

Copper(I) halide supramolecular networks linked by N-heterocyclic donor bridging ligands

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Abstract: We are pursuing the construction of extended supramolecular networks based upon inorganic co-ordination polymers using a building block methodology to control network structure. We have been attracted by the rich structural chemistry of copper(I) halides and pseudo-halides in order to form neutral networks with N-heterocyclic donor bridging ligands. By using the potentially tridentate ligand, 1,3,5-triazine, three-dimensional supramolecular networks containing unusual columnar $(\text{CuX})_\infty$ or sheet $(\text{CuI})_\infty$ motifs can be prepared. With bidentate bridging ligands, $[\text{Cu}(\text{SCN})]_\infty$ sheet motifs have been obtained.

INTRODUCTION

There is intense current interest in the construction of channelled inorganic co-ordination polymers with chemical architectures that mimic some of the characteristics of zeolite and mineral materials (ref. 1). We are using a building-block approach for the construction of three-dimensional co-ordination polymers (ref. 2); however, in contrast to many researchers, we are attempting to incorporate the anion as an essential element of the framework. This strategy allows for the synthesis of uncharged architectures in which channels remain unblocked by anions and are, therefore, free for solvent and guest inclusion. By following this approach we have identified the halides and pseudo-halides of copper(I) as effective building-blocks (ref. 3).

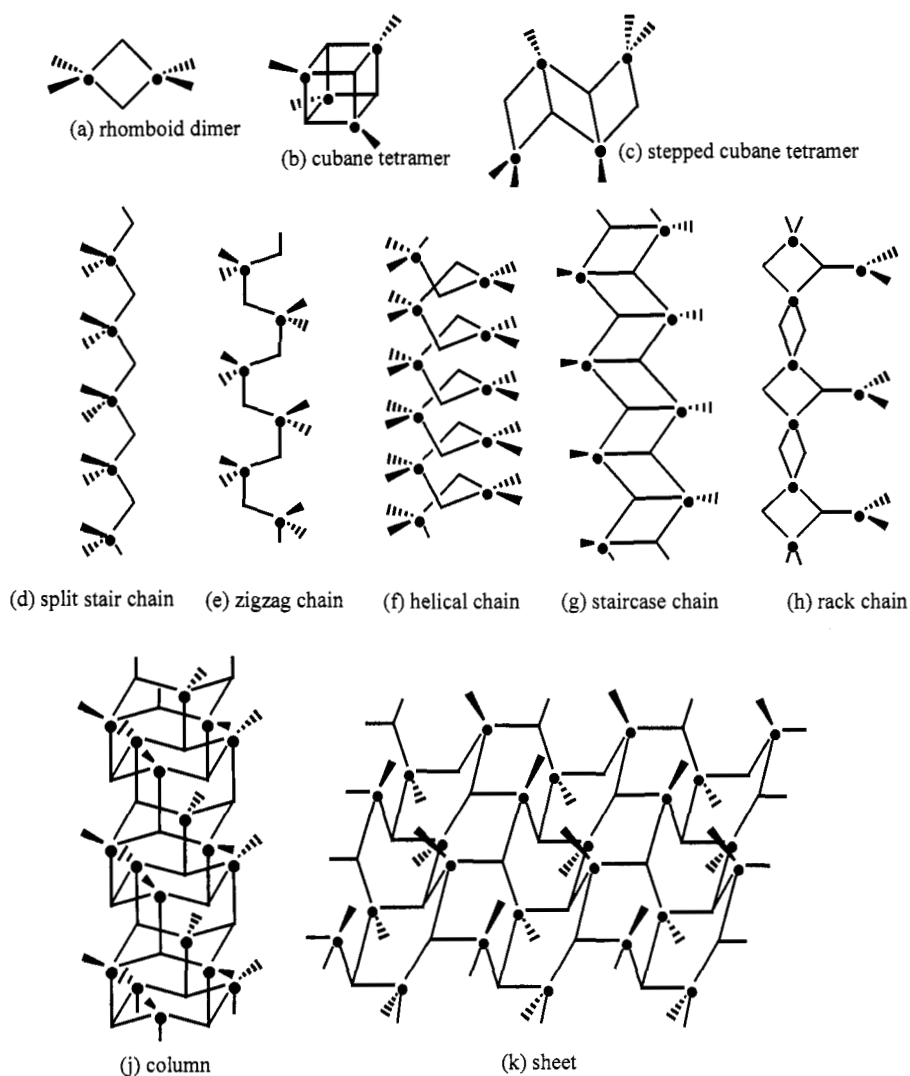
Complex formation between copper(I) halides and monodentate or bidentate chelating ligands has been studied extensively (ref. 4). More recently, bidentate bridging ligands have been considered (ref. 5-12). A rich diversity of copper(I) halide structural chemistry (Scheme 1), including discrete molecular units - rhomboid dimers [scheme 1(a)], cubane tetramers [scheme 1(b)] and stepped cubane tetramers [scheme 1(c)] - and extended polymeric chains - split stair [scheme 1(d)], zigzag [scheme 1(e)], helical [scheme 1(f)], staircase [scheme 1(g)], rack [scheme 1(h)] and columnar [scheme 1(j)] - have been observed. Although extended polymeric sheets have not been noted previously for neutral copper(I) halide constructions, a two-dimensional lattice has been recently described for the Cu_3Br_4^- anion (ref.5).

The observed copper(I) halide architecture depends upon the ligand and halogen used, and upon the stoichiometry of the complex. For example, the copper(I) bromide architecture in complexes of stoichiometry $[\text{Cu}_2\text{Br}_2\text{L}]_\infty$ ranges from staircase chains (for L = phenazine) (ref. 6, 7) through rack chains (for L = 2-cyanoguanidine) (ref. 11) and helical chains (for L = tetrakis(methylthio)tetrathiafulvalene) (ref. 6, 10), to rhomboid dimers (ref. 6) (for L = 2,11-dithia[3,3]paracyclophane). Variations with halide are more subtle. For example, $[\text{Cu}_2\text{X}_2(\text{phenazine})]_\infty$ forms either rhomboid dimers ($\text{X} = \text{I}$) or staircase chains ($\text{X} = \text{Br}$ or Cl), (ref. 6, 7), while $[\text{Cu}_2\text{X}_2(\text{tetrakis(methylthio)tetrathiafulvalene})]_\infty$ forms either rhomboid dimers (for $\text{X} = \text{I}$), helical chains (for $\text{X} = \text{Br}$) or zigzag chains (for $\text{X} = \text{Cl}$), (ref. 6, 10). The effect of stoichiometry is seen in copper(I) halide complexes of 2-cyanoguanidine (cnge) where split stair chains are observed for $[\text{CuX}(\text{cnge})]_\infty$ and rack chains for $[\text{Cu}_2\text{X}_2(\text{cnge})]_\infty$ (ref. 11).

Bridging bidentate ligands give rise to more complicated copper(I) halide architectures than do monodentate or bidentate chelating ligands, and we have now extended this theme to include the tridentate bridging ligand, triazine, which generates even more complex copper(I) halide architectures.

Copper(I) thiocyanate complexes also exhibit a range of different structural architectures. Structures related to those reported for copper(I) halides such as chain, (ref. 13) staircase (ref. 13,14) and sheet (ref. 3a) motifs have been observed in CuSCN compounds, as well as simpler dimeric and monomeric species.

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Scheme 1. Structural motifs observed for copper(I) halides. The copper(I) ions are those sites designated \bullet ; the other sites are halide anions.

COPPER(I) HALIDES BRIDGED BY 1,3,5-TRIAZINE.

Treatment of copper(I) bromide or iodide with triazine (tri) yields four crystalline products of stoichiometry $[\text{Cu}_2\text{X}_2(\text{triazine})]$ and $[\text{Cu}_3\text{X}_3(\text{triazine})]$ ($\text{X} = \text{Br}$ or I). The structures of these compounds are based on copper(I) halide polymeric frameworks, including zigzag chains [scheme 1(e)], columns [scheme 1(j)] or sheets [scheme 1(k)], bridged by triazine molecules to generate complex three-dimensional constructions.

In $[\text{Cu}_3\text{X}_3(\text{tri})]_\infty$ ($\text{X} = \text{Br}, \text{I}$) (Fig. 1) the triazine molecules use all three nitrogens to bridge $(\text{CuX})_\infty$ columns [scheme 1(j)]. Each $(\text{CuX})_\infty$ column is linked to six adjacent $(\text{CuX})_\infty$ columns to generate a system with non-crystallographically imposed three-fold symmetry (Fig. 1). The only difference between the structures is that of space group (*Prma* for $[\text{Cu}_3\text{I}_3(\text{tri})]_\infty$ and *Pbca* for $[\text{Cu}_3\text{Br}_3(\text{tri})]_\infty$). The columnar form of $(\text{CuI})_\infty$ has only been observed previously for $\{[(\text{CuI})(N\text{-methylpyrazine})]^+\}_\infty$ (ref. 15).

The structure of $[\text{Cu}_2\text{Br}_2(\text{tri})]_\infty$ (Fig. 2) is related to that of $[\text{Cu}_3\text{Br}_3(\text{tri})]_\infty$ in so much as both contain a $(\text{CuBr})_\infty$ columnar motif [scheme 1(j)]. In $[\text{Cu}_2\text{Br}_2(\text{tri})]_\infty$, however, each $(\text{CuBr})_\infty$ column is linked through tridentate triazine molecules to zigzag $(\text{CuBr})_\infty$ chains [scheme 1(e)] rather than other $(\text{CuBr})_\infty$ columns, as observed in $[\text{Cu}_3\text{Br}_3(\text{tri})]_\infty$. In $[\text{Cu}_2\text{Br}_2(\text{tri})]_\infty$, each $(\text{CuBr})_\infty$ chain is linked through other triazines to four other $(\text{CuBr})_\infty$ chains as well as a second $(\text{CuBr})_\infty$ column. The entire system has three-fold symmetry as shown in the schematic diagram (Fig. 2) depicting the arrangement of $(\text{CuBr})_\infty$.

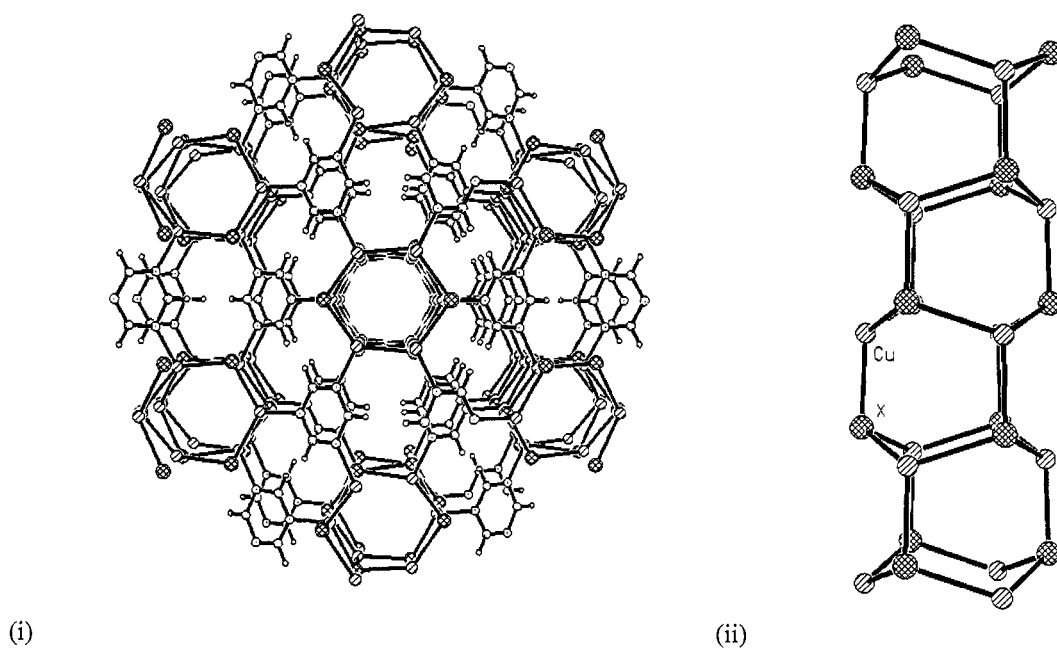


Fig. 1 (i) View of the X-ray structure of $[\text{Cu}_3\text{X}_3(\text{tri})]_\infty$ ($\text{X} = \text{Br}, \text{I}$) and (ii) the $(\text{CuX})_\infty$ column motif observed in $[\text{Cu}_3\text{X}_3(\text{tri})]_\infty$ ($\text{X} = \text{Br}, \text{I}$) and $[\text{Cu}_2\text{Br}_2(\text{tri})]_\infty$ (Cu hatched, X cross-hatched).

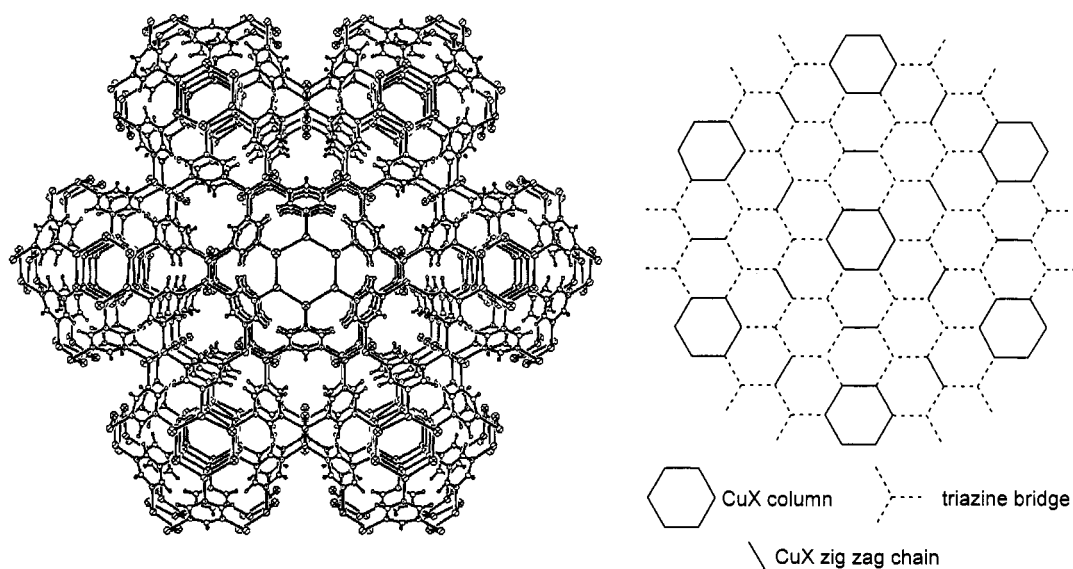


Fig. 2 View of the X-ray structure and schematic representation of $[\text{Cu}_2\text{Br}_2(\text{tri})]_\infty$.

chains, $(\text{CuBr})_\infty$ columns and triazine molecules perpendicular to the three-fold axis of symmetry (Fig. 2).

Despite its identical stoichiometry to $[\text{Cu}_2\text{Br}_2(\text{tri})]_\infty$, $[\text{Cu}_2\text{I}_2(\text{tri})]_\infty$ has a completely different, somewhat simpler, structure (Fig. 3). In $[\text{Cu}_2\text{I}_2(\text{tri})]_\infty$, the triazine ligand acts as a bidentate bridging ligand linking $(\text{CuI})_\infty$ sheets [Scheme 1(k)] to give alternating copper(I) iodide and triazine layers. The alignment of the triazine molecules is such that the unco-ordinated nitrogen atom points directly at the centre of an adjacent triazine molecule (Fig. 3). To our knowledge this is the first example of this particular sheet-form of $(\text{CuI})_\infty$. Although the triazine co-ordinates through two *meta*-N donors in $[\text{Cu}_2\text{I}_2(\text{tri})]_\infty$, behaving as though it were pyrimidine (pym), the three-dimensional architecture of $[\text{Cu}_2\text{I}_2(\text{pym})]_\infty$ (Fig. 4) differs from that of $[\text{Cu}_2\text{I}_2(\text{tri})]_\infty$. In $[\text{Cu}_2\text{I}_2(\text{pym})]_\infty$, the pyrimidine ligands bridge $(\text{CuI})_\infty$ staircase chains [(scheme 1(g)] to give two dimensional sheets comprising alternating stacks of copper(I) iodide and pyrimidine (Fig. 4). Adjacent sheets are stacked such that the $(\text{CuI})_\infty$ staircase chains are positioned on top of each other.

The structures of the three different $(\text{CuX})_\infty$ polymeric frameworks found in the triazine compounds can be traced to the three-dimensional wurtzite structure of copper(I) halides. The zigzag chain [Scheme 1(e)] in which two co-ordinate halide atoms link distorted tetrahedral copper(I) centres, which have X_2N_2 donation, is the simplest. The columnar structural form [Scheme 1(j)] can be described as three zigzag chains arranged with three-fold symmetry, each chain being connected to its two neighbours by Cu-X contacts. An alternative description is the stacking of Cu_3X_3 chairs, alternately rotated by 60° and linked by Cu-X contacts. The sheets, which have a corrugated appearance [Scheme 1(k)], are based on a series of zigzag chains aligned parallel but with cations and anions in adjacent positions on alternate chains. The resulting Cu-X contacts give rise to the sheet construction. For both the column and sheet architectures, each halide anion is three co-ordinate and links distorted tetrahedral copper(I) centres which have X_3N coordination.

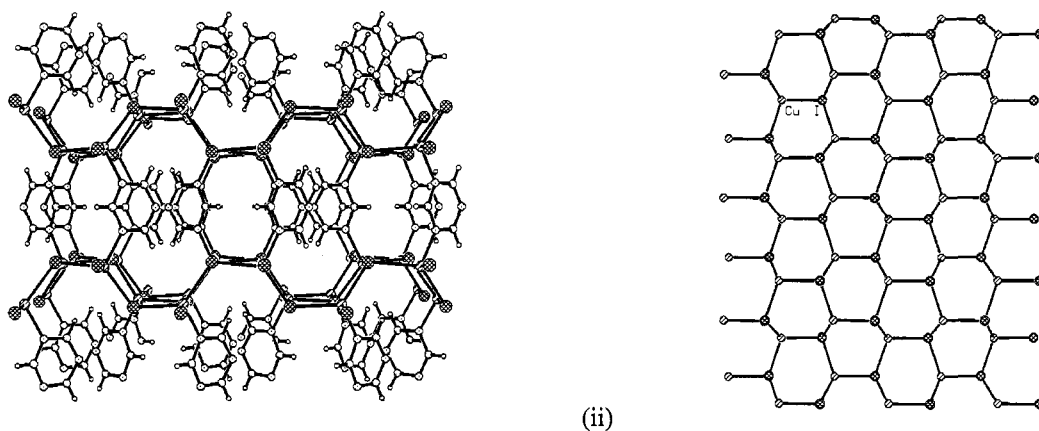


Fig. 3 (i) View of the X-ray structure of $[\text{Cu}_2\text{I}_2(\text{tri})]_\infty$ and (ii) the $(\text{CuI})_\infty$ sheet observed therein (Cu hatched, I cross-hatched).

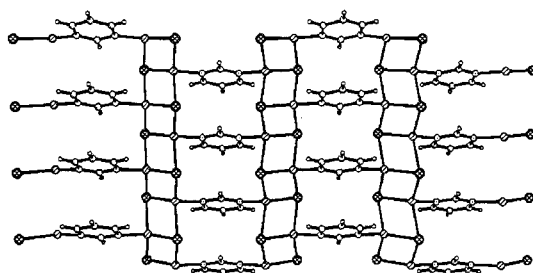


Fig. 4 View of the X-ray structure of $[\text{Cu}_2\text{I}_2(\text{pym})]_\infty$ (Cu hatched, I cross-hatched).

COPPER(I) THIOCYANATE AND BIDENTATE BRIDGING LIGANDS

Reaction of CuSCN in $\text{NH}_4\text{OH}(\text{aq})$ with ethanolic solutions of bpe {1,2-*trans*-bis(4-pyridyl)ethene} affords $[\text{Cu}_2(\text{SCN})_2(\text{bpe})]_\infty$ (Fig. 5). This complex forms two-dimensional sheets in the solid-state which are related to those observed for $[\text{Cu}_2\text{I}_2(\text{pym})]_\infty$. These sheets consist of $[\text{Cu}(\text{SCN})]_\infty$ stair-polymers linked by bridging bpe ligands. Each copper(I) centre is co-ordinated to three ($\mu_2\text{S}$, N) thiocyanate ligands and to one pyridyl donor. Adjacent sheets are staggered so that the $[\text{Cu}(\text{SCN})]_\infty$ stair-polymers in alternate sheets are related by half a translation with respect to each other. The stair-polymer arrangement observed in this complex has been reported before for related copper(I) thiocyanate compounds with pyridyl donor ligands, such as $[\text{Cu}(\text{SCN})(2\text{-methylpyridine})]_\infty$ (ref. 13) and $[\text{Cu}(\text{SCN})(\text{quinoline})]_\infty$ (ref. 14).

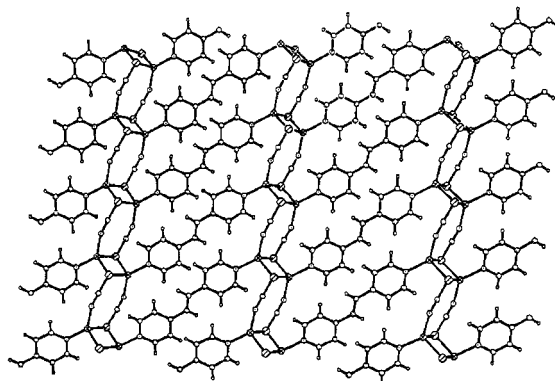


Fig. 5 View of the X-ray structure of $[\text{Cu}_2(\text{SCN})_2(\text{bpe})]_\infty$ (Cu cross-hatched, S hatched)..

In contrast to $[\text{Cu}_2(\text{SCN})_2(\text{bpe})]_\infty$ the reaction of either pyrazine (pyz) or 4,4'-bipy with CuSCN affords three-dimensional networks. Both $[\text{Cu}_2(\text{SCN})_2(\text{pyz})]_\infty$ (ref. 3a) and $[\text{Cu}_2(\text{SCN})_2(4,4'\text{-bipy})]_\infty$ exist as three-dimensional networks consisting of sheets of $[\text{Cu}(\text{SCN})]_\infty$ linked by pyrazine or 4,4'-bipy bridges (Figs. 6 and 7). In both cases each copper(I) centre is co-ordinated by three ($\mu_2\text{S}$, N) thiocyanate ligands and a heterocyclic N-donor (Fig. 7). This arrangement leads to the formation of ten-membered Cu-S-Cu-NCS-Cu-SCN rings. Because of the rigid rod-like nature of SCN^- , each ten-membered ring adopts a pseudo-chair conformation and is fused to six other rings to give a honeycomb sheet. The rings are joined to each other in two different ways, *cis* and *trans*. For $[\text{Cu}_2(\text{SCN})_2(\text{pyz})]_\infty$ (ref. 3a) the rings are *trans*-fused to each other in the direction of the *c*-axis while in the direction of the *a*-axis they are *cis*-fused. The propagation of this *cis*-fusion gives rise to an undulating sheet. In contrast, the ten-membered rings in the $[\text{Cu}(\text{SCN})]_\infty$ sheets of $[\text{Cu}_2(\text{SCN})_2(4,4'\text{-bipy})]_\infty$ are *trans*-fused in the direction of the *a*-axis and *cis*-fused along direction of the *c*-axis. The nature of fusion between adjacent ten-membered rings is also different between $[\text{Cu}_2(\text{SCN})_2(\text{pyz})]_\infty$ and $[\text{Cu}_2(\text{SCN})_2(4,4'\text{-bipy})]_\infty$. In $[\text{Cu}_2(\text{SCN})_2(4,4'\text{-bipy})]_\infty$ the rings are *trans*-fused through the SCN "edges" whereas in $[\text{Cu}_2(\text{SCN})_2(\text{pyz})]_\infty$ the rings are *cis*-fused through the SCN "edges" of the rings (Fig. 8). The arrangement within the $[\text{Cu}(\text{SCN})]_\infty$ sheets in $[\text{Cu}_2(\text{SCN})_2(\text{L})]_\infty$ (L = pyz, 4,4'-bipy) is analogous to that seen in the [011] set of lattice planes in zinc blende (ref. 16). Although ten-membered rings exist in the α - (ref. 17) and β -modifications (ref. 18) of Cu(SCN) or $\{[\text{Cu}_2(\text{SCN})_3]\}_\infty$ (ref. 19), the sheets observed in these structures are not the same as those in $[\text{Cu}_2(\text{SCN})_2(\text{L})]_\infty$ (L = pyz, 4,4'-bipy). In these latter complexes the remaining fourth co-ordination site of each tetrahedral copper(I) centre is occupied by a heterocyclic N-donor ligand which bridges adjacent $[\text{Cu}(\text{SCN})]_\infty$ sheets. For each $[\text{Cu}(\text{SCN})]_\infty$ sheet, the available co-ordination sites are arranged such that on one side all the sites are axial with respect to the ten-membered ring while on the other they are all equatorial. Adjacent sheets are linked by the heterocyclic N-donor ligands in an axial-axial and equatorial-equatorial manner giving rise to a herring-bone pattern (Figs. 6 and 7).

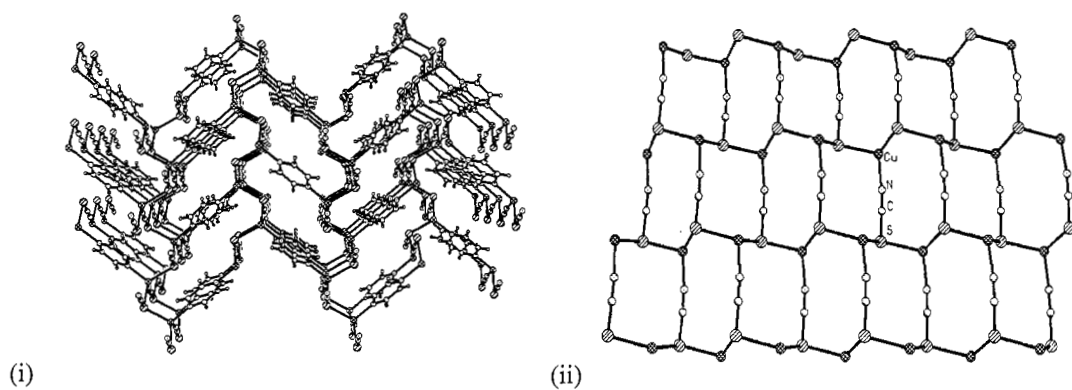


Fig. 6 (i) View of the X-ray structure of $[\text{Cu}_2(\text{SCN})_2(\text{pyz})]_\infty$ and (ii) a view of the $[\text{Cu}(\text{SCN})]_\infty$ sheet (Cu cross-hatched, S hatched).

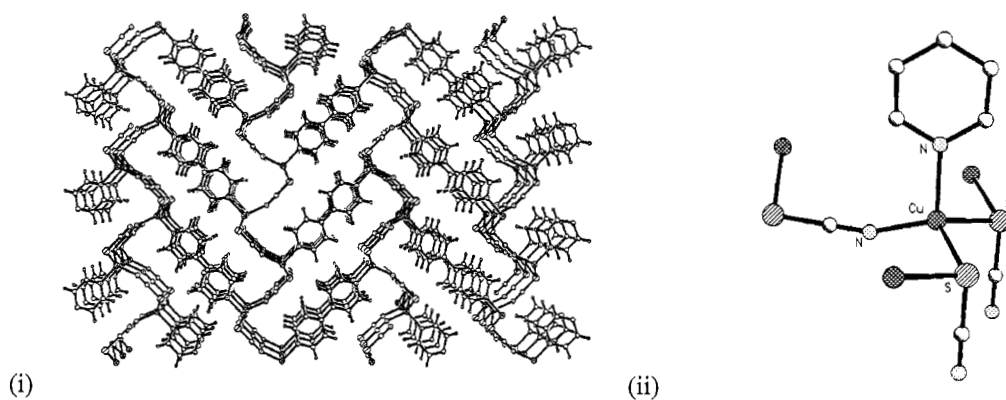


Fig. 7 (i) View of the X-ray structure of $[\text{Cu}_2(\text{SCN})_2(4,4'\text{-bipy})]_\infty$ and (ii) the copper(I) environment as observed in both $[\text{Cu}_2(\text{SCN})_2(4,4'\text{-bipy})]_\infty$ and $[\text{Cu}_2(\text{SCN})_2(\text{pyz})]_\infty$ (Cu cross-hatched, S hatched, N dotted).

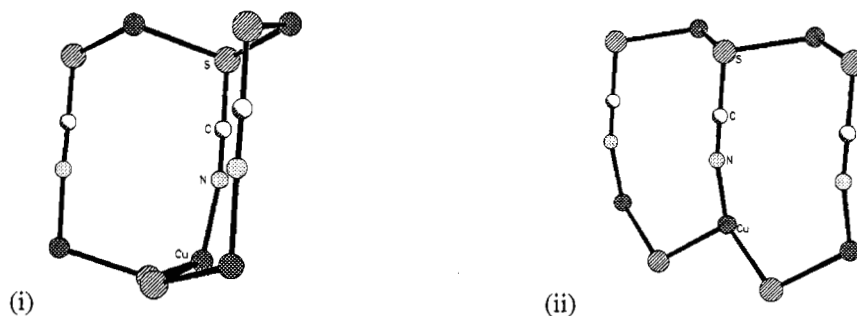


Fig. 8 (i) *Cis*- and (ii) *trans*-fused ten-membered rings as seen in $[\text{Cu}_2(\text{SCN})_2(\text{pyz})]_\infty$ and $[\text{Cu}_2(\text{SCN})_2(4,4'\text{-bipy})]_\infty$ respectively (fusion through the "SCN edges") (Cu cross-hatched, S hatched, N dotted).

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