

# Banded ribbons of $\text{Cu}_6\text{I}_6$ hexamers and multimodal thioether pyrazine ligands linked by self-complementary $\text{N} \cdots \text{H}-\text{C}$ synthons

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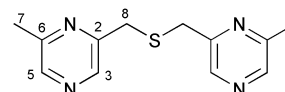
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The multimodal coordinating ability of a new thioether pyrazine ligand was used in conjunction with  $\text{CuI}$  to construct one-dimensional banded ribbons containing  $\text{Cu}_6\text{I}_6$  hexamers which formed two-dimensional sheets through (pyrazine) $\text{N} \cdots \text{H}-\text{C}$ (methylene) interactions.

The synthesis of organic–inorganic hybrid materials generally relies upon using bifunctional linking ligands such as pyrazine or 4,4'-bipyridine and an extended inorganic matrix such as metal oxides,<sup>1</sup> or  $\text{CuX}$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{CN}, \text{SCN}$ ) scaffolds.<sup>2</sup> In this way a great variety of structures has been engineered. However, such an approach often leads to alternating infinite strands of inorganic matrix and organic connector.<sup>1,2</sup> One of the major challenges in the area of coordination-polymer chemistry is to control the assembly of these hybrid materials and being able to generate a diverse range of structural features is an important step along this path.<sup>1,3</sup> In an attempt to incorporate some new design features into the engineering of coordination polymers, we have shown that it is possible to intersperse an inorganic matrix with an organic connector to give a banded-ribbon polymer. In order to achieve our purpose, rather than simply using bifunctional ligands as linkers to engineer coordination polymers, we have begun exploring the use of flexible multimodal thioether pyrazine ligands. These ligands have a number of advantages over bifunctional and rigid multimodal ligands. Like conventional multimodal ligands they offer chemically distinct binding sites<sup>4</sup> but their conformational flexibility enhances the use of other interactions such as  $\pi-\pi$  interactions and may allow for greater micro-structural diversity.<sup>5</sup> The fact that these flexible ligands have a number of energetically available conformations means that the requirements of the ligand are less likely to dominate structure formation than in the case of more rigid ligands. Often in rigid multimodal ligands it has been found that not all of the available donor atoms are able to form significant interactions.<sup>4</sup> However, flexible multimodal ligands with access to various conformations and therefore different spatial arrangements of donor atoms are more likely to be able to form significant interactions using all their donor atoms. Such donor atoms not only hold the structure together through metal–ligand interactions but also through their participation in various supramolecular synthons. Some of the most versatile molecular synthons for this purpose are the various forms of hydrogen bonding.<sup>6</sup> Hydrogen bonding may assist with the ordering and stabilization of hybrid materials, thereby facilitating their preparation and isolation.<sup>2b,c</sup> In certain circumstances, hydrogen bonding may also provide for greater solubility, although this was not the case with our system. We have found that the less commonly used  $\text{N} \cdots \text{H}-\text{C}$  hydrogen bonding, the nature of which has been subject to some recent controversy,<sup>6,7</sup> can be used as a means of linking together banded ribbons into two-dimensional sheets. Herein we describe the synthesis of a new multimodal thioether pyrazine ligand **L** (Scheme 1) and the unusual array it forms when reacted with  $\text{CuI}$ .

The new multimodal ligand **L** was prepared in moderate



Scheme 1 Diagram showing the conventional numbering scheme for ligand **L**. †

yield by the reaction of 6-methyl-2-(chloromethyl)pyrazine<sup>8</sup> with thioacetamide under basic conditions. † The use of thioacetamide, rather than  $\text{Na}_2\text{S}$ , gave a higher overall yield. Reaction of **L** with  $\text{CuI}$  in a 1 : 2 molar ratio in MeCN gave an orange solid which was isolated in low yield by precipitation with diethyl ether. Surprisingly microanalysis of the bulk complex was consistent with a ligand : metal ratio of 1 : 3. Despite careful workup of the reaction filtrate no other products, with different ligand : metal ratios, could be isolated. Subsequently, slow diffusion of the reactants produced X-ray quality crystals which gave microanalyses consistent with the bulk material. ‡

X-Ray structure analysis§ of **1** revealed one-dimensional polymeric ribbons with self-complementary (pyrazine)- $\text{N} \cdots \text{H}-\text{C}$ (methylene) interactions linking the ribbons to form a two-dimensional sheet structure (Fig. 1). The asymmetric unit

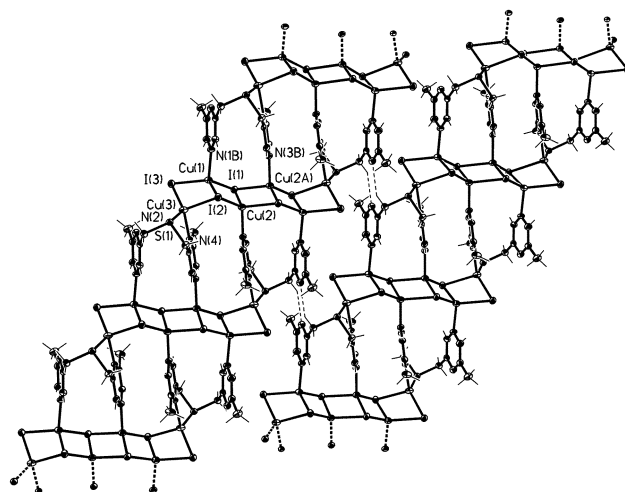


Fig. 1 View of infinite two-dimensional sheets of  $[\text{Cu}_3\text{LI}_3]_n$  showing banded ribbons of  $\text{Cu}_6\text{I}_6$  hexamers, and ligands joined by (pyrazine) $\text{N} \cdots \text{H}-\text{C}$ (methylene) synthons (50% probability ellipsoids). Selected bond lengths (Å), and angles (°):  $\text{Cu}(1)-\text{I}(1)$  2.6855(7),  $\text{Cu}(1)-\text{I}(2)$  2.6392(7),  $\text{Cu}(1)-\text{I}(3)$  2.6323(7),  $\text{Cu}(1)-\text{N}(1\text{B})$  2.069(4),  $\text{Cu}(2)-\text{I}(1)$  2.6101(7),  $\text{Cu}(2)-\text{I}(2)$  2.5993(6),  $\text{Cu}(2\text{A})-\text{I}(1)$  2.7040(7),  $\text{Cu}(2\text{A})-\text{N}(3\text{B})$  2.052(4),  $\text{Cu}(3)-\text{I}(2)$  2.8348(7),  $\text{Cu}(3)-\text{I}(3)$  2.5055(7),  $\text{Cu}(3)-\text{N}(4)$  2.071(3),  $\text{Cu}(3)-\text{S}(1)$  2.357(1);  $\text{Cu}(1)-\text{I}(1)-\text{Cu}(2)$  67.05(2),  $\text{Cu}(1)-\text{I}(1)-\text{Cu}(2\text{A})$  104.70(2),  $\text{Cu}(1)-\text{I}(2)-\text{Cu}(3)$  60.35(2),  $\text{Cu}(1)-\text{I}(2)-\text{Cu}(2)$  67.90(2),  $\text{Cu}(2)-\text{I}(1)-\text{Cu}(2\text{A})$  59.91(2),  $\text{Cu}(2)-\text{I}(2)-\text{Cu}(3)$  93.51(2),  $\text{Cu}(1)-\text{I}(3)-\text{Cu}(3)$  64.84(2),  $\text{N}(1\text{B})-\text{Cu}(1)-\text{I}(3)$  101.2(1),  $\text{N}(1\text{B})-\text{Cu}(1)-\text{I}(2)$  112.0(1),  $\text{I}(2)-\text{Cu}(1)-\text{I}(3)$  114.64(2),  $\text{N}(1\text{B})-\text{Cu}(1)-\text{I}(1)$  102.3(1),  $\text{I}(1)-\text{Cu}(1)-\text{I}(3)$  115.00(2),  $\text{I}(1)-\text{Cu}(1)-\text{I}(2)$  110.59(2),  $\text{N}(4)-\text{Cu}(3)-\text{S}(1)$  87.0(1),  $\text{N}(4)-\text{Cu}(3)-\text{I}(3)$  126.4(1),  $\text{S}(1)-\text{Cu}(3)-\text{I}(3)$  130.44(4),  $\text{N}(4)-\text{Cu}(3)-\text{I}(2)$  104.6(1),  $\text{S}(1)-\text{Cu}(3)-\text{I}(2)$  88.14(3),  $\text{I}(2)-\text{Cu}(3)-\text{I}(3)$  112.23(1),  $\text{I}(1)-\text{Cu}(2)-\text{I}(2)$  114.35(2),  $\text{N}(3\text{B})-\text{Cu}(2\text{A})-\text{I}(1)$  98.4(1). (Symmetry codes: A  $1-x, -y, 1-z$ ; B  $1+x, y-1, z$ ).

contained one ligand, three Cu(I) ions and three I<sup>-</sup> ions. The ligand was folded in an *endo-syn* conformation where the pyrazine rings were  $\pi$  stacked with an intra-ligand centroid-to-centroid distance of 3.79 Å. The two pyrazine rings on each ligand were orientated so that methyl groups pointed in the same direction and the rings were tilted by 22.5° with respect to each other. The one-dimensional polymeric ribbon consisted of two alternating building blocks, a unique Cu<sub>6</sub>I<sub>6</sub> hexameric ladder<sup>9</sup> and a pair of ligands, which gave rise to a banded structure propagating in the [1 1 0] direction (Fig. 1). Each ligand in the pair was related in a centrosymmetric fashion with respect to the other so that the S donors on each of the two ligands pointed in opposite directions. In each pair of ligands, inter-ligand  $\pi$ -stacking occurred with a centroid-to-centroid distance of 3.64 Å.

The three different Cu(I) ions in the centrosymmetric hexameric ladder all had different distorted-tetrahedral geometries. Two of the Cu(I) ions had I<sub>3</sub>N coordination spheres; the central Cu(I) ion was coordinated to three  $\mu_3$ -I anions and a 4-substituted pyrazine N donor and the adjacent Cu(I) ion was coordinated to two  $\mu_3$ -I and one  $\mu$ -I anions and a 4-substituted pyrazine N donor. The terminal Cu(I) ion had an I<sub>2</sub>NS coordination sphere and was coordinated to  $\mu_3$ -I and  $\mu$ -I anions and chelated by S and 1-substituted pyrazine N donors. The Cu(I) ions were separated by distances of Cu(2)  $\cdots$  Cu(2A) 2.655(1) Å, Cu(1)  $\cdots$  Cu(3) 2.7565(8) Å and Cu(1)  $\cdots$  Cu(2) 2.9256(9) Å which were typical values for both discrete<sup>9-11</sup> and polymeric<sup>9,12</sup> CuI ladders. No previous examples of Cu<sub>6</sub>I<sub>6</sub> hexameric ladders could be found in a search of the Cambridge Structural Database. However, a number of similar Cu<sub>4</sub>I<sub>4</sub> stepped cubane crystal structures have been obtained,<sup>9,10</sup> as well as a number of other related discrete oligomeric CuI structures.<sup>11</sup> Each ligand was chelated to one hexameric ladder through N and S donors and was bound in a monodentate fashion through two other N donors to an adjacent hexameric ladder. In this way chelation of the Cu(I) ion by the ligand was possibly responsible for terminating the growth of a CuI staircase chain and producing the hexameric fragment rather than an infinite staircase. Also the ligand was probably not well suited to effective coordination to other commonly found smaller CuI structures such as the cubanes or dinuclear complexes.<sup>9</sup>

For every ligand one, 1-substituted pyrazine, N atom closest to the edge of the ribbon was not coordinated to a Cu(I) ion. Instead these N atoms were involved in the formation of hydrogen-bonding synthon interactions<sup>6,7</sup> between the edges of the ribbons, forming the ribbons into two-dimensional sheets (Fig. 1). The synthons were formed through two self-complementary H-bonding interactions between pyrazine N and methylene H atoms on two different ribbons. For the N  $\cdots$  H–C interaction, the angle was 151(5)° and the N  $\cdots$  H and N  $\cdots$  C distances were 2.45(6) and 3.348(6) Å, respectively. The corresponding sums of the van der Waals radii were 2.75 and 3.25 Å.<sup>13</sup> The values for this H-bonding interaction were within experimental error of previously reported mean values.<sup>7</sup> The sheets were stacked upon each other with the ribbons in each sheet being directly above those in the sheet below (Fig. 2). The sheets were held together by weak I  $\cdots$  H–C interactions ranging from 2.99 to 3.18 Å.

In conclusion, it was unusual to find a new oligomer based on the well recognised CuI staircase polymer motif. The formation of the Cu<sub>6</sub>I<sub>6</sub> hexamer and its placement in a banded ribbon structure were a consequence of the flexibility and multimodal nature of the ligand. The flexibility of the ligand allowed for the more effective use of donor atoms and resulted in a less conventional type of hydrogen bonding being employed to link the ribbons into sheets. We are currently investigating the coordination-polymer chemistry of these new flexible multimodal ligands.

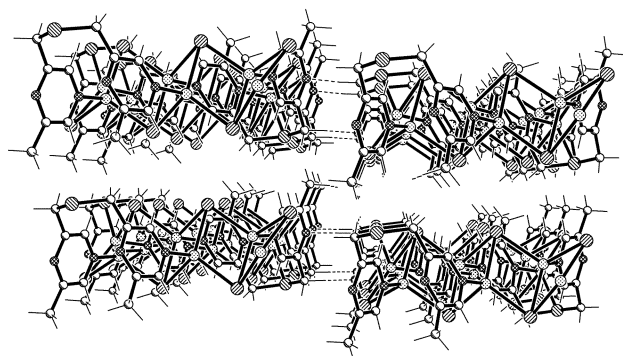


Fig. 2 View along the [1 1 0] diagonal axis showing the stacking of the two-dimensional sheets.

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## Notes and references

† Synthesis of bis(6-methyl-2-pyrazylmethyl)sulfide **L**: KOH (5.0 g, 89 mmol) dissolved in H<sub>2</sub>O (10 mL) together with 6-methyl-2-(chloromethyl)pyrazine (15.43 g, 108.2 mmol) and thioacetamide (4.77 g, 63.5 mmol) were refluxed overnight in a 250 mL benzene-ethanol (1 : 1 v/v) solution. The solution was filtered and the solvent removed *in vacuo* to give a black oil. This oil was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (200 mL) before being washed with H<sub>2</sub>O (8  $\times$  150 mL), and the solvent was removed *in vacuo* to give a crude red-black oil (yield 10.1 g, 75.9%). Purification on a silica gel column (10% hydrated v/v) eluted with CH<sub>2</sub>Cl<sub>2</sub> followed by CHCl<sub>3</sub> gave **L** as an analytically pure red-black oil (1.29 g, 9.65%). NMR:  $\delta_{\text{H}}$  (300 MHz, CDCl<sub>3</sub>) 8.44 (2H, s, H3), 8.33 (2H, s, H5), 3.82 (4H, s, H8), 2.56 (6H, s, H7);  $\delta_{\text{C}}$  (300 MHz, CDCl<sub>3</sub>) 153.65 (C6), 153.10 (C2), 143.09 (C5), 141.81 (C3), 35.15 (C8) and 21.88 (C7). Anal. calc. for C<sub>12</sub>H<sub>14</sub>N<sub>4</sub>S: C, 58.50; H, 5.73; N, 22.75; S, 13.02. Found: C, 58.70; H, 5.90; N, 22.58; S, 12.93%.

‡ Synthesis of [Cu<sub>3</sub>LI<sub>3</sub>]<sub>n</sub>: CuI (104.4 mg, 0.5482 mmol) dissolved in degassed MeCN (25 mL) was added *via* cannula to **L** (63.9 mg, 0.259 mmol) dissolved in degassed MeCN (25 mL) and stirred for 48 h. The resulting solution was concentrated to 5 mL and diethyl ether (10 mL) was added. The orange solid, which immediately precipitated, was filtered and dried *in vacuo* (yield 28.3 mg, 18.9% based on CuI). Red X-ray quality crystals were grown from the slow diffusion of a CH<sub>3</sub>NO<sub>2</sub> solution (2 mL) of **L** (22.9 mg, 0.0930 mmol) layered with ethyl acetate (2 mL) and a MeCN solution (5 mL) of CuI (28.9 mg, 0.152 mmol). Anal. calc. for C<sub>12</sub>H<sub>14</sub>N<sub>4</sub>SCu<sub>3</sub>I<sub>3</sub>: C, 17.63; H, 1.73; N, 6.85; S, 3.92. Found: C, 17.93; H, 1.48; N, 6.43; S, 3.66%.

§ Crystal data for [Cu<sub>3</sub>LI<sub>3</sub>]<sub>n</sub>: C<sub>12</sub>H<sub>14</sub>N<sub>4</sub>SCu<sub>3</sub>I<sub>3</sub>, *M* = 817.66, triclinic, *P* $\bar{1}$  (no. 2), *a* = 8.3841(2), *b* = 9.2406(2), *c* = 13.7990(4) Å,  $\alpha$  = 87.937(1),  $\beta$  = 86.209(1),  $\gamma$  = 67.204(1)°, *U* = 983.34(4) Å<sup>3</sup>, *T* = 123(2) K, *Z* = 2,  $\mu$ (Mo-K $\alpha$ ) = 8.031 mm<sup>-1</sup>, 7319 reflections measured, 4480 independent reflections (*R*<sub>int</sub> = 0.0262), [3606, *I*  $\geq$  2 $\sigma$ (*I*)], *R*<sub>1</sub> = 0.0295, 0.0446 (all data), *wR*<sub>2</sub> = 0.0589, 0.0628 (all data). CCDC reference number 197840. See <http://www.rsc.org/suppdata/dt/b2/b212365g/> for crystallographic data in CIF or other electronic format.

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