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Fused pyridazines: rigid multidentates for designing and fine-tuning the structure of hybrid organic/inorganic frameworks †

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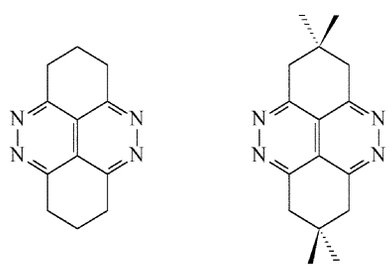
Fused pyridazines (1,2,3,6,7,8-hexahydro-cinnolino[5,4,3-*cde*]cinnoline, L and its 2,2,7,7-tetramethyl derivative, Me_4L) are designed as rigid multidentate ligands for the construction of framework solids. In combination with copper(I) bromide (iodide) they provide excellent structural examples for predictive engineering and the possibilities for further fine-tuning of the framework architectures facilitated by the tetradentate function of the ligands and effective cooperation of organic and inorganic bridges. This study features control over helical structures for $(CuX)_n$ chains and homo/heterochiral combination of the helices in the lattice, the design of a range of channelled and tubular CuX networks and the structural significance of ligand shape complementarity. 3D tetragonal $Cu_2X_2(L)$ frameworks exist either as chiral or achiral supramolecular isomers $Cu_2I_2(Me_4L)$ and $Cu_{12}I_{12}\{Cu(CH_3CN)\}_3(L)_6$-$Cu_3I_6{\cdot}CH_3CN$ illustrate 3D hexagonal channelled and tubular arrays; $Cu_2I_2(Me_4L)(CH_3CN)$ and $Cu_4I_4(L)(CH_3CN)_2$ complexes are 1D polymers.

Introduction

The development of new ligand systems is an important aspect for the chemistry of coordination polymers since the properties of such composites[1] are closely related to their structure and may be predetermined by the geometry of available multiple binding sites of the organic connector.[1–3] An attractive assembly scenario is when neutral organic and anionic inorganic bridging groups cooperate for interconnection of the metal centres and produce hybrid organic/inorganic framework solids[4,5] that often are thermally stable and chemically robust and can satisfy requirements for practical use. Some of these crystal lattices are able to adsorb small molecules from the gaseous phase and behave as zeolites.[3,4]

There are significant difficulties designing open structures of rigid hybrid organic/inorganic polymers. The organic ligands, which are able to maintain a parity of structural functions with small inorganic linkers (OH^-, halogenide and halcogenide ions, *etc*) for interconnection of closely separated metal ions,[6] are hardly suitable for the generation of open structures. Thus, the paradigmatic pyridazine connectors are perfectly complementary with the inorganic bridged –M–X–M– portion; this combination, however, produces the simplest molecular or 1D polymeric motifs[6,7] rather than extended frameworks.

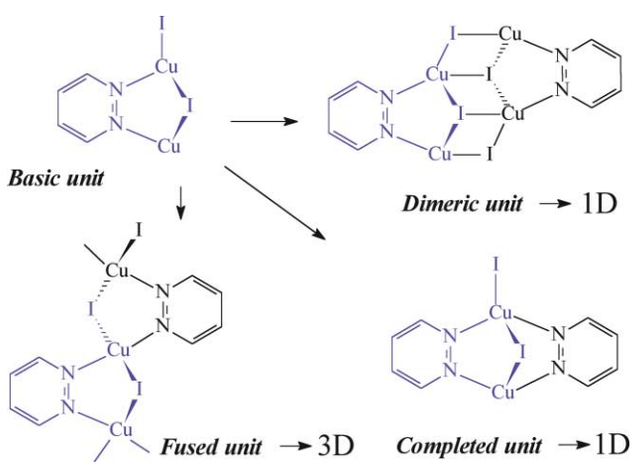
Herein we report a ligand system that combines the ability to bridge closely situated metal ions and the potential for larger organic connectors (Scheme 1). The fusion of two pyridazine fragments within a single molecular frame provides tectons that feature bridging of metal ions at two sets of distances 3.2–3.3 Å and 9–9.5 Å, effective cooperation of organic and inorganic linkers for assembly of a hybrid framework with four-fold immobilization of the organic tecton as well as possibilities for the design and fine-tuning of the structure by considering a combination of simple inorganic motifs and rigid organic tetradentates.



Scheme 1 Fused pyridazine tetradentates used in this study.

Results and discussion

The copper(I) iodide (bromide) coordination patterns have a common motif (Scheme 2): the pyridazine nuclei and halide ion cooperate to connect a copper ion pair at 3.2–3.3 Å and provide hybrid organic/inorganic bridging. These basic units are self-complementary through unsaturated coordination positions of



Scheme 2 Representative copper(I) pyridazine patterns as a result of the cooperation of organic and inorganic bridges.

† Electronic supplementary information (ESI) available: crystal structure determination and refinement details for **1**–**8**. See http://www.rsc.org/suppdata/dt/b3/b316561b/

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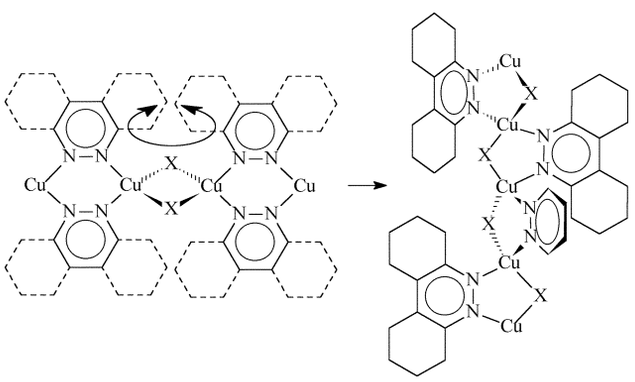
both metal centres and nucleophilic character of halide ions, and thus they are able to dimerize, to coordinate additional ligands and to associate into chains or large cyclic compounds. All these possibilities illustrate "supramolecular synthons" for pyridazine coordination polymers and predetermine an amazing structural diversity of the resulting solids originating in the simplicity of the ligand and its mode of coordination bridging.

One of such clear motifs involves infinite 1D $(CuX)_n$ subunits, where pyridazine –N–N– donors bridge the adjacent copper centres and stabilize the chain with saturated four-fold copper coordination. The atoms of this "1D building block" cannot become either collinear and coplanar as the nearly tetrahedral angles at the copper(I) centres dictate a more complicated geometry of the chain, unlike those observed for three-coordinated $(CuX)_n$ structures.[8] Realistic and attractive shape motifs for such metal-halide chains are helices,[9] and the components can be readily arranged into this chiral array since the pyridazine bridges stabilize a chain of tetrahedra $CuX_2(N_2)_2$ sharing opposite edges $[X(N_2)]$. Also, for control over the helical structure, the steric effect of cylohexane rings fused with the pyridazine frame precludes interligand stacking interactions (as may be seen from comparison of copper(I) iodide complexes with acridine[8a] and octahydroacridine[10]) and does not allow any coplanarity with neighboring pyridazine molecules along the chain (Scheme 3), similar to copper halide complexes with pyridazine.[11]



Scheme 3 Function of fused cyclohexane frames as a design tool for stabilizing the desired helical architecture over formation of typical molecular rhombics Cu_2I_2.

Description of structures

The designed model exists as a helix with a repeating unit involving four pyridazine connectors situated orthogonally (Figs. 1 and 2), and the ligands serve to propagate this 1D architecture with formation of a tetragonal network $Cu_2Br_2(L)\cdot CH_2Cl_2$ **1** (Table 1). The network contains a system of channels, with inner dimensions *ca.* 4 × 5 Å,[12] running in two intersecting directions. Copper and bromide ions form helices with a pitch at 12.77 Å and the structure incorporates helices of opposite handedness (Fig. 1B) in equal proportions thus eliminating bulk chirality of the architecture that is a common feature of helical self-assembly structures.[13]

However, a genuine chiral tetragonal architecture is also feasible and it exists as a pattern incorporating only one sort of $(CuBr)_n$ helices, *i.e.* for self-resolution into enantiomeric chiral crystals.[14] Complex $Cu_2Br_2(L)$ **2** (See Experimental) has a similar CuBr–ligand interaction motif and is related to structure **1** by alignment of $(CuBr)_n$ helices bridged by pyridazine connectors. Structure **2** is a channelled chiral network supported by homochiral alignment of the subunits. These observations could be generalized also for the copper(I) iodide system where simple $(CuI)_n$ helical arrangements are uncommon. Complexes $Cu_2I_2(L)$ **3** and $Cu_2I_2(L)\cdot CHCl_3$ **4** exactly retain the structure of bromide analogs **1** and **2**.

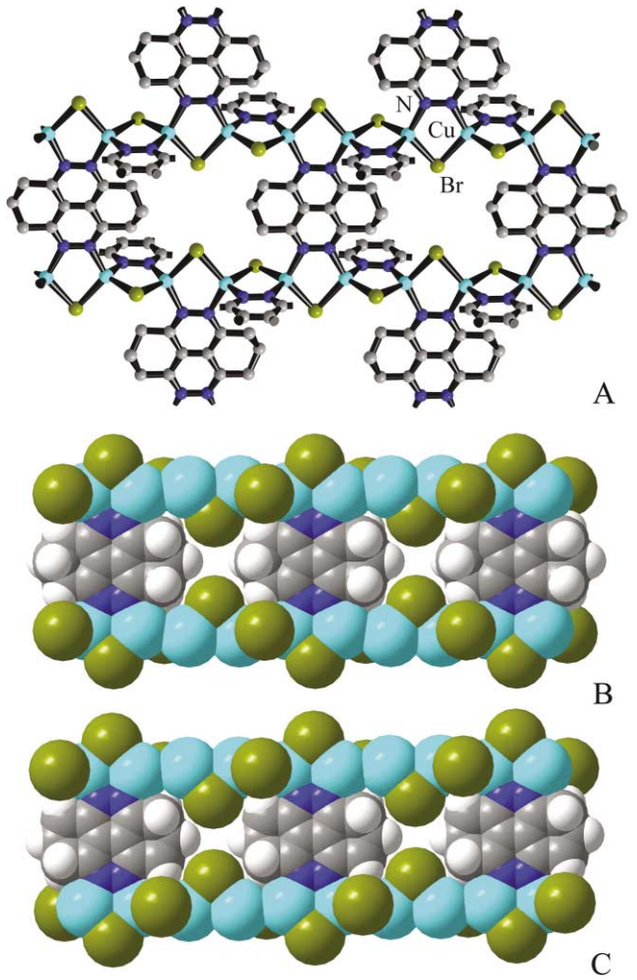


Fig. 1 Tetragonal motif designed for structures $Cu_2Br_2(L)$ that are based on interconnecting $(CuBr)_n$ helices by the organic tetradentate (A), and either "racemic" $(Cu_2Br_2(L)\cdot CH_2Cl_2$ **1,** B) and homochiral ($Cu_2Br_2(L)$ **2**, C) alignment of the helices is feasible. Note that the ligand is perfectly shape complementary with both combinations of the helices.

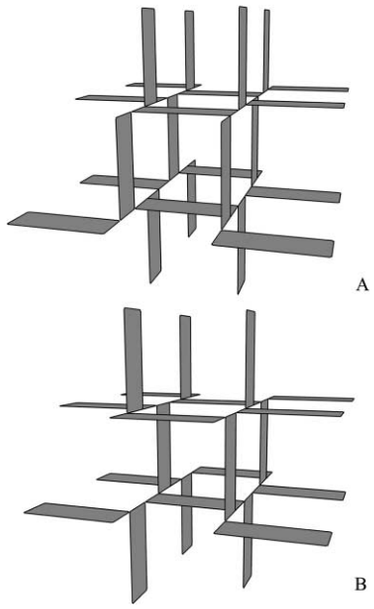


Fig. 2 Topological diagram for achiral (A) and chiral (B) supramolecular isomers of tetragonal networks $Cu_2X_2(L)$ (**1**–**4**), represented as Cu_4 rectangles that are adopted around each ligand and share the same vertices.

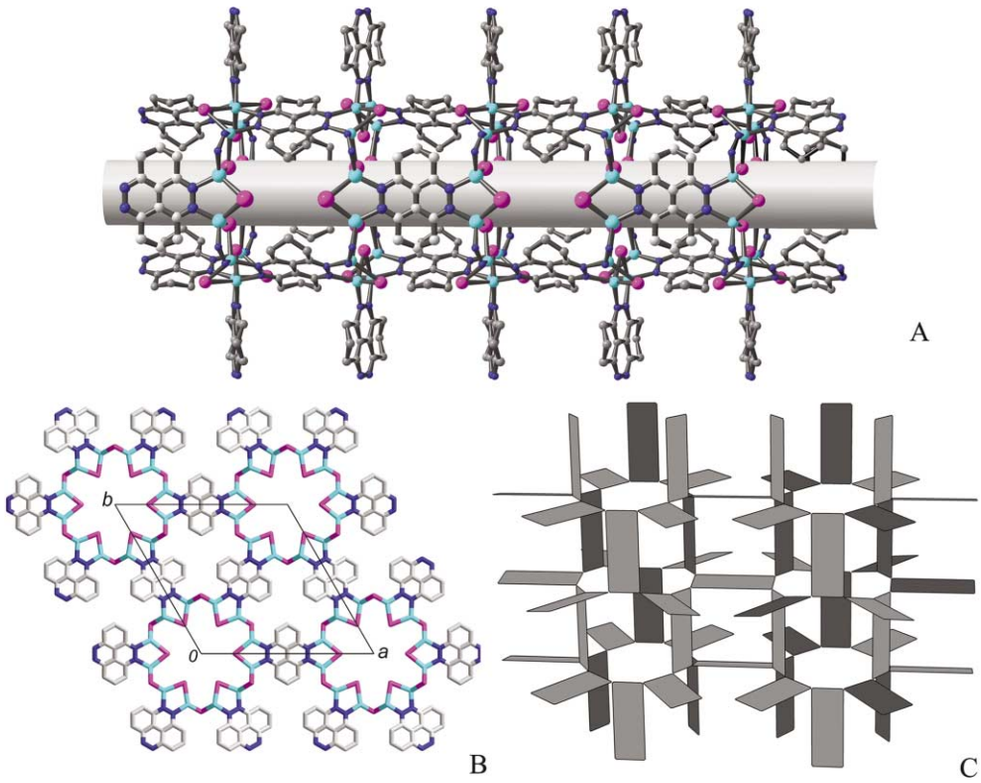


Fig. 3 $Cu_{12}I_{12}\{Cu(CH_3CN)\}_3(L)_6Cu_3I_6\cdot CH_3CN$ structure **5**: Assembly of large tubes by interconnection of $Cu_{12}I_{12}$ cycles (A); fragment of the network showing how four adjacent tubes are interlinked by an additional set of the ligands (B) and the entire topology diagram (C). Note a significance of shape complementary relationships in the structure. Selected bond distances (Å) and angles (°): Cu–N 2.056(4), 2.066(4); Cu–I 2.6231(8), 2.6521(8); N–Cu–N 113.8(2), I–Cu–I 110.04(3).

Table 1 Selected bond distances (Å) and angles (°) for complexes **1**–**4**

$Cu_2Br_2(L)\cdot CH_2Cl_2$ **1** (a: 0.5 − *y*, *x*, −0.25 + *z*)			
Cu(1)–N(1)	2.066(8)	N(1)–Cu(1)–N(2a)	107.0(3)
Cu(1)–N(2a)	2.042(8)	N(1)–Cu(1)–Br(1)	112.9(2)
Cu(1)–Br(1)	2.468(2)	Br(1)–Cu(1)–Br(1a)	106.21(3)
Cu(1)–Br(1a)	2.457(2)		
$Cu_2Br_2(L)$ **2** (a: 1.5 − *x*, *y*, −0.25 − *z*; b: 1.5 − *y*, *x*, −0.25 + *z*)			
Cu(1)–N(1)	2 × 2.051(3)	N(1)–Cu(1)–Br(1)	106.9(1)
Cu(1)–Br(1)	2 × 2.4813(6)	N(1)–Cu(1)–N(1a)	106.4(2)
		Br(1)–Cu(1)–Br(1b)	109.61(3)
$Cu_2I_2(L)$ **3** (a: 1.5 − *x*, *y*, −0.25 − *z*; b: 1.5 − *y*, *x*, −0.25 + *z*)			
Cu(1)–N(1)	2 × 2.078(3)	N(1)–Cu(1)–I(1)	107.4(1)
I(1)–Cu(1)	2 × 2.6463(5)	N(1)–Cu(1)–N(1a)	106.7(2)
		I(1)–Cu(1)–I(1b)	108.17(3)
$Cu_2I_2(L)\cdot CHCl_3$ **4** (a: 0.75 − *y*, 0.75 − *x*, 0.25 − *z*; b: −0.25 + *y*, 0.75 − *x*, 0.25 + *z*)			
Cu(1)–N(1)	2 × 2.083(5)	N(1)–Cu(1)–I(1)	113.7(1)
I(1)–Cu(1)	2 × 2.6153(8)	N(1)–Cu(1)–N(1a)	104.4(3)
		I(1)–Cu(1)–I(1b)	107.29(4)

In **1**, dichloromethane solvate molecules are situated inside the channels and, according to TGA data, the compound loses the incorporated solvent (13.5 mass% *vs.* calculated value of 14.5%) at 165° C. Decomposition of the remaining compound proceeds above 350° C. Desolvated material as well as solvent-free complex **2** are unable to uptake small molecules into the lattice pores as was found from experiments for gaseous nitrogen adsorption at 293 K, following out-gassing at 383 K for 12–15 h (10^{-4} Torr).

The structure $Cu_{12}I_{12}\{Cu(CH_3CN)\}_3(L)_6Cu_3I_6\cdot CH_3CN$ **5** is spectacular and has many new features (Fig. 3). It may be best described as built up from $Cu_{12}I_{12}$ rings, a finite copper–iodide pattern, one of the largest as yet entirely inorganic macrocycles. Molecular structures containing $[Cu^{I}_6Cl_6]$[15] and $[Cu^{II}_{10}Cl_{10}]$[16] cycles are also known. The $Cu_{12}I_{12}$ units are stacked exactly one on the top of another and are interlinked by the ligands into large tubes (Fig. 3A) and an additional set of bridging ligands serve for integration of the tubes into a 3D hexagonal network. All the copper ions of this network display tetrahedral four-fold coordination. The inner diameter of the tubes is *ca.* 4.1 Å and it allows the accommodation of linear acetonitrile molecules. According to TGA data, their total elimination occurs at 150 °C. Each large $Cu_{12}I_{12}$ cycle has the conformation of a crown and enclatrathes three disordered copper cations that form bonds with three iodide ions and the nitrogen atom of the acetonitrile molecule. To allow for charge compensation the network also incorporates unique $Cu_3I_6^{3-}$ anions inside the holes. The anion has a shape of a mesytilene hydrocarbon with three copper and three iodide ions arranged into a planar hexagon (Cu–I 2.51 Å). This is the second homologue for the hypothetical class of planar cyclic ions $Cu_nI_{2n}^{n-}$, with the simplest member being $Cu_2I_4^{2-}$.[17] The topology of network **5** is important considering the design principles for tubular structures that may be anticipated for large bridged cyclic compounds, for example copper(I) thiolates.[18]

Any of the unusual and attractive architectures **1**–**5** have a symmetry imprint and organic connector shape complementarity that can afford a very symmetric tight packing without shortened van der Waals contacts. Substitution in the methylene linkage of the ligand allows further tuning of the architecture. Tetramethyl substituted fused pyridazine Me_4L cannot provide either tetragonal motifs as seen in compounds **1**–**4** or an hexagonal array **5** due to a possible interference of methyl groups with adjacent halogenide ions. The increased steric volume of the ligand forces a higher degree of mutual rotation of the ligands associated with the $(CuI)_n$ "1D building block" and this results in formation of three- (instead of four-) fold helices and generation of the hexagonal network $Cu_2I_2(Me_4L)\cdot CH_2Cl_2$ **6** (Fig. 4). This structure integrates $(CuI)_n$ helices of opposite chirality and is centrosymmetric. We were not successful in the preparation of homochiral networks of this type.

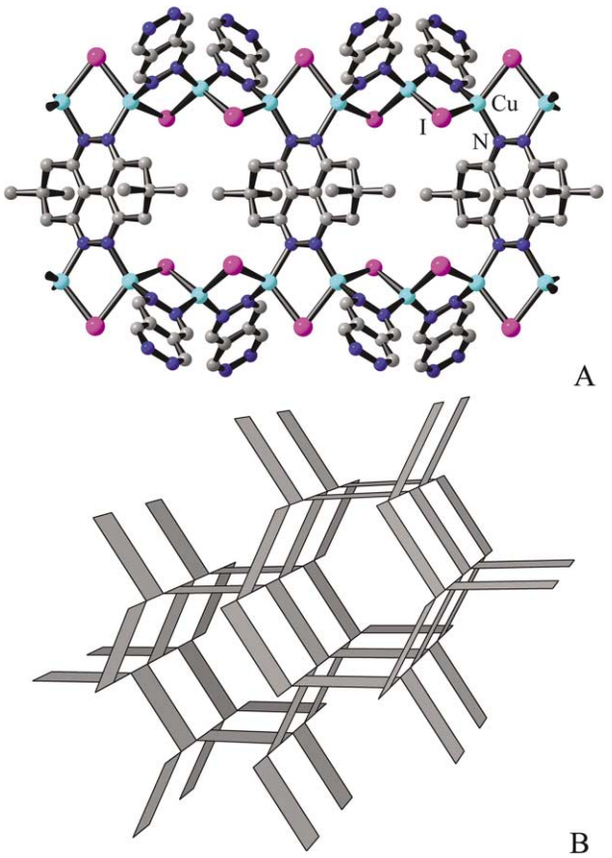


Fig. 4 Three-fold $(CuI)_n$ helices interconnected by Me_4L bridges in the $Cu_2I_2(Me_4L)\cdot CH_2Cl_2$ structure **5** (A) and the entire topology of the network (B). This is an evolution of the pattern seen for **1**–**4** affected by steric repulsion of methyl substitutes and a loss of shape complementarity between the four-fold helix and organic connector. Selected bond distances (Å) and angles (°): Cu–N 2.048(6) Cu–I 2.6461(9) × 2; N–Cu–N 126.9(3), I–Cu–I 118.39(5), N–Cu–I 94.9(2) and 111.91(14).

The simpler coordination polymer $Cu_2I_2(Me_4L)(CH_3CN)$ **7** (Fig. 5, Table 2) has a one-dimensional structure. The Cu_2I_2 unit involves four-coordinated copper ions, it does not form a typical "rhombic" structure[19] and remains open. The related 1D polymer $Cu_4I_4(L)(CH_3CN)_2$ **8** was also isolated for an unsubstituted ligand, as a minor co-product of complex **5**. The pyridazine ligands bridge copper iodide tetramers that are constituted of three fused molecular Cu_2I_2 rhombics and terminal acetonitrile ligands (Fig. 5B). Such a structure of Cu_4I_4 linkage is stabilized by pyridazine bridges that preclude formation of typical "cubes".[20]

Conclusion

Our results introduce a new ligand system for the synthesis of coordination polymers and crystal engineering of network solids. The fused pyridazine frame provides multiple binding sites for coordination with metal centres and for an especially effective integration of the ligand into extended superstructures. These possibilities are important from a materials design perspective since an increased number of binding sites of the connector under cooperation with rigid inorganic bridging facilitates the preparation of very open stable architectures for adsorption and gas storage applications. Further tuning of spatial alignment of fused pyridazine nuclei is possible utilizing design principles of fused hydrocarbon chemistry[21] and will lead to rigid multidentates for hybrid organic/inorganic open networks. Similar to the reported ligand system, many of the condensed pyridazines are readily available and are inexpensive species[22] that can be employed for the preparation of new materials. Our study also provides examples of the role of shape-complementarity of the organic ligands in coordination chemistry, as a suitable tool for the design of new attractive metal–organic topologies.

Table 2 Selected bond distances (Å) and angles (°) for complexes **7** and **8**

$Cu_2I_2(Me_4L)(CH_3CN)$ **7** (a: x, 0.5 − y, z)

Cu(1)–N(1)	2.106(2) × 2	I(2)–Cu(1)–I(1)	104.85(2)
Cu(1)–I(1)	2.7362(6)	N(1)–Cu(1)–N(1a)	94.84(11)
Cu(1)–I(2)	2.5873(6)	N(2)–Cu(2)–N(2a)	101.23(11)
Cu(2)–N(2)	2.087(2) × 2	N(3)–Cu(2)–I(1)	112.58(9)
Cu(2)–N(3)	1.977(3)		
Cu(2)–I(1)	2.5820(5)		

$Cu_4I_4(L)(CH_3CN)_2$ **8** (a: 1 − x, 2 − y, 1 − z)

Cu(1)–I(1)	2.6630(10)	Cu(1)–N(3)	2.023(6)
Cu(2)–I(1)	2.6438(9)	Cu(2)–N(2a)	2.065(5)
Cu(2)–I(2)	2.6670(9)	Cu(2)–I(1)–Cu(1)	64.51(3)
Cu(1)–I(2a)	2.6187(9)	N(3)–Cu(1)–N(1)	112.0(2)
Cu(2)–I(2a)	2.7731(10)	N(3)–Cu(1)–I(1)	103.9(2)
Cu(1)–N(1)	2.069(5)	I(1)–Cu(2)–I(2)	102.15(3)

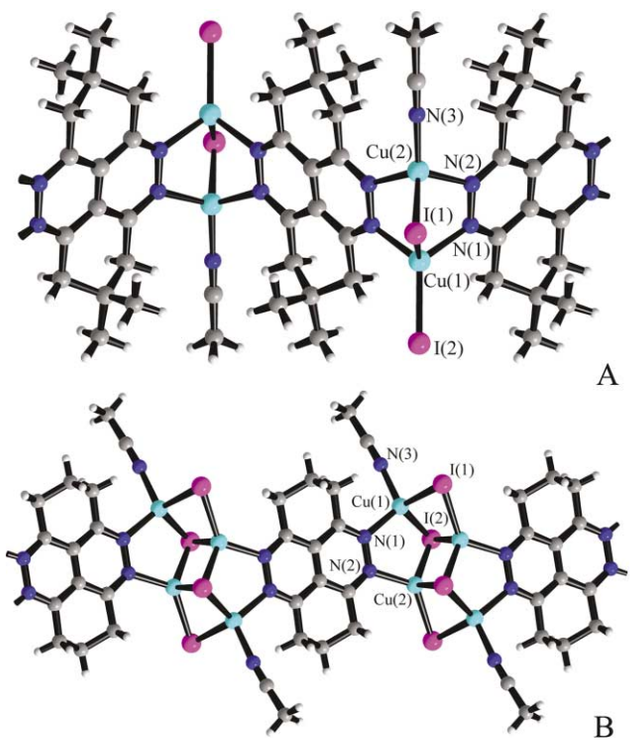


Fig. 5 1D coordination pyridazine polymers involving copper(I) iodide dimers, $Cu_2I_2(Me_4L)(CH_3CN)$ **7** (A) and tetramers $Cu_4I_4(L)(CH_3CN)_2$ **8** (B).

Experimental

1,2,3,6,7,8-Hexahydro-cinnolino[5,4,3-*cde*]cinnoline (L) and its 2,2,7,7-tetramethyl derivative (Me_4L) were prepared in one stage reacting 1,3-cyclohexanedione (5,5-dimethyl-1,3-cyclohexanedione) and hydrazine.[23]

Solvent dependence of structures

Solvent/structure relationships for copper(I) bromide (iodide) compounds illustrate how an achiral media could assist in homochiral alignment of the helices over formation of a '3D racemate'. As was proved by examination of the unit cell parameters, the complex $Cu_2Br_2(L)$ crystallizes in the above form **1** under the many different conditions used, irrespectively of the nature of solvent (alcohols, acetonitrile and their mixtures with chloroform, dichloromethane and 1,1,1-trichloroethane), temperature (5 to 35° C) and of the

valence state of copper in the starting material since both copper(I) and copper(II) bromides provide the same product. However, even minor quantities of chlorobenzene in acetonitrile or methanol solutions dramatically influenced the pathway of self-assembly and led to the chiral supramolecular isomer $Cu_2Br_2(L)$ **2**. Bromobenzene, 1-bromonaphthalene and 1,2-dichlorobenzene had the same obvious effect although the resulting network does not intercalate them. Such a templating effect of "unwelcome guests" was also observed for fluorinated aromatics.[24]

The copper(I) iodide chiral tetragonal network $Cu_2I_2(L)$ **3** also crystallizes in systems containing the above aromatic species as a possible templating component, while the achiral isomer $Cu_2I_2(L)\cdot CHCl_3$ **4** was prepared from a benzonitrile–chloroform mixture. In non-aromatic media the products of interactions of **5** and **8** were not isomorphous with bromide analogs.

For substituted pyridazine Me_4L, crystallization of copper(I) idodide compounds is also solvent-dependent. It was possible to prepare complex **6** in butyronitrile–dichloromethane media, while reaction in acetonitrile solution led to compound **7**.

Synthesis of coordination polymers

For the preparation of a $Cu_2Br_2(L)\cdot CH_2Cl_2$ **1** complex, a solution of 0.028 g (0.2 mmol) CuBr in 3 ml acenonitrile was layered over a solution of the ligand (0.042 g, 0.2 mmol) in 5 ml dichloromethane–acetonitrile 1 : 1 v/v mixture. Slow interdiffusion of the components afforded, in a 15 d period, 0.041 g (70%) of black prisms. The same product was formed, in a lower yield of 45%, when 0.044 g (0.2 mmol) $CuBr_2$ was used as a starting material, in either acetonitrile and methanol mixtures with CH_2Cl_2.

Complex $Cu_2Br_2(L)$ **2** was prepared layering a solution of 0.028 g (0.2 mmol) CuBr in 3 ml acetonitrile over a solution of the ligand (0.042 g, 0.2 mmol) in 5 ml methanol and 2 ml chlorobenzene. The yield of brown–black prismatic crystals was 0.039 g (78%). Complex $Cu_2I_2(L)$ **3** was prepared in a similar fashion in a 75% yield. Dark-brown prisms of its supramolecular isomer $Cu_2I_2(L)\cdot CHCl_3$ **4** were isolated in 80% yield from a 1 : 1 v/v mixture of benzonitrile and chloroform. Interdiffusion of 0.038 g (0.2 mmol) copper(I) iodide solutions in 10 ml acetonitrile and 0.042 g (0.2 mmol) L in 5 ml 1 : 1 acetonitrile–dichloromethane mixture in a 1 month period provides 0.036 g (65%) of pure $Cu_{12}I_{12}\{Cu(CH_3CN)\}_3(L)_6\cdot Cu_3I_6\cdot CH_3CN$ **5** as large black hexagonal prisms. This compound was also formed in acetonitrile–chloroform solutions, in a mixture with red–brown needles of $Cu_4I_4(L)(CH_3CN)_2$ **8**. The latter grew in a period of 3–4 d and then dissolved.

In a similar fashion, 0.019 g (0.1 mmol) CuI and 0.027 g (0.01 mmol) Me_4L in a butyronitrile–dichloromethane mixture provided, in a 20 d period, black crystals $Cu_2I_2(Me_4L)\cdot CH_2Cl_2$ **5** (0.020 g, 55%), while the reaction of the components in acetonitrile–dichloromethane (or chloroform) solution gave 0.018 g (52%) pure $Cu_2I_2(Me_4L)(CH_3CN)$ **7,** red–brown blocks.

Crystallography

Crystallographic measurements were made using a Siemens SMART CCD area-detector diffractometer (empirical absorption corrections using SADABS) and Stoe IPDS diffractometer for **7** and **8** (graphite monochromated Mo-Kα radiation, λ = 0.71073 Å). The structures were solved by direct methods and refined in the anisotropic approximation using SHELXS-86 and SHELXL-97[25] (Table 3). All hydrogen atoms were placed in calculated positions with their isotropic U values set invariant at 0.08 Å^2. In structures **2** and **3** the side methylene group of the ligands is disordered over two positions relative to the planar aromatic frame, and very similarly, structure **6** shows disorder of the $C(CH_3)_2$ fragment. Therefore the hydrogen atoms were not included. In complex **2** three fragments of

Table 3 Crystal data for $Cu_2Br_2(L)\cdot CH_2Cl_2$ **1**, $Cu_2Br_2(L)$ **2**, $Cu_2I_2(L)$ **3**, $Cu_2I_2(L)\cdot CHCl_3$ **4** $Cu_{12}I_{12}\{Cu(CH_3CN)\}_3(L)_6Cu_3I_6\cdot CH_3CN$ **5**, $Cu_2I_2(Me_4L)\cdot CH_2Cl_2$ **6**, $Cu_2I_2(Me_4L)(CH_3CN)$ **7** and $Cu_4I_4(L)(CH_3CN)_2$ **8**

	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**
Formula	$C_{13}H_{14}Br_2Cl_2Cu_2N_4$	$C_{12}H_{12}Br_2Cu_2N_4$	$C_{12}H_{12}Cu_2I_2N_4$	$C_{13}H_{13}Cl_3Cu_2I_2N_4$	$C_{80}H_{84}Cu_{18}I_{18}N_{28}$	$C_{17}H_{22}Cl_2Cu_2I_2N_4$	$C_{18}H_{23}Cu_2I_2N_5$	$C_{16}H_{18}Cu_4I_4N_6$
M	584.08	499.16	593.14	712.50	4865.67	734.17	690.29	1056.12
Crystal system	Tetragonal	Tetragonal	Tetragonal	Tetragonal	Hexagonal	Trigonal	Orthorhombic	Triclinic
Space group, Z	$I4_1md$, 8	$I4_122$, 4	$I4_122$, 4	$I4_1/amd$, 8	$P6_3/mmc$, 2	$R\bar{3}m$, 9	$Pmna$, 4	$P\bar{1}$, 1
a/Å	17.730(2)	12.318(1)	12.347(1)	17.614(2)	20.463(2)	26.190(1)	24.063(3)	7.6797(9)
b/Å							13.557(2)	7.7125(9)
c/Å	12.601(1)	12.772(2)	13.212(1)	13.136(2)	17.989(2)	9.610(1)	6.8122(8)	11.315(1)
α, β, γ/°								104.415(2), 104.170(2), 96.141(2)
U/Å^3	3961.3(7)	1937.8(4)	2014.3(3)	4076(1)	6524(1)	5708.3(7)	2222.4(5)	619.2(1)
μ(Mo-Kα)/cm^{-1}	64.53	63.13	51.72	55.14	71.71	43.30	47.05	83.90
D_c/g cm^{-3}	1.959	1.711	1.956	2.322	2.477	1.922	2.063	2.832
$2\theta_{max}$/°	57.4	58.2	58.3	55.9	55.0	54.2	55.7	57.2
Meas./unique reflns	13973/2554	5730/1217	5437/1251	11844/1295	38755/2792	5412/1422	12648/2834	3844/2851
R_{int}	0.078	0.017	0.032	0.038	0.038	0.056	0.030	0.031
Data/parameters	2554/108	1217/52	1251/52	1295/61	2792/133	1422/95	2834/134	2851/137
$R1$, $wR2$ ($I > 2\sigma(I)$)	0.056, 0.144	0.030, 0.079	0.027, 0.070	0.053, 0.103	0.043, 0.102	0.062, 0.149	0.025, 0.058	0.048, 0.133
$R1$, $wR2$ (all data)	0.090, 0.156	0.030, 0.080	0.027, 0.070	0.062, 0.106	0.047, 0.103	0.065, 0.151	0.026, 0.060	0.051, 0.136
Max., min. peak/e Å^{-3}	1.52, −0.50	1.00, −0.43	1.06, −0.63	1.23, −0.86	2.26, −1.03	1.75, −1.49	0.76, −0.58	1.51, −1.94

$Cu(NCCH_3)$ are located inside the $Cu_{12}I_{12}$ "crown" and are disordered over the six-fold axis. It was not possible to completely resolve the disorder of the guest CH_2Cl_2 and CH_3CN molecules in structures **1** and **5**. Details of the crystal structure refinement and presentation of refined disordering schemes is given as ESI.† A graphical visualisation of the structures was made using the program Diamond.[26]

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See http://www.rsc.org/suppdata/dt/b3/b316561b/ for crystallographic data in CIF or other electronic format.

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