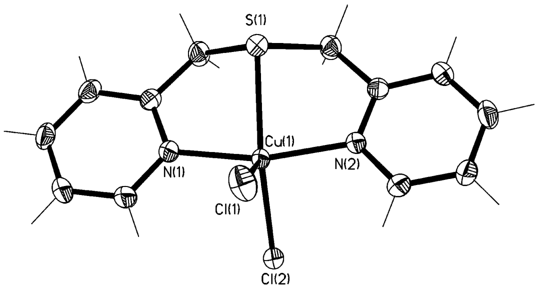

Fig. 1 Perspective view (crystallographic numbering) of **1**. Thermal ellipsoids are drawn at the 50% probability level. The water molecule is not shown. Selected bond lengths (Å) and angles (°): Cu(1)–N(1) 2.008(3), Cu(1)–N(2) 2.001(3), Cu(1)–S(1) 2.388(1), Cu(1)–Cl(1) 2.467(1), Cu(1)–Cl(2) 2.298(1); N(1)–Cu(1)–N(2) 161.9(1), N(1)–Cu(1)–Cl(1) 97.0(1), N(1)–Cu(1)–Cl(2) 95.7(1), N(1)–Cu(1)–S(1) 82.5(1), N(2)–Cu(1)–Cl(1) 96.7(1), N(2)–Cu(1)–Cl(2) 93.2(1), N(2)–Cu(1)–S(1) 82.6(1), S(1)–Cu(1)–Cl(1) 105.06(4), S(1)–Cu(1)–Cl(2) 153.54(3), Cl(1)–Cu(1)–Cl(2) 101.30(4).

be less planar.[15] All Cu–S, Cu–N and Cu–Cl bond lengths were within the normal range.[16] Two intermolecular π–π stacking interactions (centroid–centroid distances = 3.69 and 3.81 Å)[6] were observed between the pyridine rings of the complex which generated a two-dimensional brick wall pattern (Fig. 2). In addition, the complex was associated with one H_2O of crystallisation. These water molecules were involved in O–H ··· Cl (2.09–2.28 Å) and C–H ··· ·O (2.27–2.49 Å) interactions which gave rise to the three-dimensional packing.

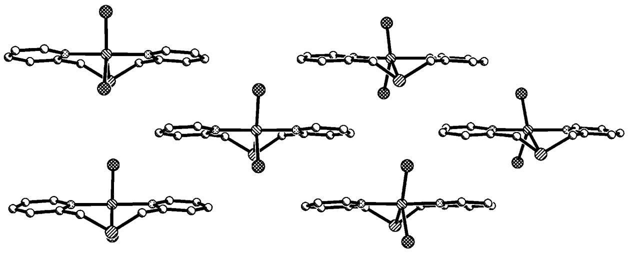

Fig. 2 A view of the π–π interactions between adjacent molecules of $CuCl_2$**L′**. Water molecules and hydrogens are omitted for clarity.

Four transition metal complexes of **L′** have been reported previously.[10,17] However, only the silver complex of **L′**, $[Ag_2(\mathbf{L'})_2](PF_6)_2$, has been structurally characterised.[10] In addition, a $Cu(CF_3SO_3)_2$ complex of bis(6-methyl-2-pyridylmethyl)sulfide, a methylated analogue of **L′**, has been prepared and shows many structural similarities to **1**.[18] In that complex the Cu(II) ion also adopted a distorted square-pyramidal environment ($\tau = 0.42$) with the five donor atoms provided by the two $CF_3SO_3^-$ ions and the meridionally N_2S coordinated ligand.

Synthesis of Cu_2Cl_4L 2

A 1 : 2 molar ratio of **L** and $CuCl_2$ was reacted to give a green precipitate, which had an analysis consistent with Cu_2Cl_4**L**. Two different types of crystals with distinctly different crystal morphologies and colours were grown at different times from the slow diffusion of diethyl ether into a MeCN solution of the complex. The first type grown were small block-shaped crystals, which were emerald-green in colour. Despite many attempts, the only emerald-green crystals obtained were always very small, often twinned and of poor quality. However, a data set was obtained and the structure was solved to a level which unambiguously established that the complex was present as the *anti* isomer **2a**. Attempts to re-grow the crystals often produced lime-green crystals with a needle morphology. The X-ray structure of a lime-green crystal showed the complex was present as the *syn* isomer **2b**.

***Anti* isomer 2a.** The asymmetric unit of **2a** contained one Cu(II) ion, two Cl^- ions, half a ligand and one MeCN solvent molecule. The complex was centrosymmetric such that **L** was coordinated to two Cu(II) centres with regular square-pyramidal geometries ($\tau = 0.07$)[14] (Fig. 3). Each Cu(II) ion was coordinated in the basal plane by a $N_{py}N_{pz}Cl_2$ donor set (N_{py} = pyridine N donor and N_{pz} = pyrazine N donor), with the elongated axial site occupied by a S donor. The ligand adopted an *anti–fac* conformation in which the pyridine rings were in a stepped arrangement, with one pyridine ring above the plane of the pyrazine ring and one pyridine ring below it.

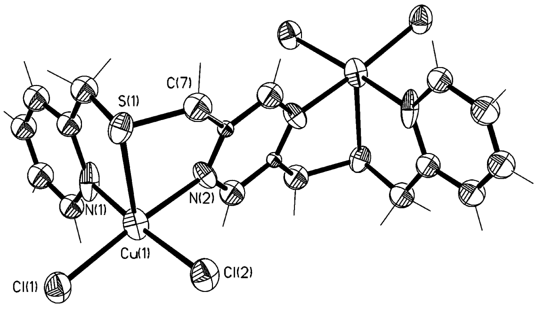

Fig. 3 Perspective view (crystallographic numbering) of **2a**. Thermal ellipsoids are drawn at the 50% probability level. The MeCN molecule is not shown. Selected bond lengths (Å) and angles (°): Cu(1)–N(1) 1.94(3), Cu(1)–N(2) 2.08(2), Cu(1)–Cl(1) 2.260(7), Cu(1)–Cl(2) 2.27(1), Cu(1)–S(1) 2.577(7); N(1)–Cu(1)–Cl(1) 89.7(7), N(1)–Cu(1)–Cl(2) 173.7(6), N(1)–Cu(1)–S(1) 83.1(7), N(1)–Cu(1)–N(2) 86.6(9), N(2)–Cu(1)–Cl(1) 169.7(6), N(2)–Cu(1)–Cl(2) 87.6(7), N(2)–Cu(1)–S(1) 81.3(6), Cl(1)–Cu(1)–Cl(2) 95.6(3), Cl(1)–Cu(1)–S(1) 107.8(3), Cl(2)–Cu(1)–S(1) 98.3(3).

The *anti*-Cu_2Cl_4**L** dinuclear units associated with each other through weak semi-coordinate Cu ··· Cl interactions [Cu ··· Cl 3.465(9) Å] to form one-dimensional proto-polymer chains running parallel to the *a* axis (Fig. 4). Semi-coordinate Cu ··· Cl bonding has previously been reported for coordination polymers to range from 2.78 to 4.14 Å.[19] Each Cl^- ion *trans* to a N_{py} donor was involved in semi-coordinate interactions. The semi-coordinate interactions completed an axially distorted octahedral arrangement about each copper and created pseudo Cu_2Cl_2 bridges between adjacent dinuclear units. The remaining Cl^- ion, *trans* to the pyrazine moiety, was not involved in any interactions with the adjacent unit (Fig. 4). Two-dimensional sheets were formed in the *ac* plane through π-stacking interactions (centroid–centroid distance = 3.64 Å)[6] between adjacent proto-polymer chains (Fig. 4). The MeCN

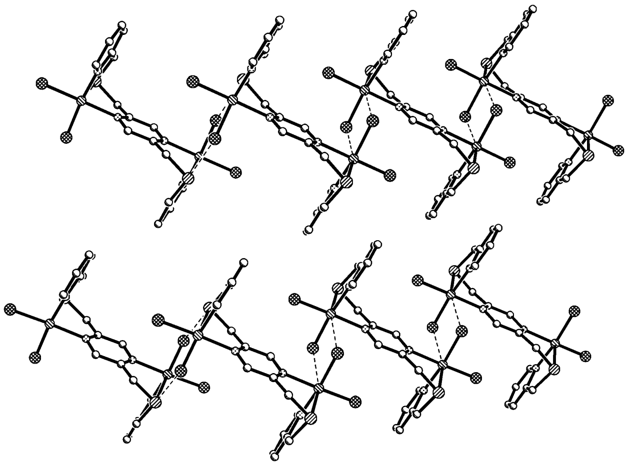

Fig. 4 A view of the proto-polymeric chains of **2a**, illustrating the intermolecular π-stacking interactions. Hydrogens and MeCN molecules are omitted for clarity.

solvent molecules were found to occupy the structural voids between the sheets.

While the model complex **1** correctly predicted a five-coordinate square-pyramidal arrangement for the Cu(II) centres in **2a**, there were significant differences between the two structures. These differences were due to the arrangements of the ligands about the Cu(II) ion. In **1** the ligand adopted a meridional arrangement, while in **2a** the ligand adopted a facial arrangement.

***Syn* isomer 2b.** The asymmetric unit of **2b** contained two Cu(II) ions, four Cl⁻ ions, one ligand and a MeCN solvent molecule. The complex was dinuclear and non-centrosymmetric (Fig. 5). Both Cu(II) ions adopted distorted square-pyramidal arrangements [τ = 0.32 for Cu(1) and Cu(2)].[14] They were coordinated in the basal plane by a $N_{py}SCl_2$ donor set, with the elongated axial site occupied by a N_{pz} donor. This was in contrast to **2a** which also contained square-pyramidal Cu(II) ions, but had an N_2Cl_2 basal plane and an axial S donor. The ligand was arranged in a *syn* conformation with both pyridine rings oriented on the same side of the pyrazine ring and tilted at 23.9° to each other (Fig. 5).

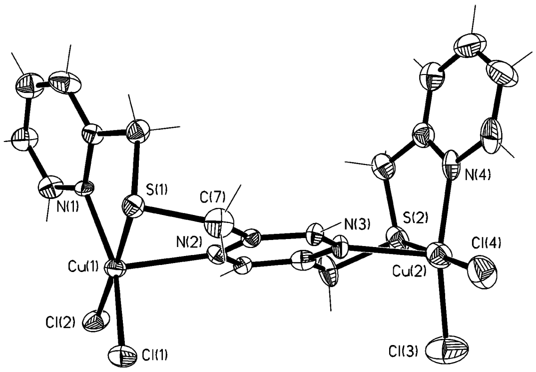

Fig. 5 Perspective view (crystallographic numbering) of **2b**. Thermal ellipsoids are drawn at the 50% probability level. The MeCN molecule is not shown. Selected bond lengths (Å) and angles (°): Cu(1)–N(1) 2.056(8), Cu(1)–N(2) 2.255(8), Cu(1)–S(1) 2.336(3), Cu(1)–Cl(1) 2.300(3), Cu(1)–Cl(2) 2.240(3), Cu(2)–N(3) 2.274(9), Cu(2)–N(4) 2.052(8), Cu(2)–S(2) 2.349(4), Cu(2)–Cl(3) 2.260(3), Cu(2)–Cl(4) 2.258(4); N(1)–Cu(1)–N(2) 101.1(3), N(1)–Cu(1)–Cl(1) 158.6(2), N(1)–Cu(1)–Cl(2) 95.9(2), N(1)–Cu(1)–S(1) 83.4(2), N(2)–Cu(1)–Cl(1) 94.9(2), N(2)–Cu(1)–Cl(2) 101.4(2), N(2)–Cu(1)–S(1) 80.8(2), Cl(1)–Cu(1)–Cl(2) 94.8(1), Cl(1)–Cu(1)–S(1) 85.2(1), Cl(2)–Cu(1)–S(1) 177.8(1), N(3)–Cu(2)–N(4) 93.4(3), N(3)–Cu(2)–Cl(3) 103.1(2), N(3)–Cu(2)–Cl(4) 98.8(3), N(3)–Cu(2)–S(2) 79.8(3), N(4)–Cu(2)–Cl(3) 158.0(3), N(4)–Cu(2)–Cl(4) 96.8(3), N(4)–Cu(2)–S(2) 83.3(3), Cl(3)–Cu(2)–Cl(4) 94.9(1), Cl(3)–Cu(2)–S(2) 85.4(1), Cl(4)–Cu(2)–S(2) 178.6(1).

The *syn*-Cu_2Cl_4**L** dinuclear units were linked together *via* Cl ··· H interactions of moderate strength (2.66–2.77 Å) to form one-dimensional proto-polymer chains which ran parallel to the *b* axis (Fig. 6).[5d] The individual *syn*-folded dinuclear units all faced in the same direction along the polymeric axis, but were slightly skewed with respect to each other, such that each chain had a zigzag arrangement. In addition to the Cl ··· H interactions along the polymeric chain, C–H ··· arene(pyrazine) and C–H ··· arene(pyridine) interactions of 2.75 and 2.88 Å, respectively, were also present.[20]

The polymeric chains formed two-dimensional sheets in the *ab* plane through relatively short S ··· S interactions [3.298(4) Å] (Fig. 6).[21] Furthermore, a three-dimensional network was formed from additional Cl ··· H interactions (2.70–2.89 Å) between the two-dimensional sheets.

As in the case of **2a**, the square-pyramidal coordination geometry of the Cu(II) ions in **2b** was modelled by **1**, however the arrangement of the ligand about the metal centres was still significantly different. The isolation of *anti* and *syn* isomers of **2** was somewhat surprising. However, examination of an orthogonal fit through the pyrazine rings of **2a** and **2b** highlighted the reason for differences between the isomers. That is, the structures of the *syn* and *anti* isomers were similar until the ligand arrangements diverged at the C7 methylene joint where the pyridine arms were arranged in different directions (Figs. 3 and 5). This rotation of the pyridine arm meant that the flexible ligand **L** could readily adopt two different conformations while maintaining a square-pyramidal arrangement about the Cu(II) centres. Hence, it was possible to crystallise two isomeric structures of **2**. The ability of this flexible ligand to form isomeric compounds with Ag(I) has recently been reported.[11] In contrast to the topological isomerism observed for the Ag(I) polymers of **L**, **2a** and **2b** were strict isomers of each other and contained the same solvent molecules. Furthermore, an associated dinuclear Cu(II) complex of a flexible polypyridyl ligand containing a pyrazine bridging group has been isolated in two different crystalline forms.[22] One form adopted a distorted trigonal-bipyramidal arrangement about the Cu centre and was solvated by MeOH while the other adopted a distorted square-pyramidal geometry and did not contain any solvent. Similarly other related dinuclear Cu(II) complexes were also found with both square-pyramidal and trigonal-bipyramidal geometries.[23]

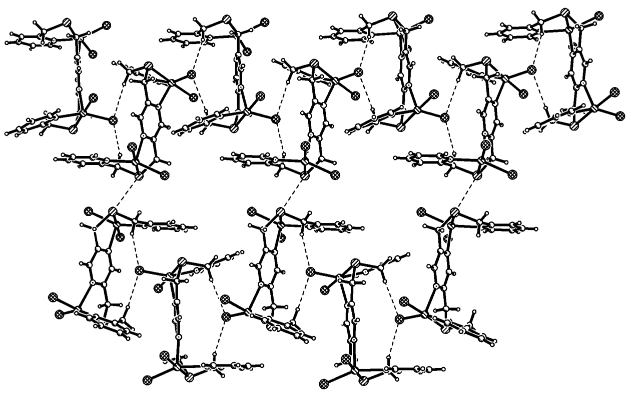

Fig. 6 A view of Cl ··· H interactions which generate the proto-polymeric chains of **2b** and the S ··· S interactions which link the chains into two-dimensional sheets. MeCN solvent molecules are omitted for clarity.

The different arrangements of the ligand in **2a** and **2b** also affected the way in which the complexes formed proto-polymeric chains. The stepped arrangement of the ligand in **2a** allowed interaction between the metal centres of adjacent ligands in the form of semi-coordinate Cu ··· Cl interactions to give pseudo-Cu_2Cl_2 bridges. The unusual arrangement of the *syn*-folded Cu(II) isomer prevented such Cu ··· Cl interactions from occurring and instead the complex adopted H ··· Cl and C–H ··· arene interactions to form one-dimensional proto-polymeric chains.

A powder X-ray diffraction study of the bulk material of **2** failed to establish the *anti* : *syn* ratio present in the powder before crystallisation. The sample was not particularly crystalline and showed a very high background suggesting a substantial amorphous component. Only a few broad and some narrow Bragg peaks were observed. These could not be confidently assigned to either the *anti* or *syn* powder patterns, which were calculated from their respective crystal structures.

Synthesis and structure of $Cu_2I_2L'_2$ 3

The potential for **L** to form polymeric chains through the formation of Cu_2X_2 bridges was indicated by the X-ray structure of **2a**. Cu(I) halides have been shown to form these types of bridges with simple monotopic and ditopic ligands.[2,8,24] Hence, as part of our investigation of **L′** as a probe for ditopic ligands we reacted **L′** with CuI.

A 1 : 1 molar ratio of CuI and **L**′ was reacted and gave a cream powder. Microanalysis showed the complex was consistent with a 1 : 1 metal-to-ligand ratio. The ^{1}H NMR spectrum of **3** in CD_2Cl_2 was consistent with a symmetrical complex. In addition, the presence of only one methylene signal at 4.07 ppm indicated that fluxional processes were occurring in solution at 298 K. Electrospray mass spectroscopy under normal operating conditions in MeCN–H_2O (1 : 1 v/v) showed three major peaks which had the correct isotopic patterns for $[Cu(\mathbf{L}')]^+$ at *m*/*z* 279, $[Cu(\mathbf{L}')_2]^+$ at 495 and $[Cu_2(\mathbf{L}')_2I]^+$ at 687. The presence of the peak at *m*/*z* 687 suggested that the complex might exist as a dimer in solution.

The dimeric nature of the complex was confirmed by X-ray structure analysis. The dimer was formed from two **L**′ ligands, joined together by an asymmetric Cu_2I_2 core, related by a centre of symmetry at the mid-point between the two Cu(I) atoms (Fig. 7). The Cu(I) ions adopted a distorted tetrahedral geometry which was provided by a N_2I_2 coordination sphere. Each ligand coordinated to two N donors in a NN bidentate fashion forming an eight-membered chelate ring, with the S atoms remaining non-bonding and in an *exo* orientation. Similar dimeric Cu(I) halide compounds containing related ligands also tend to bind the heterocyclic N donors rather than the donor atom in the flexible linker.[24a,25] Uneven Cu–I bond distances of 2.6357(5) and 2.7560(5) Å resulted in the distorted asymmetric Cu_2I_2 core. The Cu_2I_2 core was strictly planar with a Cu(1) ··· Cu(1A) distance of 3.1695(5) Å, which was at the long end of the range for other complexes with Cu_2I_2 cores (2.566–3.452 Å).[26,27] The two Cu atoms and the four N atoms resided in a Cu_2N_4 plane with a mean deviation from planarity of only 0.023 Å. This plane was at right angles to the Cu_2I_2 core. The ligand adopted a stretched out and twisted *exo*–*anti* conformation in which the pyridine rings were tilted at 46.1° to each other. The twist in the ligands meant that one of the S atoms in the dimer was above the Cu_2N_4 plane and the other was below the plane. The ligand in **1** had a similar *anti* conformation to **3**, although in **1** the pyridine rings were planar with respect to each other and the S donor was *endo* and bound to the Cu(II) centre.

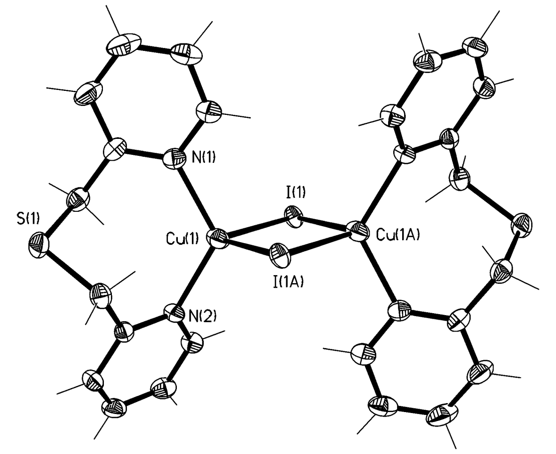

Fig. 7 Perspective view (crystallographic numbering) of **3**. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (°): I(1)–Cu(1) 2.6357(5), Cu(1)–I(1A) 2.7560(5), Cu(1) ··· Cu(1A) 3.1695(5), Cu(1)–N(1) 2.060(3), Cu(1)–N(2) 2.029(3); N(2)–Cu(1)–N(1) 121.8(1), N(2)–Cu(1)–I(1) 110.78(8), N(1)–Cu(1)–I(1) 104.76(7), N(2)–Cu(1)–I(1A) 108.25(7), N(1)–Cu(1)–I(1A) 102.33(7), I(1)–Cu(1)–I(1A) 108.03(1). (Symmetry code: A $-x + 1$, $-y + 2$, $-z + 2$.)

One-dimensional polymeric chains, which propagated along the [102] diagonal axis, were formed from strongly π-stacked pyridine rings (centroid–centroid distance 3.65 Å)[6] (Fig. 8). Each dimeric unit was involved in a number of relatively weak intermolecular C–H ··· I interactions (3.09–3.24 Å)[5d] leading to the formation of an overall three-dimensional network. No solvent accessible volume was available within the crystal structure.[28]

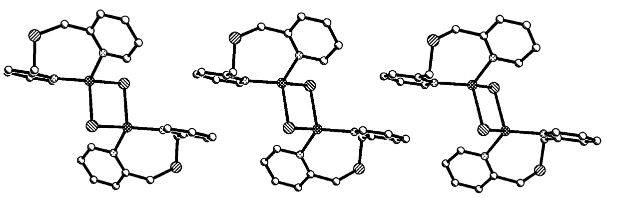

Fig. 8 A view of the polymeric chain of **3**, illustrating the intermolecular π-stacking. Hydrogen atoms are omitted for clarity.

Synthesis and structure of $[Cu_2I_2L]_\infty$ 4

The dimeric nature of **3**, in combination with the protopolymeric structure of **2a** prompted us to investigate the complexation of **L** with CuI. The reaction of **L** and CuI in a 1 : 2 mole ratio immediately produced an orange precipitate, which had an analysis consistent with Cu_2I_2L.

In the X-ray crystal structure of **4** the asymmetric unit contained one Cu(I) ion, one I^- ion and half a ligand. The complex was centrosymmetric such that **L** was coordinated to two Cu(I) centres with distorted tetrahedral arrangements. Each Cu(I) centre was $N_{py}N_{pz}$ coordinated to a compartment of the ditopic ligand with two bridging I^- ions completing the arrangement about each metal centre. The presence of the Cu_2I_2 core and the $N_{py}N_{pz}$ binding of **L** to the metal centre was identical to the coordination observed for complex **3**. An orthogonal fit of the non-hydrogen atoms of **3** with an equivalent fragment of **4** gave a weighted root mean square deviation of just 0.391 Å.

Complex **4** formed a one-dimensional polymer along the *b* axis such that adjacent ligands were joined by Cu_2I_2 moieties (Fig. 9). This was in contrast to the non-bonding interactions that formed the proto-polymeric chains in **2a** and **2b**. The symmetric Cu_2I_2 moiety was strictly planar with a Cu(1) ··· Cu(1A) distance [2.858(1) Å] in the middle of the range for similar systems.[26,27] The $N_2Cu_2N'_2$ atoms formed a plane (0.0088 Å mean deviation from planarity), that was perpendicular to the Cu_2I_2 core. As in **3**, the S donors remained uncoordinated to the soft Cu(I) centres and were exodentate, which resulted in eight-membered chelate rings. It was somewhat surprising that in complexes **3** and **4** the thioether donor did not coordinate to the Cu(I) ion, while in complexes **1**, **2a** and **2b** it did coordinate to the Cu(II) ion. Generally the Cu(I) ion has been shown to behave as a ‘soft’ metal and would be expected to preferentially coordinate to the ‘soft’ sulfur atom rather than the Cu(II) ion, which has been shown to be a ‘harder’ metal centre. The inability of Cu(I) to bind the S atom may have been due to the formation of the thermodynamically more favourable Cu_2I_2 core for **3** and **4**, and the presence of the somewhat softer pyridine N donors. Recently we have found in a series of related CuI complexes containing Cu_2I_2 cores that

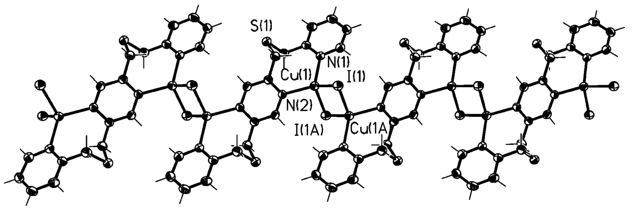

Fig. 9 Perspective view (crystallographic numbering) of **4**. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (°): Cu(1)–I(1) 2.6686(6), Cu(1)–I(1A) 2.6334(6), Cu(1)–N(1) 2.080(3), Cu(1)–N(2) 2.104(3), Cu(1) ··· Cu(1A) 2.858(1); N(1)–Cu(1)–N(2) 119.2(1), I(1A)–Cu(1)–I(1) 114.76(2), N(1)–Cu(1)–I(1) 103.89(9), N(1)–Cu(1)–I(1A) 108.55(9), N(2)–Cu(1)–I(1) 106.71(9), N(2)–Cu(1)–I(1A) 104.99(9). (Symmetry code: A $-x + 1$, $-y$, $-z + 2$.)

S coordination did occur in some cases.[29] Thus the energy difference between the presence or absence of the copper–sulfur bond in such thioether–pyridine systems must be small.

The exodentate S atoms in **4** allowed the ligand to adopt a stretched-out linear arrangement, with one S donor slightly above the $N_2Cu_2N'_2$ plane and one S donor slightly below the plane. The two pyridine rings adopted a stepped arrangement with respect to the pyrazine ring, with the pyridine rings twisting in opposite directions away from the pyrazine ring. The two pyridine rings were strictly parallel with respect to each other and were tilted by 59.5° with respect to the central pyrazine ring. The stretched-out linear arrangement placed the pyridine rings of **L** on the outside of the polymeric chain. Weak S ··· S interactions (3.55 Å)[21] existed between adjacent chains and offset π–π interactions (centroid–centroid distance = 3.83 Å)[6] between pyridine rings were also observed. This succession of π–π interactions and weak S ··· S interactions linked neighbouring polymeric chains together to form two-dimensional sheets in the *ab* plane (Fig. 10).

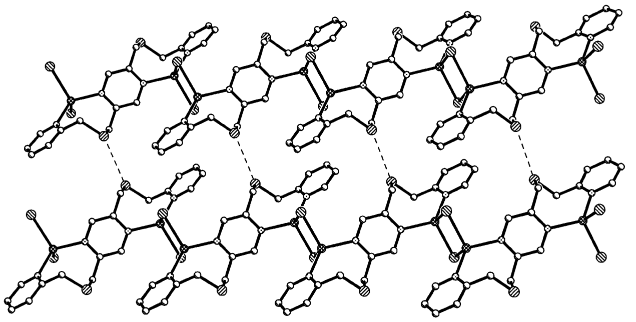

Fig. 10 A view of the polymeric chain of **4**, illustrating the intermolecular π-stacking and S ··· S interactions which generate the two-dimensional sheets. Hydrogen atoms are omitted for clarity.

In addition, the intermolecular π-stacking which existed between pyridine rings of adjacent dimers of **3**, when viewed from above, exactly mimicked the polymeric chain found in **4** (Fig. 11). That is, the two π-stacked pyridine rings in **3** mapped exactly with the pyrazine ring in **4**. The structure of **4** contrasts with the CuI complex of a related 1,4-bis(2-pyridylmethylsulfanylmethyl)benzene ligand, in which the S donors were coordinated to the Cu(I) ion.[8] This may have been due to the lack of N donors available for chelation on the spacer head unit of that complex.

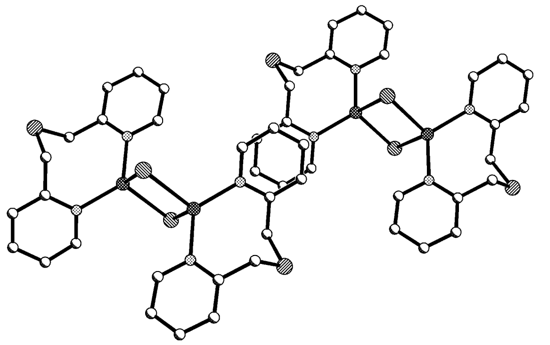

Fig. 11 View from above the two π-stacked pyridine rings of **3** which shows a structure analogous to **4**. Hydrogen atoms are omitted for clarity.

Conclusion

While **1** predicted the coordination geometry of the Cu(II) ions in **2a** and **2b**, it was unsuccessful at predicting the supramolecular structures. However, comparison of **3** with the polymeric structure of **4** showed it to be an accurate model for the Cu(I) coordination sphere and the polymeric chain. Furthermore, the success of **3** as a model for **4** was consistent with previous findings for some Ag(I) complexes of **L′** and **L**.[11,12] These results illustrate the use of simple ligand analogues as probes for the structures of more complicated ligands and will continue to be investigated.

Experimental

General

The ligands **L′** and **L** were prepared by literature methods.[11,30] Elemental analyses were performed by the Campbell Microanalytical laboratory at the University of Otago. Samples were pre-dried under vacuum to remove volatile solvent residues. The solid-state electronic spectrum was collected as a $BaSO_4$ diluted sample with a Perkin-Elmer Lambda-9 UV/vis/nir spectrophotometer and a 60 mm MgO coated integrating sphere diffuse reflectance attachment. Powder X-ray diffraction (PXD) data were collected using a Philips XPERT θ–2θ diffractometer with Cu-Kα radiation in flat plate Bragg–Brentano geometry. Diffraction data were collected over a duration of 16 h in the range 5–80° 2θ with step size 0.02° 2θ at 298 K. Theoretical powder patterns were calculated by POWDERCELL 2.0[31] using the single crystal diffraction data generated for the isomers, **2a** and **2b** as models.

Complexes

$CuCl_2L'\cdot H_2O$ 1. $CuCl_2$ (31 mg, 0.23 mmol) dissolved in EtOH (20 mL) was added to **L′** (50 mg, 0.23 mmol) dissolved in EtOH (20 mL) and allowed to stir for 1 h. The resulting green solution was concentrated to 2 mL and pentane (10 mL) was added. The green solid, which immediately precipitated, was filtered and dried *in vacuo* (yield 54 mg, 67%). Green crystals were grown from the slow evaporation of a EtOH solution. (Found: C, 39.0; H, 3.4; N, 7.5; S, 8.8. Calc. for $C_{12}H_{12}N_2SCuCl_2\cdot H_2O$: C, 39.1; H, 3.8; N, 7.6; S; 8.7%). UV/vis/nir ($BaSO_4$)/nm: 901, 1106.

Cu_2Cl_4L 2. **L** (50 mg, 0.14 mmol) dissolved in EtOH (20 mL) was added dropwise over 0.5 h to $CuCl_2$ (38 mg, 0.28 mmol) dissolved in EtOH (20 mL) and allowed to stir for 0.5 h. The green solid, which immediately precipitated, was filtered and dried *in vacuo* (yield 67 mg, 77%). Emerald green (*anti* isomer) and lime-green (*syn* isomer) crystals were grown separately from the slow diffusion of diethyl ether into a MeCN solution of the complex. (Found: C, 34.5; H, 2.8; N, 8.7; S, 10.1. Calc. for $C_{18}H_{18}N_4S_2Cu_2Cl_4$: C, 34.7; H, 2.9; N, 9.0; S; 10.3%).

$Cu_2I_2L'_2$ 3. CuI (176 mg, 0.925 mmol) dissolved in degassed MeCN (20 mL) was added *via* cannula to **L′** (200 mg, 0.925 mmol) dissolved in degassed MeCN (20 mL) under a N_2 atmosphere and allowed to stir for 1 h. The cream precipitate which formed was filtered, washed with diethyl ether and dried *in vacuo* (yield 246 mg, 66%). Pale yellow crystals were grown from the slow evaporation of a CH_2Cl_2 solution. (Found: C, 35.8; H, 3.2; N, 7.0; S, 7.6. Calc. for $C_{12}H_{12}N_2SCuI$: C, 35.4; H, 3.0; N, 6.9; S, 7.9%); ^1H NMR (CD_2Cl_2): δ 8.81 [2H, d, ^3J(HH) 4.0], 7.69 [2H, t, ^3J(HH) 8.0 Hz], 7.29 (4H, br d) and 4.07 (4H, s); ES MS: *m*/*z* 279 $[Cu(L')]^+$, 495 $[Cu(L')_2]^+$ and 687 $[Cu_2(L')_2I]^+$.

$[Cu_2I_2L]_\infty$ 4. CuI (53 mg, 0.28 mmol) dissolved in degassed MeCN (20 mL) was added *via* cannula to **L** (50 mg, 0.14 mmol) dissolved in degassed MeCN under a N_2 atmosphere and allowed to stir for 1 h. The orange solid, which immediately precipitated was filtered and dried *in vacuo* (67 mg, 65%). Dark red crystals were grown from the slow diffusion of a $CHCl_3$ solution (2 mL) of **L** (20 mg, 0.056 mmol) layered with CH_2Cl_2 (1 mL) and a MeCN solution (5 mL) of CuI (23 mg, 0.12

Table 1 Crystallographic data for complexes **1**–**4**

	1·H_2O	**2a**	**2b**	**3**	**4**
Formula	$C_{12}H_{14}Cl_2CuN_2OS$	$C_{22}H_{24}Cl_4Cu_2N_6S_2$	$C_{20}H_{21}Cl_4Cu_2N_5S_2$	$C_{24}H_{24}Cu_2I_2N_4S_2$	$C_9H_9CuIN_2S$
M	368.77	705.47	664.46	813.51	367.70
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P\bar{1}$	$P2_1/c$	$P2_1/c$	$P2_1/n$
a/Å	8.077(2)	7.735(2)	14.363(5)	8.0239(5)	10.033(1)
b/Å	13.919(4)	7.989(2)	11.881(3)	18.710(1)	8.7293(8)
c/Å	12.956(3)	11.949(2)	15.710(5)	9.5160(6)	12.374(1)
α/°		86.02(3)			
β/°	94.728(3)	77.61(3)	107.664(5)	110.112(1)	91.421(1)
γ/°		71.18(3)			
U/Å^3	1451.6(6)	682.6(3)	2554(1)	1341.5(1)	1083.4(2)
Z	4	1	4	2	4
T/K	170(2)	153(2)	158(2)	168(2)	158(2)
μ/mm^{-1}	2.008	2.127	2.267	4.063	5.018
Reflections collected	18180	1768	4243	17040	7329
Unique reflections (R_{int})	2951 (0.0434)	1381 (0.0533)	3305 (0.0958)	2747 (0.0389)	2085 (0.0218)
$R1$ indices [$I > 2\sigma(I)$]	0.0363	0.1773	0.0596	0.0276	0.0290
$wR2$ (all data)	0.0789	0.4752	0.1073	0.0715	0.0729

mmol). (Found: C, 29.6; H, 2.5; N, 7.7; S, 8.6. Calc. for $C_{18}H_{18}N_4S_2Cu_2I_2$: C, 29.4; H, 2.5; N, 7.6; S; 8.7%).

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[32] and a multiscan absorption correction[33] was applied. The structures were solved by direct methods (SHELXS)[34] and refined on F^2 using all data by full-matrix least-squares procedures (SHELXL 97).[35] As outlined in the text, considerable difficulties were experienced in growing crystals for isomer **2a** and when obtained crystals were always of poor quality. In addition, technical difficulties experienced during data collection gave a truncated data set. Such problems were reflected in the poor but unambiguous structure solution. Consequently, the structure showed a number of peaks between 2.1 to 1.3 e Å^{-3} located at about 1.0 Å from the Cu and Cl atoms. Crystallographic data for the five structures are listed in Table 1.

CCDC reference numbers 175744–175748.

See http://www.rsc.org/suppdata/dt/b1/b111176k/ for crystallographic data in CIF or other electronic format.

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