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Controlling copper(I) halide framework formation using *N*-donor bridging ligand symmetry: use of 1,3,5-triazine to construct architectures with threefold symmetry

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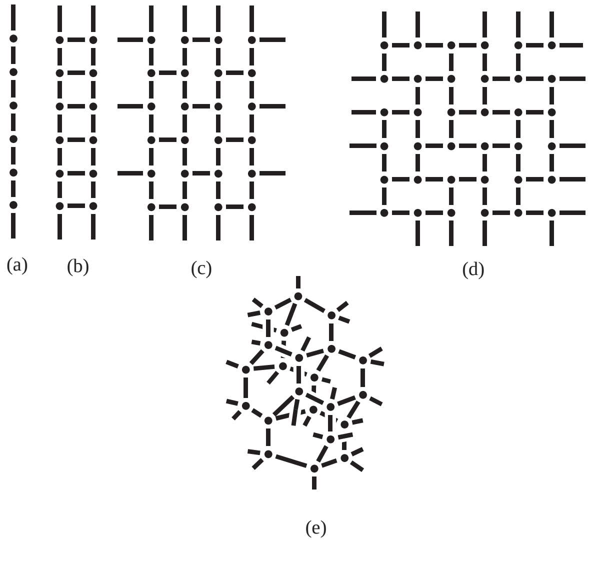
The formation of co-ordination polymers between copper(I) halides and 1,3,5-triazine (tri), a potentially tridentate *N*-donor bridging ligand with threefold symmetry, has been studied. Complexes with both 3 : 1 and 2 : 1 molar ratios are formed by both CuBr and CuI. The compounds $[Cu_3X_3(tri)]_\infty$ (X = Br or I) are structurally similar, despite crystallising in different space groups. They are composed of $(CuX)_\infty$ columns linked by triazine molecules to generate three-dimensional constructions with non-crystallographically imposed threefold symmetry. The $(CuX)_\infty$ columnar motif can be described as a series of perpendicularly stacked Cu_3X_3 chairs, alternately rotated by 60° and linked by Cu–X contacts. The tetrahedral co-ordination geometry of the copper centres is completed by a tridentate triazine bridge which links two copper atoms in separate columns. Thus, each $(CuX)_\infty$ column is linked to six adjacent $(CuX)_\infty$ columns. The structure of $[Cu_2Br_2(tri)]_\infty$ comprises $(CuBr)_\infty$ columns and castellated $(CuBr)_\infty$ chains linked by triazine molecules to generate a construction with crystallographically imposed threefold symmetry. The $(CuBr)_\infty$ columns are similar to but more regular than those found in $[Cu_3Br_3(tri)]_\infty$. In this case, however, each column is linked to six adjacent chains. The $(CuBr)_\infty$ castellated chain motif is very unusual. The tetrahedral copper centres are co-ordinated by two adjacent bromide anions and by two triazine molecules each of which links a second chain and a column. Consequently, each chain is linked to four neighbouring chains and two neighbouring columns. Despite a stoichiometry identical to that of $[Cu_2Br_2(tri)]_\infty$, $[Cu_2I_2(tri)]_\infty$ has a completely different structure. The triazine molecules act as bidentate bridging ligands to link $(CuI)_\infty$ layers thereby giving alternating inorganic and organic layers. The tetrahedral co-ordination geometry of the copper centres in the $(CuI)_\infty$ layers, which are effectively undulating hexagonal nets, is provided by three iodide anions from the layers and by a bridging triazine molecule.

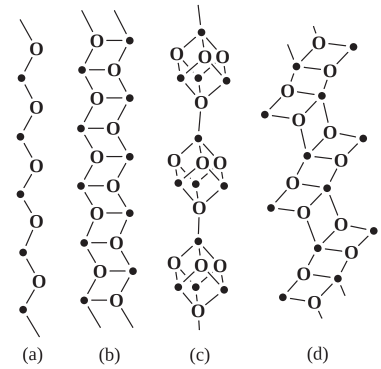
Co-ordination polymers are normally constructed by linking transition metal centres through bridging ligands and a rich diversity of architectures has been reported ranging from simple one-dimensional chains to three-dimensional matrices (Scheme 1).[1] The anions in these systems act either as co-ordinated, non-bridging, spectator ligands or as non-co-ordinated, void-filling species. Copper(I) halides, however, can themselves form both oligomeric (normally dimers or tetramers) and polymeric frameworks.[2–7] Consequently, copper(I) halide co-ordination polymers can be solely metal-halide based (Scheme 2), solely metal–ligand based with oligomeric molecular units linked by bridging ligands (Scheme 3), or a combination of both with metal-halide frameworks linked by bridging ligands (Scheme 4).

The influence of ligand geometry and/or symmetry on the metal–ligand co-ordination assembly is self-evident.[1] In this paper we report the syntheses and structures of copper(I) halide frameworks linked by *N*-donor ligands and provide considerable evidence to support the contention that ligand geometry and/or symmetry also influences metal–halogen framework formation.

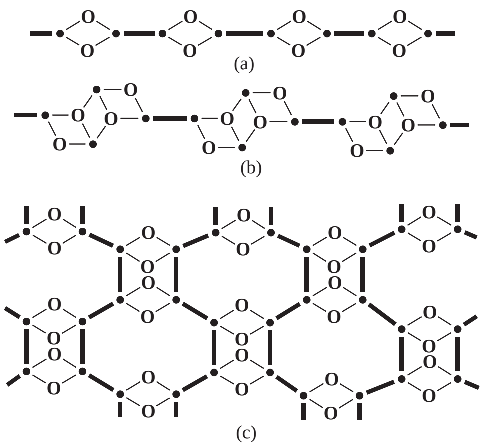
With monodentate *N*-donor ligands, the copper(I) halide frameworks range from mononuclear species through dinuclear and tetranuclear discrete molecular moieties to polymeric



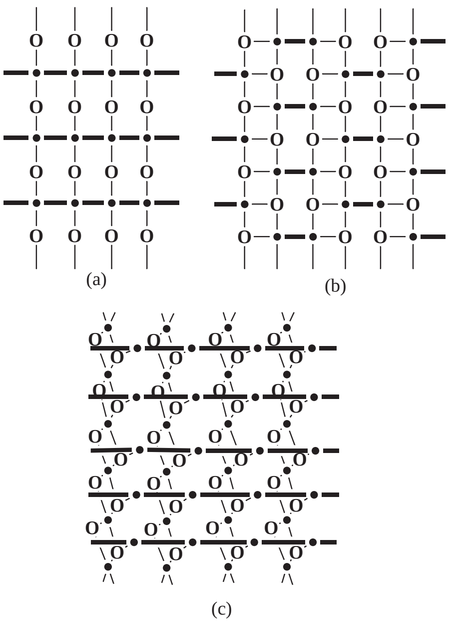
Scheme 1 Co-ordination polymers formed by linking transition metal centres (●) through molecular rods (▬): (a, b) one-dimensional chains, (c, d) two-dimensional sheets and (e) three-dimensional matrices.



Scheme 2 Copper(I) halide frameworks: (a, b, c, d) one-dimensional chains. ● Copper(I) cations; ○, halide anions.



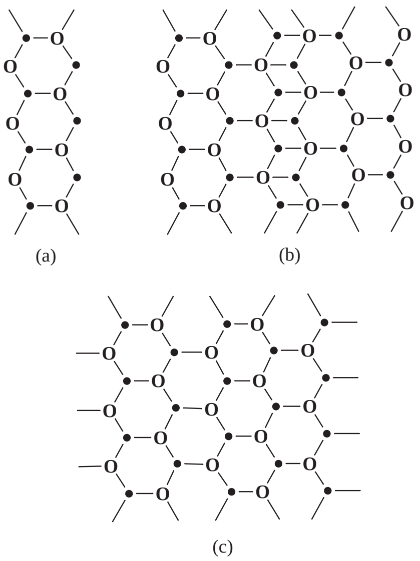
Scheme 3 Co-ordination polymers formed by linking copper(I) halide molecular units through molecular rods (▬): (a, b) one-dimensional chains, (c) two-dimensional sheets. ●, Copper(I) cations; ○, halide anions.



Scheme 4 Co-ordination polymers (two-dimensional sheets) formed by linking copper(I) halide frameworks through molecular rods. Key as in Scheme 3.

structures.[2–9] The less sterically demanding the ligand, the greater the complexity of the copper(I) halide architectures. The mononuclear species comprise two- and three-co-ordinate molecular units of stoichiometry $[\mathrm{CuXL}]$[8] or $[\mathrm{CuXL_2}]$[9] (X = halide, L = *N*-donor ligand). The dinuclear species are based on rhomboid dimers of stoichiometry $[\mathrm{Cu_2X_2L_2}]$[2,8] or $[\mathrm{Cu_2X_2L_4}]$[3,5,9] and the tetranuclear species on cubane[2,10] or stepped cubane[2] tetramers of stoichiometry $[\mathrm{Cu_4X_4L_4}]$ and $[\mathrm{Cu_4X_4L_6}]$, respectively (X = halide, L = *N*-donor ligand). All the copper(I) halide polymeric species are based on one-dimensional chains; no examples of two-dimensional sheets have been observed. Although the majority of the chains are single-strand split-stair[2–4] or double-strand staircase[3,5,6] frameworks of stoichiometry $[\mathrm{CuXL}]_\infty$, there are a limited number of examples containing linked cubane tetramers[2] or stepped-cubane[7] tetramers of stoichiometry $[\mathrm{Cu_4X_4L_3}]_\infty$ and $[\mathrm{Cu_4X_4L_4}]_\infty$, respectively (X = halide, L = *N*-donor ligand).

Bidentate bridging *N*-donor ligands have immense influence on the metal–halogen framework adopted. They are best classified according to the disposition of their lone pairs, which varies from linear (bridging angle 180°; *e.g.* pyrazine) through obtuse (bridging angle 120°, *e.g.* pyrimidine) and acute (bridging angle 60°, *e.g.* pyridazine) to parallel (bridging angle 0°; *e.g.* 1,8-naphthyridine). The copper(I) halide frameworks formed in the presence of parallel bridging *N*-donor ligands are complex chain, ribbon or layer motifs (Scheme 5).[11,12] They are all based on fused $\mathrm{Cu_3Br_3}$ hexagons, two copper atoms of which are spanned by the bidentate ligand. It is the small bridging angle which dictates the relative positioning of the copper centres and hence the geometry of the copper(I) halide frameworks. With dipyrido(1,2-*a*:2′,3′-*d*)imidazole (dpi),[11] CuCl forms $[\mathrm{Cu_2Cl_2(dpi)}]_\infty$ chains, which comprise a linear array of hexagons (Scheme 5a); in contrast, CuBr forms $[\mathrm{Cu_3Br_3(dpi)}]_\infty$ ribbons, which comprise two chains linked by a conventional $[\mathrm{CuBr}]_\infty$ staircase chain (Scheme 5b). With acrylonitrile (acn), CuCl forms $[\mathrm{Cu_2Cl_2(acn)}]_\infty$ layers in which the chains are fused to generate a buckled, severely distorted, hexagonal net (Scheme 5c).[12]



Scheme 5 Copper(I) halide $[\mathrm{CuX}]_\infty$ co-ordination polymers generated from parallel bridging bidentate ligands: (a) one-dimensional chain, (b) one-dimensional ribbon and (c) two-dimensional layer.

Only a small number of copper(I) halide co-ordination polymers have been obtained with obtuse bridging bidentate *N*-donor ligands. 2-Cyanoguanidine (cnge), which uses its nitrile and imino nitrogens to give a bridging angle of 120°,[13] forms with CuX (X = Cl or Br) a two-dimensional structure in which parallel $(\mathrm{CuX_2Cu})_\infty$ rack chains (Scheme 4c) are linked by cnge molecules.

Linear bidentate bridging *N*-donor ligands, so-called molecular rods, favour linear frameworks[14] which in turn generate one-dimensional copper(I) halide frameworks. Thus, pyrazine (pyz) forms two complexes with CuCl both of which adopt two-dimensional sheet structures; in $[CuCl(pyz)]_\infty$ the pyrazine molecules link $(CuCl)_\infty$ split stair chains (Scheme 4a),[15] whereas in $[Cu_2Cl_2(pyz)]_\infty$ they link $(CuCl)_\infty$ staircase chains (Scheme 4b).[16] Phenazine (phz) forms 1:2 complexes $[Cu_2X_2(phz)]_\infty$ (X = Cl or Br) structurally similar to $[Cu_2Cl_2(pyz)]_\infty$.[17] 4-Cyanopyridine (pyridine-4-carbonitrile; pycn), a molecular rod with both pyridinyl and nitrile bases, gives 1:1 complexes $[CuX(pycn)]_\infty$ (X = Cl or Br) which adopt a two-dimensional sheet structure analogous to that of $[CuCl(pyz)]_\infty$, with 4-cyanopyridine molecules linking $(CuCl)_\infty$ split-stair chains.[18]

The remaining copper(I) halide frameworks found in co-ordination polymers containing linear bidentate bridging *N*-donor ligands are discrete dinuclear or tetranuclear species. In $[Cu_2I_2(phz)]_\infty$, phenazine molecules link Cu_2I_2 rhomboids to form a one-dimensional chain structure (Scheme 3a).[17] A similar one-dimensional chain structure occurs in $[Cu_4I_4(pycn)_5]_\infty$ in which $[Cu_4I_4(pycn)_4]$ stepped cubane tetramers are linked by a fifth bidentate bridging pycn molecule (Scheme 3b).[18] The extended structure of $[CuCl(4,4'\text{-bipy})]_\infty$, comprises an interpenetrated arrangement of mutually perpendicular sheets based on an hexagonal arrangement of Cu_2Cl_2 rhomboids linked by alternating single and double 4,4′-bipyridine (4,4′-bipy) bridges (Scheme 3c).[19]

To support our contention that the choice of copper(I) halide framework is dependent on ligand symmetry, we now report the results of our study of complex formation between the tridentate bridging ligand 1,3,5-triazine (tri) and copper(I) halides. Thus far, only two co-ordination polymers involving triazine have been reported; they are both silver(I) complexes, $[Ag(tri)(CF_3SO_3)]\cdot H_2O$[20] and $[Ag_6(tri)_8][BF_4]_6\cdot H_2O$.[21] Whereas all of the triazine molecules in the former are triconnected, only six are triconnected in the latter, the other two acting as bidentate ligands.

Results and discussion

Treatment of copper(I) bromide or iodide with triazine has yielded four crystalline products of stoichiometry $[Cu_3X_3(tri)]$ (X = Br **1** or I **2**) and $[Cu_2X_2(tri)]$ (X = Br **3** or I **4**). Good quality crystals of all four products were obtained by conventional crystallisation techniques. Crystals of **1**–**3** were obtained by layering solutions of CuX (X = Br or I) in MeCN and solutions of 1,3,5-triazine in CH_2Cl_2 or Et_2O. Crystals of **4** were obtained by vapour phase diffusion of Et_2O into a mixture of CuI in MeCN and 1,3,5-triazine in CH_2Cl_2. The four products were characterised by single crystal X-ray diffraction methods. Although $[Cu_2X_2(tri)]_\infty$ (X = Br or I) adopt markedly different structures, $[Cu_3X_3(tri)]_\infty$ (X = Br or I) are similar, although they adopt different space groups (*Pbca* for $[Cu_3Br_3(tri)]_\infty$ and *Pnma* for $[Cu_3I_3(tri)]_\infty$). The molecular structures of the complexes are shown in Figs. 1–4; selected interatomic distances and angles are summarised and compared in Table 1.

The reactivity of the products increases markedly from the iodides, which were prepared in bulk, to the bromides, which could only be obtained in very limited quantity as crystalline samples. The chlorides were so sensitive that analogous experiments with copper(I) chloride were unsuccessful despite the careful application of Schlenk methods.

Crystal and molecular structure of $[Cu_3X_3(tri)]_\infty$ (X = Br or I)

The structures of $[Cu_3X_3(tri)]_\infty$ (X = Br **1** or I **2**) are composed of $(CuX)_\infty$ columns linked by triazine molecules to generate three-dimensional constructions with non-crystallographically imposed threefold symmetry (Fig. 1a). The numbering schemes for the asymmetric unit of **1**, which contains three copper cations, three bromide anions and a single triazine molecule, and **2**, which contains two copper cations and two iodide anions, of which Cu(3) and I(1) lie on a mirror plane, and half a triazine molecule of which C(1) and N(2) lie on a mirror plane, are shown in Fig. 2a and 2b, respectively. The location, in **2**, of one of the copper cations on a symmetry element results in a more symmetrical network and different packing of the triazine molecules.

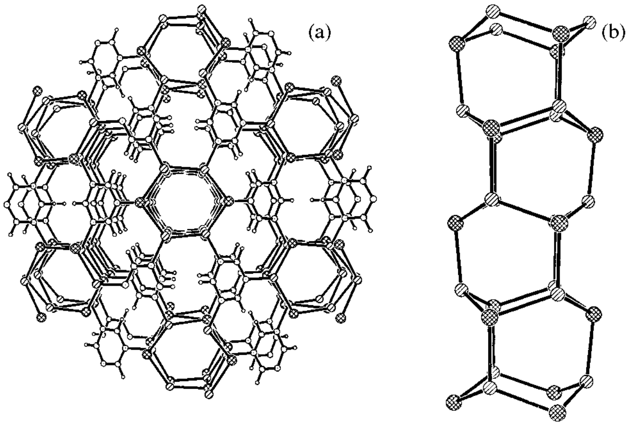


Fig. 1 Molecular structure of $[Cu_3X_3(tri)]_\infty$ (X = Br or I): (a) view down the columnar axis and (b) view of the one-dimensional columnar framework (Cu, hatched; X, cross-hatched; N, dotted; C, shaded).

The $(CuX)_\infty$ columnar framework motif (Fig. 1b; Scheme 6b) has been observed once before, in the *N*-methylpyrazinium iodocuprate, $[Cu_2I_3(Mepyz)]$.[22] The motif can be described as a series of perpendicularly stacked Cu_3X_3 chairs, alternately rotated by 60° and linked by Cu–X contacts [for **1**, Cu···Br 2.418(1)–2.491(1), average 2.46 Å; for **2**, Cu···I 2.588(1)–2.621(1), average 2.61 Å]. Each of the three copper atoms in a chair is linked through a tridentate triazine bridge [for **1**, Cu···N 2.058(4)–2.090(4), average 2.07 Å; for **2**, Cu···N 2.082(5), 2.083(8) Å] to two copper atoms in separate columns (Fig. 2a). Thus, each column is linked to six adjacent columns (Fig. 1a) to give the three-dimensional construction.

Crystal and molecular structure of $[Cu_2Br_2(tri)]_\infty$

The structure of $[Cu_2Br_2(tri)]_\infty$ **3** (Fig. 3a) comprises $(CuBr)_\infty$ columns (Fig. 3b; Scheme 6b), similar to those found in **1**, and castellated $(CuBr)_\infty$ chains (Fig. 3c; Scheme 6a) linked by triazine molecules to generate a construction with crystallographically imposed threefold symmetry (Fig. 3a). The numbering scheme for the asymmetric unit, which contains two copper cations and two bromide anions, all of which lie on mirror planes, and half a triazine molecule of which C(4) and N(2) lie on a mirror plane, is shown in Fig. 2c.

The castellated $(CuBr)_\infty$ chains (Fig. 3c; Scheme 6a) in complex **3** are unusual. Much less common than split-stair chains, castellated chains have been observed previously only in conjunction with the bidentate chelating *S*-donor ligand, tetrakis(methylsulfanyl)tetrathiafulvalene (tmtttf). In $[Cu_2Cl_2(tmtttf)]_\infty$,[23] tmtttf molecules bridge parallel castellated $(CuCl)_\infty$ chains to form two-dimensional sheets.

The $(CuBr)_\infty$ column in complex **3** is more regular than that in **1**. The Cu···Br interatomic distances within the column of **3** [2.423(3), 2.485(2) Å] are similar to those in the column of **1** [2.418(1)–2.491(1) Å] and cover a narrower range than those in the chain of **3** [2.394(3), 2.523(3) Å].

Each of the three copper atoms in a chair of the column in complex **3** is co-ordinated by a triazine molecule, Cu···N 2.076(13) Å, which uses its other two nitrogen atoms to bridge to two copper atoms, Cu···N 2.095(9) Å, in separate chains (Fig. 2b). Owing to the alternating 60° rotation of the chairs a view down the column shows sixfold symmetry as each column is linked to six adjacent chains (Fig. 3a). Each copper atom of a chain is co-ordinated by two triazine molecules, Cu···N 2.095(9) Å, each of which links to a second chain and a column.

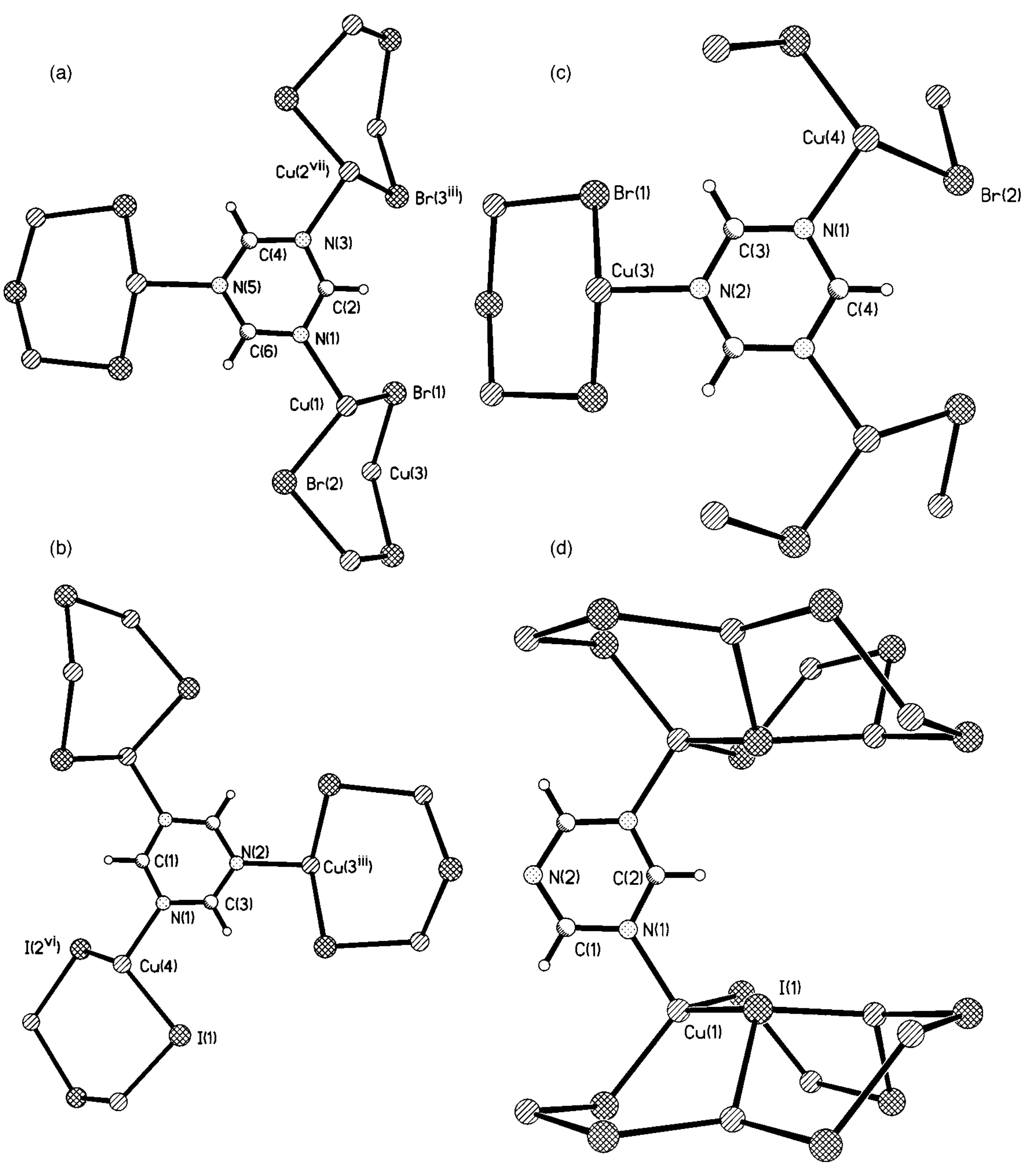


Fig. 2 Co-ordination properties of triazine in $[Cu_3X_3(tri)]_\infty$ [X = Br (a) or I (b)], $[Cu_2Br_2(tri)]_\infty$ (c) and $[Cu_2I_2(tri)]_\infty$ (d) showing the numbering schemes [Cu, hatched; X, cross-hatched; N, dotted; C, shaded; symmetry codes: (a) iii $-x$, $-0.5 + y$, $0.5 - z$; vii $-x$, $0.5 + y$, $0.5 - z$; (b) iii $-x$, $-y$, $1 - z$; vi $1 + x, y, z$].

Consequently, each chain is linked through triazine molecules to four other neighbouring chains and two neighbouring columns. The entire system has threefold symmetry as shown in the schematic diagram depicting the arrangement of chains, tubes and triazine molecules perpendicular to the threefold axis of symmetry (Fig. 3d). A corollary of the non-centrosymmetric character of the complex is the fact that all the triazine molecules point in the same direction (Fig. 3a), giving rise to a polar crystal structure.

Crystal and molecular structure of $[Cu_2I_2(tri)]_\infty$

Despite a stoichiometry identical to that of complex **3**, $[Cu_2I_2(tri)]_\infty$ **4** has a completely different structure (Fig. 4). It comprises $(CuI)_\infty$ sheets (Fig. 4b; Scheme 6c) linked by triazine molecules acting as bidentate bridging ligands (Fig. 2d). The numbering scheme for the asymmetric unit, which contains one copper cation, one iodide anion, and half a triazine molecule of which C(2) and N(2) lie on a mirror plane, is shown in Fig. 2d.

The $(CuI)_\infty$ layer (Fig. 4b; Scheme 6c) is effectively an undulating hexagonal net, each six-membered ring adopting a boat conformation. It is similar to, but much more regular than, the $(CuCl)_\infty$ sheet found in $[Cu_2Cl_2(acn)]_\infty$.[12] The geometrical parameters in **4** [Cu–I 2.5864(10)–2.6338(9), average 2.616 Å; I–Cu–I 108.39(3)–117.10(4), average 112.5°; Cu–I–Cu 105.55(3)–110.06(3), average 107.8°] fall into much more limited ranges than those in $[Cu_2Cl_2(acn)]_\infty$ [Cu–Cl 2.269(5)–2.720(4), average 2.398 Å; Cl–Cu–Cl 96.52(13)–107.30(13), average 101.8°; Cu–Cl–Cu 104.2(2)–127.0(2), average 116.3°].[12] The fourth position of the tetrahedral copper centre in **4** is occupied by a nitrogen, Cu–N 2.064(5) Å, of a triazine which bridges to a copper atom in a second $(CuI)_\infty$ layer (Fig. 2d) giving alternating copper(I) iodide and triazine layers (Fig. 4a). The alignment of the triazine molecules is such that the unco-ordinated nitrogen atom points directly at the centre of an adjacent triazine molecule (dihedral angle between triazine rings = 82.2°; nitrogen–ring centre distance = 2.93 Å; Fig. 4).

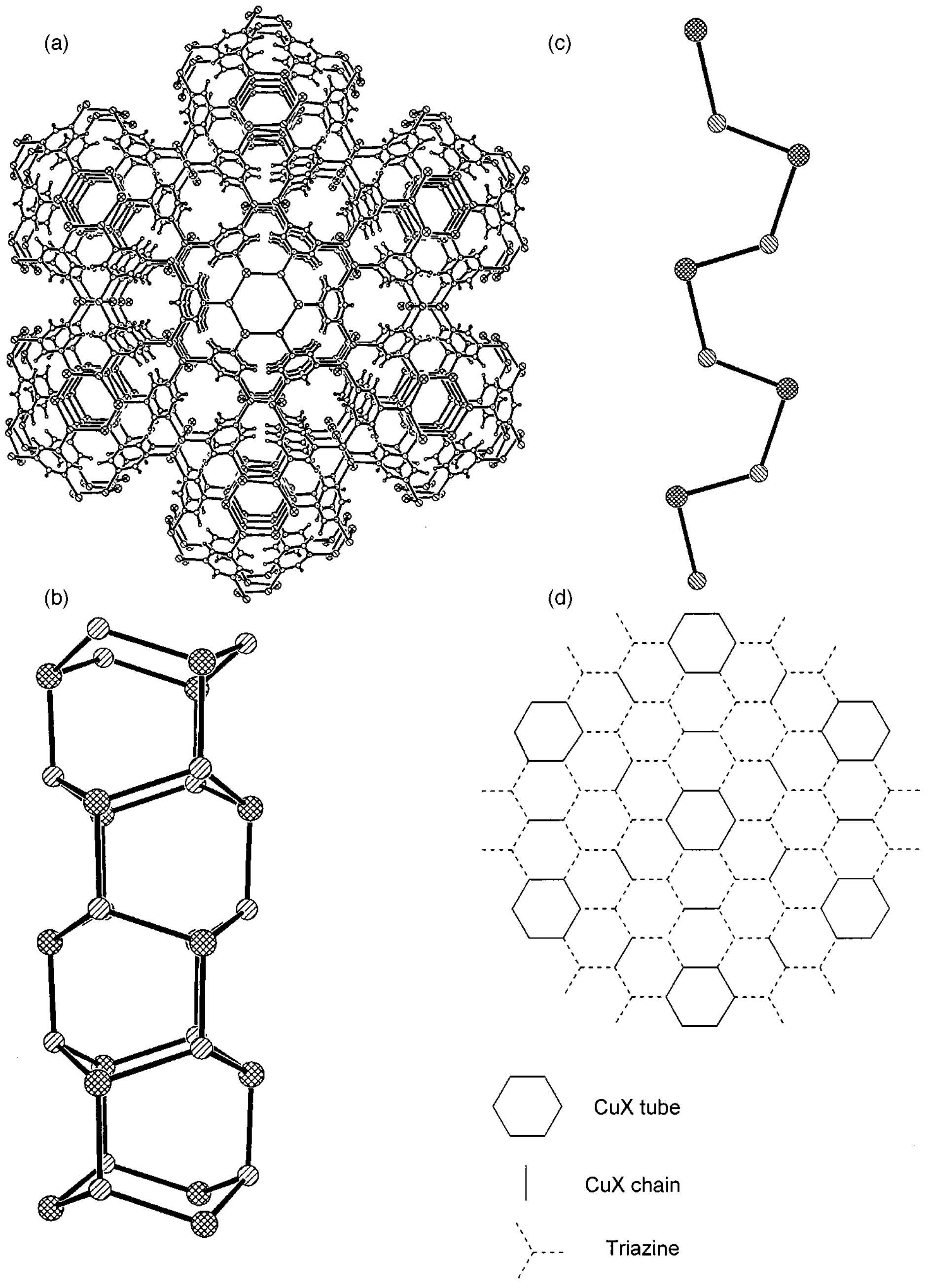


Fig. 3 Molecular structure of $[Cu_2Br_2(tri)]_\infty$: (a) view down the columnar axis, (b) view of the one-dimensional columnar framework, (c) view of the one-dimensional castellated chain and (d) schematic representation of the structure showing the threefold symmetry of the extended assembly (Cu, hatched; Br, cross-hatched; N, dotted; C, shaded).

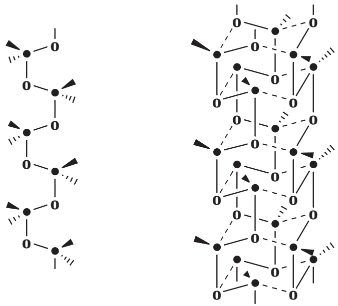
This structure may be considered to be a new topological type as replacement of copper by silicon, iodine by nitrogen and triazine by oxygen generates the Si_2N_2O (Sinoite) structure.[24]

Copper halide frameworks

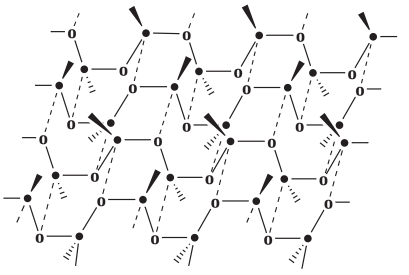
All three copper halide polymeric frameworks, chains, tubes and sheets found in the four compounds can be traced to the three-dimensional wurtzite structure of copper(I) halides.[24] The one-dimensional castellated chain (Scheme 6a) is the simplest, with distorted tetrahedral copper centres linked by two-co-ordinate halides leaving two co-ordination sites free to bind separate triazine molecules. The novel columnar structural form (Scheme 6b), although previously described as a series of perpendicularly stacked Cu_3X_3 chairs, alternately rotated by 60° and linked by Cu–X contacts, can also be described as three parallel castellated chains arranged with threefold symmetry, each chain being connected to its two neighbours by Cu–X contacts. The sheets, which have a corrugated appearance (Scheme 6c), are constructed in a similar fashion to the columns, a series of parallel castellated chains being connected by Cu–X contacts. They have essentially the same geometry as the (100) plane of the wurtzite structure.[24] For both the columnar and sheet architectures, distorted tetrahedral copper centres are linked by three co-ordinate halides leaving a single co-ordination site free to bind a triazine molecule.

1,3,5-Triazine co-ordination

The triazine ligand bridges the copper halide frameworks to generate complex three-dimensional constructions. The dispositions of the copper(I) halide frameworks around the triazine molecules are compared in Fig. 2. Although potentially tridentate, the triazine molecule does not invariably use all three *N*-donor sites. In **4** it acts as a bidentate ligand by linking two copper iodide sheets (Fig. 2d) to give alternating copper iodide and triazine layers (Fig. 4). The triazine is tridentate in the other three componds. In **1** and **2** each triazine co-ordinates to



(a) castellated chain (b) column



(c) sheet

Scheme 6 Novel copper(I) halide frameworks formed in triazine based co-ordination polymers: (a) one-dimensional castellated chains, (b) one-dimensional $[CuX]_\infty$ columns and (c) two-dimensional $[CuX]_\infty$ sheets.

three copper(I) centres in adjacent columns (Fig. 2a and 2b) to generate a system with non-crystallographically imposed threefold symmetry (Fig. 1). The packing of the triazine molecules differs in the two co-ordination polymers, the location, in **2**, of one of the copper centres on a mirror plane resulting in a more symmetrical network. In **3** each triazine molecule bridges a column and two castellated chains (Fig. 2c), to give the three-dimensional structure (Fig. 3).

Conclusion

Co-ordination polymers of copper(I) halides with *N*-donor ligands dramatically exemplify the influence of ligand geometry and/or symmetry on the type of copper(I) halide framework geometry observed. Thus, monodentate ligands generate either molecular units or one-dimensional chains; parallel bidentate bridges form one-dimensional chains or ribbons and two-dimensional layers all of which are based on distorted hexagonal Cu_3X_3 building blocks; linear bidentate bridges encourage formation of linear arrays in the form of staircase or split-stair chains and the trigonal symmetry of the tridentate triazine molecule promotes the formation of a copper(I) halide framework with threefold symmetry in the form of the columnar constructions in **1**, **2** and **3**.

Experimental

Synthesis; general procedures

All reagents (Aldrich) were used as received. When using CuBr all procedures were carried out under argon and all solvents were freshly distilled, degassed and dried by literature procedures.[25] Elemental analysis (C, H, N) was performed by the Nottingham University School of Chemistry Microanalytical Service using a Perkin-Elmer 240B instrument. Infrared spectra were obtained (as KBr pressed pellets) using either a Perkin-Elmer 1600 series or a Nicolet Avatar 360 FTIR spectrometer.

$[Cu_3Br_3(tri)]_\infty$ 1. A solution of CuBr (0.050 g; 3.49×10^{-4} mol) in dry MeCN (10 cm^3) was added to a solution of 1,3,5-triazine (0.0094 g; 1.16×10^{-4} mol) in dry MeCN (10 cm^3). Dry Et_2O was added and the resultant orange precipitate filtered off, washed with dry MeCN and dry Et_2O and dried *in vacuo* (yield: 0.043 g, 0.84×10^{-4} mol, 72%) [Found (calc. for CHBrCuN): C, 7.00 (7.05); H, 0.50 (0.60); N, 8.00 (8.20)%]. IR $\tilde{\nu}$/cm^{-1} (triazine unless stated otherwise): 1556s, 1406s, 1171w, 705m and 699m. Orange block-shaped crystals suitable for X-ray diffraction studies were grown by layering a solution of triazine in Et_2O on top of a CuBr solution in MeCN (molar ratio 1 : 3).

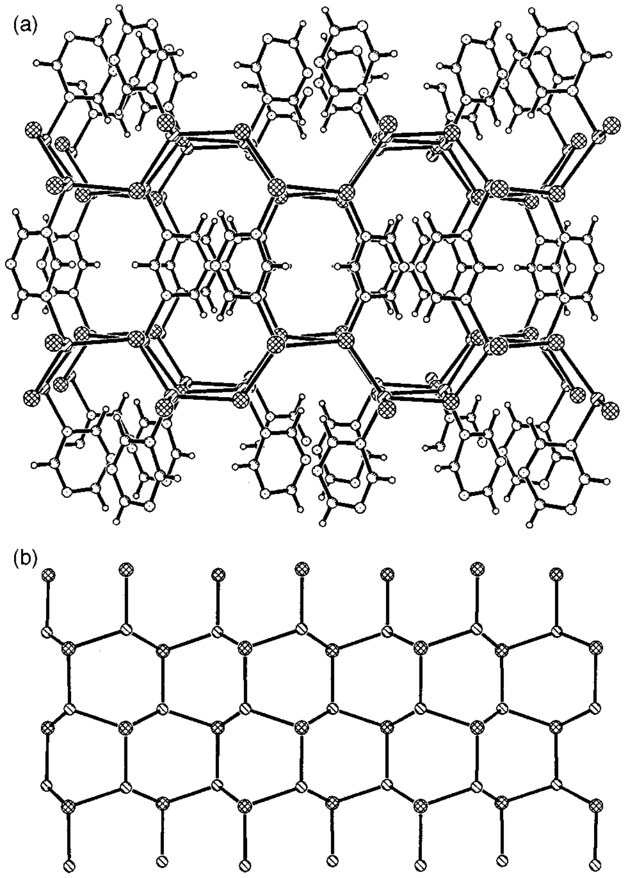


Fig. 4 Molecular structure of $[Cu_2I_2(tri)]_\infty$: (a) view showing the alternating $[CuI]_\infty$ and triazine layers and (b) view of the two-dimensional $[CuI]_\infty$ layer (Cu, hatched; I, cross-hatched; N, dotted; C, shaded).

$[Cu_3I_3(tri)]_\infty$ 2. A solution of CuI (0.050 g; 2.63×10^{-4} mol) in MeCN (10 cm^3) was added to a solution of 1,3,5-triazine (0.0071 g; 0.88×10^{-4} mol) in Et_2O (20 cm^3). The mixture was left at room temperature overnight and the resulting red crystalline precipitate filtered off, washed with CH_2Cl_2 and dried *in vacuo* (yield: 0.0125 g, 0.19×10^{-4} mol, 22%) [Found (calc. for CHCuIN): C, 5.50 (5.50); H, 0.40 (0.45); N, 6.30 (6.45)%]. IR $\tilde{\nu}$/cm^{-1} (triazine unless stated otherwise): 1554s, 1406s and 1172m. Red block-shaped crystals suitable for X-ray diffraction studies were grown either by slow evaporation of a 2 : 1 CuI : triazine solution in MeCN or CH_2Cl_2 or by layering a solution of triazine in Et_2O on top of a CuI solution in MeCN (molar ratio 1 : 3).

$[Cu_2Br_2(tri)]_\infty$ 3. Orange acicular crystals suitable for X-ray diffraction studies were grown by layering a CuBr solution in pre-dried MeCN on top of a solution of triazine in pre-dried Et_2O. All attempts to prepare the product in bulk resulted in the formation of $[Cu_3Br_3(tri)]_\infty$ (by microanalysis and X-ray powder diffraction analysis).

$[Cu_2I_2(tri)]_\infty$ 4. A solution of CuI (0.020 g; 1.05×10^{-4} mol) in MeCN (10 cm^3) was added to a solution of 1,3,5-triazine (0.0043 g; 0.53×10^{-4} mol) in CH_2Cl_2 (10 cm^3). The mixture was left at room temperature overnight and the resulting yellow precipitate filtered off, washed with CH_2Cl_2 and dried *in vacuo* (yield: 0.0167 g, 0.36×10^{-4} mol, 68%) [Found (calc. for

Table 1 Selected bond lengths and angles for $[Cu_3Br_3(tri)]_\infty$ **1**, $[Cu_3I_3(tri)]_\infty$ **2**, $[Cu_2Br_2(tri)]_\infty$ **3** and $[Cu_2I_2(tri)]_\infty$ **4**

1[a]		**2**[b]		**3**[c]		**4**[d]	
Cu–X/Å							
Cu(1)–Br(1)	2.4779(10)	Cu(3)–I(1)	2.592(2)	Cu(3)–Br(1)	2.423(3)	Cu(1)–I(1)	2.6286(14)
Cu(1)–Br(2)	2.4204(8)	Cu(4)–I(1)	2.5875(12)	Cu(3$^{\text{i}}$)–Br(1)	2.485(2)	Cu(1$^{\text{i}}$)–I(1)	2.5864(10)
Cu(1)–Br(3)	2.4832(9)	Cu(3)–I(2)	2.6206(12)	Cu(4)–Br(2)	2.523(3)	Cu(1$^{\text{ii}}$)–I(1)	2.6338(9)
Cu(2)–Br(1)	2.4565(8)	Cu(4$^{\text{i}}$)–I(2)	2.616(2)	Cu(4$^{\text{ii}}$)–Br(2)	2.394(3)		
Cu(2$^{\text{i}}$)–Br(3)	2.4898(9)	Cu(4$^{\text{ii}}$)–I(2)	2.620(2)				
Cu(2$^{\text{ii}}$)–Br(3)	2.4184(8)						
Cu(3)–Br(1)	2.4708(8)						
Cu(3$^{\text{i}}$)–Br(2)	2.4305(9)						
Cu(3$^{\text{ii}}$)–Br(2)	2.4912(8)						
Cu–N/Å							
Cu(1)–N(1)	2.090(4)	Cu(3)–N(2$^{\text{iii}}$)	2.083(8)	Cu(3)–N(2)	2.076(13)	Cu(1)–N(1)	2.064(5)
Cu(2)–N(3$^{\text{iii}}$)	2.076(4)	Cu(4)–N(1)	2.082(5)	Cu(4)–N(1$^{\text{iii}}$)	2.095(9)		
Cu(3)–N(5$^{\text{iv}}$)	2.058(4)						
Angles at X/°							
Cu(1)–Br(1)–Cu(3)	103.71(3)	Cu(4)–I(1)–Cu(4$^{\text{iv}}$)	97.71(5)	Cu(3$^{\text{i}}$)–Br(1)–Cu(3)	107.34(7)	Cu(1$^{\text{i}}$)–I(1)–Cu(1)	105.55(3)
Cu(2)–Br(1)–Cu(1)	108.02(3)	Cu(4)–I(1)–Cu(3)	107.25(3)	Cu(4$^{\text{ii}}$)–Br(2)–Cu(4)	93.32(7)	Cu(1$^{\text{i}}$)–I(1)–Cu(1$^{\text{ii}}$)	110.06(3)
Cu(3)–Br(1)–Cu(1)	100.95(3)	Cu(4$^{\text{iv}}$)–I(1)–Cu(3)	107.25(3)			Cu(1)–I(1)–Cu(1$^{\text{ii}}$)	107.84(3)
Cu(1)–Br(2)–Cu(3$^{\text{i}}$)	107.71(3)	Cu(4$^{\text{i}}$)–I(2)–Cu(4$^{\text{ii}}$)	107.53(3)				
Cu(1)–Br(2)–Cu(3$^{\text{ii}}$)	100.74(3)	Cu(4$^{\text{i}}$)–I(2)–Cu(3)	103.59(4)				
Cu(3$^{\text{i}}$)–Br(2)–Cu(3$^{\text{ii}}$)	109.36(2)	Cu(4$^{\text{ii}}$)–I(2)–Cu(3)	103.25(4)				
Cu(2$^{\text{ii}}$)–Br(3)–Cu(1)	98.26(4)						
Cu(2$^{\text{ii}}$)–Br(3)–Cu(2$^{\text{i}}$)	101.68(2)						
Cu(1)–Br(3)–Cu(2$^{\text{i}}$)	107.41(3)						
Angles at Cu/°							
N(1)–Cu(1)–Br(2)	108.05(11)	N(2$^{\text{iii}}$)–Cu(3)–I(1)	114.2(2)	N(2)–Cu(3)–Br(1$^{\text{v}}$)	117.5(4)	N(1)–Cu(1)–I(1$^{\text{iii}}$)	109.9(2)
N(1)–Cu(1)–Br(1)	102.04(12)	N(2$^{\text{iii}}$)–Cu(3)–I(2)	103.09(11)	N(2)–Cu(3)–Br(1)	103.5(2)	N(1)–Cu(1)–I(1)	106.2(2)
Br(2)–Cu(1)–Br(1)	117.76(3)	I(1)–Cu(3)–I(2)	110.73(3)	Br(1$^{\text{v}}$)–Cu(3)–Br(1)	109.43(7)	I(1$^{\text{iii}}$)–Cu(1)–I(1)	112.07(4)
N(1)–Cu(1)–Br(3)	99.22(11)	N(2$^{\text{iii}}$)–Cu(3)–I(2$^{\text{iv}}$)	103.09(11)	Br(1)–Cu(3)–Br(1$^{\text{vi}}$)	113.54(12)	N(1)–Cu(1)–I(1$^{\text{iv}}$)	102.2(2)
Br(2)–Cu(1)–Br(3)	119.42(3)	I(1)–Cu(3)–I(2$^{\text{iv}}$)	110.73(3)	N(1$^{\text{ii}}$)–Cu(4)–N(1)	110.3(5)	I(1$^{\text{iii}}$)–Cu(1)–I(1$^{\text{iv}}$)	117.10(4)
Br(1)–Cu(1)–Br(3)	107.30(3)	I(2)–Cu(3)–I(2$^{\text{iv}}$)	114.64(6)	N(1$^{\text{iii}}$)–Cu(4)–Br(2$^{\text{vii}}$)	110.1(2)	I(1)–Cu(1)–I(1$^{\text{iv}}$)	108.39(3)
N(3$^{\text{iii}}$)–Cu(2)–Br(3$^{\text{v}}$)	106.26(11)	N(1)–Cu(4)–I(1)	106.5(2)	N(1$^{\text{iii}}$)–Cu(4)–Br(2)	100.4(3)		
N(3$^{\text{iii}}$)–Cu(2)–Br(1)	103.71(12)	N(1)–Cu(4)–I(2$^{\text{vi}}$)	104.5(2)	Br(2$^{\text{vii}}$)–Cu(4)–Br(2)	124.59(10)		
Br(3$^{\text{v}}$)–Cu(2)–Br(1)	119.27(3)	I(1)–Cu(4)–I(2$^{\text{vi}}$)	114.59(3)				
N(3$^{\text{iii}}$)–Cu(2)–Br(3$^{\text{vi}}$)	101.92(12)	N(1)–Cu(4)–I(2$^{\text{vii}}$)	101.3(2)				
Br(3$^{\text{v}}$)–Cu(2)–Br(3$^{\text{vi}}$)	115.96(3)	I(1)–Cu(4)–I(2$^{\text{vii}}$)	118.84(4)				
Br(1)–Cu(2)–Br(3$^{\text{vi}}$)	107.53(3)	I(2$^{\text{vi}}$)–Cu(4)–I(2$^{\text{vii}}$)	109.12(3)				
N(5$^{\text{iv}}$)–Cu(3)–Br(2$^{\text{vi}}$)	116.65(12)						
N(5$^{\text{iv}}$)–Cu(3)–Br(1)	102.10(11)						
Br(2$^{\text{vi}}$)–Cu(3)–Br(1)	111.24(3)						
N(5$^{\text{iv}}$)–Cu(3)–Br(2$^{\text{v}}$)	102.68(11)						
Br(2$^{\text{vi}}$)–Cu(3)–Br(2$^{\text{v}}$)	109.04(3)						
Br(1)–Cu(3)–Br(2$^{\text{v}}$)	114.96(3)						

Symmetry operators: [a] i $x, y + 1, z$; ii $-x + 0.5, y + 0.5, z$; iii $-x, y - 0.5, -z + 0.5$; iv $-x, -y + 1, -z + 1$; v $-x + 0.5, y - 0.5, z$; vi $x, y - 1, z$. [b] i $x - 1, y, z$; ii $x - 0.5, y, -z + 0.5$; iii $-x, -y, -z + 1$; iv $x, -y + 0.5, z$; v $x, -y - 0.5, z$; vi $x + 1, y, z$; vii $x + 0.5, y, -z + 0.5$. [c] i $x - y, x - 1, z - 0.5$; ii $-x + 2, -y + 1, z - 0.5$; iii $x, x - y, z$; iv $-x + y + 2, y, z$; v $y + 1, -x + y + 1, z + 0.5$; vi $-x + y + 2, -x + 1, z$; vii $-x + 2, -y + 1, z + 0.5$. [d] i $-x + 0.5, -y - 0.5, z + 0.5$; ii $x, -y, z + 0.5$; iii $-x + 0.5, -y - 0.5, z - 0.5$; iv $x, -y, z - 0.5$.

Table 2 Crystallographic parameters for $[Cu_3Br_3(tri)]_\infty$ **1**, $[Cu_3I_3(tri)]_\infty$ **2**, $[Cu_2Br_2(tri)]_\infty$ **3** and $[Cu_2I_2(tri)]_\infty$ **4**

	1	**2**	**3**	**4**
Chemical formula	$C_3H_3Br_3Cu_3N_3$	$C_3H_3Cu_3I_3N_3$	$C_6H_6Br_4Cu_4N_6$	$C_3H_3Cu_2I_2N_3$
Formula weight	511.43	652.40	735.97	461.96
Crystal system	Orthorhombic	Orthorhombic	Hexagonal	Orthorhombic
Space group	*Pbca*	*Pnma*	$P6_3mc$	$Cmc2_1$
T/K	220(2)	150(2)	150(2)	150(2)
a/Å	16.096(3)	6.913(4)	14.247(6)	15.380(3)
b/Å	6.5180(13)	9.777(5)	—	7.725(2)
c/Å	18.010(4)	15.570(9)	6.415(3)	6.9130(14)
V/Å^3	1889.5(7)	1064.5(10)	1127.6(9)	821.3(3)
Z	8	4	3	4
μ(Mo-Kα)/mm^{-1}	19.322	14.589	16.205	12.621
Reflections collected	6952	3125	1277	2653
Unique reflections, R_{int}	2074, 0.0959	1108, 0.0366	410, 0.0961	751, 0.1324
Observed reflections [$I > \sigma(I)$]	1776	961	377	747
$R1$ [$I > 2\sigma(I)$]	0.0391	0.0293	0.0328	0.0257
$wR2$ [all data]	0.0968	0.0755	0.0819	0.0642

$C_3H_3Cu_2I_2N_3$): C, 7.70 (7.80); H, 0.50 (0.65); N, 8.75 (9.10)%]. IR $\tilde{\nu}$/cm^{-1} (triazine unless stated otherwise): 1573s, 1545s, 1408s, 1169w, 1124w, 711s and 682m. Yellow block-shaped crystals suitable for X-ray diffraction studies were grown by layering a CuI solution in MeCN on top of a solution of triazine in CH_2Cl_2 (molar ratio 2:1).

Crystallography

Crystal data and summaries of the crystallographic analyses for complexes **1**–**4** are given in Table 2. Diffraction data were collected on either a Stoë Stadi-4 diffractometer equipped with an Oxford Cryosystems open flow cryostat[26] using ω–θ scans and graphite monochomated Mo-Kα radiation (for **2**, **3** and **4**) or a Stoë IPDS image plate diffractometer equipped with an Oxford Cryosystems open flow cryostat (for **1**).[26] Data were corrected for Lorentz and polarisation effects. Absorption corrections were applied either numerically (**2** , **3** and **4**) or using XABS2 (**1**).[27] The structures were solved by direct methods using SHELXS 97[28] and full-matrix least squares refinement undertaken using SHELXL 97.[29] All hydrogen atoms were placed in geometrically calculated positions and thereafter refined using a riding model with $U_{iso}(H) = 1.2\ U_{eq}(C)$. All non-hydrogen atoms were refined with anisotropic displacement parameters except for the carbon and nitrogen atoms in **3** which displayed poor displacement parameters and were refined isotropically. For all four structures the largest residual electron density features lie near the copper and halogen centres. The assignment of the absolute structures for **3** and **4** was confirmed by the refinement of Flack enantiopole parameters to values of $-0.02(5)$ and 0.03(5), respectively.

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See http://www.rsc.org/suppdata/dt/1999/2103/ for crystallographic files in .cif format.

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References

1 S. R. Batten and R. Robson, *Angew. Chem.*, *Int. Ed.*, 1998, **37**, 1460; O. M. Yaghi and G. Li, *Angew. Chem.*, *Int. Ed. Engl.*, 1995, **34**, 207; M. Munakata, L. P. Wu and T. Kuroda-Sowa, *Adv. Inorg. Chem.*, 1998, **46**, 17; A. J. Blake, N. R. Champness, P. Hubberstey, W.-S. Li, M. A. Withersby and M. Schröder, *Coord. Chem. Rev.*, 1999, **183**, 117; N. R. Champness and M. Schröder, *Curr. Opin. Solid State Mater. Chem.*, 1998, **3**, 419.

2 P. C. Healy, C. Pakawatchai, C. L. Raston, B. W. Skelton and A. H. White, *J. Chem. Soc.*, *Dalton Trans.*, 1983, 1905.

3 J. A. Campbell, C. L. Raston and A. H. White, *Aust. J. Chem.*, 1977, **30**, 1937.

4 P. C. Healy, J. D. Kildea, B. W. Skelton and A. H. White, *Aust. J. Chem.*, 1989, **42**, 115.

5 N. P. Roth, J. L. Maxwell and E. M. Holt, *J. Chem. Soc.*, *Dalton Trans.*, 1986, 2449.

6 K. Nilsson and A. Oskarsson, *Acta Chem. Scand.*, *Sect. A*, 1985, **39**, 663; J. P. Jasinski, N. P. Roth and E. M. Holt, *Inorg. Chim. Acta*, 1985, **97**, 91; M. Massaux, J.-M. Bernaud and M.-T. Le Bihan, *Bull. Soc. Chim. Fr.*, *Mineral Crystallogr.*, 1969, **92**, 118; M. Massaux and J.-M. Bernaud, *Acta Crystallogr.*, *Sect. B*, 1971, **27**, 2419; P. Jones, *Acta Crystallogr.*, *Sect. C*, 1992, **48**, 1307; M. Massaux and M.-T. Le Bihan, *Acta Crystallogr.*, *Sect. B*, 1976, **32**, 1586; 2032; I. D. Brown and J. D. Dunitz, *Acta Crystallogr.*, 1960, **13**, 28; E. Eitel, D. Oelkrug, W. Hiller and J. Strähle, *Z. Naturforsch.*, *Teil B*, 1980, **35**, 1247; M. Bolte and M. Massaux, *Inorg. Chim. Acta*, 1981, **52**, 191; P. C. Healy, J. D. Kildea, B. W. Skelton and A. H. White, *Aust. J. Chem.*, 1989, **42**, 79; 93.

7 M. Massaux, G. Ducreux, R. Chevalier and M.-T. Le Bihan, *Acta Crystallogr.*, *Sect. B*, 1978, **34**, 1863.

8 P. C. Healy, J. D. Kildea and A. H. White, *Aust. J. Chem.*, 1989, **42**, 137.

9 P. C. Healy, C. Pakawatchai and A. H. White, *J. Chem. Soc.*, *Dalton Trans.*, 1983, 1935.

10 V. Schramm, *Inorg. Chem.*, 1978, **17**, 714; J. C. Dyason, P. C. Healy, L. M. Engelhardt, C. Pakawatchai, V. A. Patrick, C. L. Raston and A. H. White, *J. Chem. Soc.*, *Dalton Trans.*, 1985, 831; M. R. Churchill, G. Davies, M. A. El-Sayed, J. P. Hutchinson and M. W. Rupich, *Inorg. Chem.*, 1982, **21**, 995; C. L. Raston and A. H. White, *J. Chem. Soc.*, *Dalton Trans.*, 1976, 2153; V. Schramm and K. F. Fischer, *Naturwissenschaften*, 1974, **61**, 500; V. Schramm, *Cryst. Struct. Commun.*, 1982, **11**, 1549; L. M. Engelhardt, P. C. Healy, J. D. Kildea and A. H. White, *Aust. J. Chem.*, 1989, **42**, 107.

11 J. Y. Lu, B. R. Cabrera, R.-J. Wang and J. Li, *Inorg. Chem.*, 1998, **37**, 4480.

12 M. Massaux, M.-T. Le Bihan and R. Chevalier, *Acta Crystallogr.*, *Sect. B*, 1977, **33**, 2084.

13 M. J. Begley, O. Eisenstein, P. Hubberstey, S. Jackson, C. E. Russell and P. H. Walton, *J. Chem. Soc.*, *Dalton Trans.*, 1994, 1935.

14 A. J. Blake, N. R. Brooks, N. R. Champness, P. A. Cooke, M. Crew, A. Deveson, D. Fenske, L. R. Hanton, P. Hubberstey and M. Schröder, *Crystal Engineering*, in the press.

15 J. M. Moreno, J. Suarez-Valera, E. Colacio, J. C. Avila-Rosón, M. A. Hidalgo and D. Martin-Ramos, *Can. J. Chem.*, 1995, **73**, 1591.

16 S. Kawata, S. Kitagawa, H. Kumagai, S. Iwabuchi and M. Katada, *Inorg. Chim. Acta*, 1998, **267**, 143.

17 M. Munakata, T. Kuroda-Sowa, M. Maekawa, A. Honda and S. Kitagawa, *J. Chem. Soc.*, *Dalton Trans.*, 1994, 2771.

18 A. J. Graham, P. C. Healy, J. D. Kildea and A. H. White, *Aust. J. Chem.*, 1989, **42**, 177.

19 O. M. Yaghi and G. Li, *Angew. Chem.*, *Int. Ed. Engl.*, 1995, **34**, 207.

20 D. Venkataraman, S. Lee, J. S. Moore, P. Zhang, K. A. Hirsch, G. B. Gardner, A. C. Covey and C. L. Prentice, *Chem. Mater.*, 1996, **8**, 2030.

21 M. Bertelli, L. Carlucci, G. Ciani, D. M. Proserpio and A. S. Sironi, *J. Mater. Chem.*, 1997, **7**, 1271.

22 D. Adam, B. Hirrschaft and H. Hartl, *Z. Naturforsch.*, *Teil B*, 1991, **46**, 738.

23 M. Munakata, L. P. Wu and T. Kuroda-Sowa, *Bull. Chem. Soc. Jpn.*, 1997, **70**, 1727; M. Munakata, T. Kuroda-Sowa, M. Maekawa, A. Hirota and S. Kitagawa, *Inorg. Chem.*, 1995, **34**, 2705.

24 A. F. Wells, *Structural Inorganic Chemistry*, 5th edn., Clarendon Press, Oxford, 1984.

25 D. D. Perrin and W. L. F. Armarego, *Purification of Laboratory Chemicals*, Pergamon, Oxford, 3rd edn., 1988.

26 J. Cosier and A. M. Glazer, *J. Appl. Crystallogr.*, 1986, **19**, 105.

27 S. Parkin, B. Moezzi and H. Hope, *J. Appl. Crystallogr.*, 1995, **28**, 53.

28 G. M. Sheldrick, SHELXS 97, *Acta Crystallogr.*, *Sect. A*, 1990, **46**, 467.

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

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