Chiral Copper(I) Iodide Based Porous Coordination Frameworks with Asymmetrically Substituted Bridging N-Donor Ligands

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The 2-dimensional coordination polymers $\mathcal{Z}[\{(CuI)_2(Mepyz)_2\} \cdot Mepyz]$ (1a), $\mathcal{Z}_{\mathbb{Z}}[CuX(Mepyz)]$ (2a, X = Br; 2b, X = Cl) and $\mathcal{Z}_{\mathbb{Z}}[(CuX)_2(Mepyz)]$ (3a, X = I;3b, X = Br) may be prepared by reaction of the appropriate copper(I) halide with 2-methylpyrazine (Mepyz) either in acetonitrile solution at 130 °C (2a/2b, 3a/3b) or without solvent at 20 °C (1a). Mepyz ligands bridge (CuI)₂ rhomboid dimers in the chiral network of 1a, whose resulting 24-membered rings are large enough to accomodate an Mepyz guest molecule. 1a rapidly loses these guests to afford a crystalline powder (1b), that can reversibly imbibe benzonitrile molecules into its open channels. In contrast to 1a, the sheets of 2a/2b contain zigzag infinite CuX chains, those of 3a/3b staircase $\frac{1}{2}$ [CuX] double chains as their characteristic substructures. Helical $\frac{1}{2}$ [CuI] single chains in the 3-dimensional network of $\frac{3}{2}$ [CuI(Mepip)]4 are bridged by R-2-methyl-piperazine (Mepip) ligands in a second example of a chiral coordination polymer.

Introduction

Two ever recurring goals in the rapidly expanding field of inorganic crystal engineering are the development of functional materials with zeolitelike molecular-sized cavities or channels [1 - 4] and the construction of chiral coordination networks of potential utility for nonlinear optics [5]. However, attempts to design two- or three-dimensional frameworks with larger well-defined pores have often been foiled by the self-interpenetration of multiple networks, which eliminates the void space [6]. This phenomenon is particularly typical for diamondoid polymers [3], for which as many as eight or nine interweaving frameworks can be obtained [7 - 9]. As a result, surprisingly few coordination frameworks have been reported that can clathrate organic guest molecules with a degree of shape specificity [10 - 16]. Several of these examples contain bidentate rodlike 4,4'-bipyridine as an organic spacer molecule, and tridentate ligands have also been successfully employed to construct such porous materials [11, 15].

We ourselves have recently described the assembly of two CuCN based three-dimensional frameworks $^{3}_{\infty}$ [CuCN(μ -2Mepyz)] and $^{3}_{\infty}$ [CuCN(μ -4Mepym)] (2Mepyz = 2-methylpyrazine, 4Mepym = 4-methylpyrimidine) [17], the former of which is both chiral and porous. The asymmetric bridging heterocyclic diazines, whose 2-methyl substituents protrude into the large nanometer-sized channels of $\frac{3}{\infty}$ [CuCN(μ -2Mepyz)] (dimensions 1.10×1.14 nm), are clearly instrumental in inducing the adoption of a chiral framework during the selfassembly process. As such porous networks could be of potential interest for both asymmetric catalysis and nonlinear optics we considered it to be of interest to establish whether similar copper(I) halide based polymers can be obtained. Many types of oligometric and polymetric CuX (X = Cl, Br, I)substructures have been found in their coordination frameworks with bridging spacer molecules, for instance (CuX)₂ rings, cubane-like and tricyclic Cu_4X_4 tetramers, zigzag $\frac{1}{\infty}[CuX]$ single chains and staircase or spirocyclic $\frac{1}{\infty}$ [CuX] double chains [18 - 22]. Both 2-methylpyrazine and the chiral derivative R-2-methylpiperazine (Mepip) were employed as asymmetrically substituted N-donor ligands in the present work.

Results and Discussion

Treatment of CuI with an equimolar quantity of the liquid 2-methylpyrazine at room temperature leads to slow growth of orange crystals of the chiral lamellar coordination poly-

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Fig. 1. Asymmetric unit of the ${}^2_{\mathbb{A}}[(CuI)_2(Mepy_2)_2]$ sheets of **1a**. Selected bond lengths (Å) and angles (°): Cu(1)-I(1) 2.659(3), Cu(1)-I(2) 2.737(3), Cu(2)-I(1) 2.619(3), Cu(2)-I(2) 2.575(3), Cu(1)-I(1)-Cu(2) 63.27(9), Cu(2)-I(2)-Cu(1) 62.74(9), I(1)-Cu(1)-I(2) 111.86(9), I(1)-Cu(2)-I(2) 118.79 (9).

mer ${}_{\infty}^{2}[\{(CuI)_{2}(Mepyz)_{2}\} \cdot Mepyz]$ **1a** (space group $P2_{1}2_{1}2_{1}$), which contains (CuI)₂ rings as its characteristic building blocks. In contrast, ${}_{\infty}^{2}[CuX(Mepyz)]$ (X = Br, Cl; **2a**, **2b**) and ${}_{\infty}^{2}[(CuX)_{2}$ (Mepyz)] (X = I, Br; **3a**, **3b**), which were prepared by reacting the appropriate copper (I) halide with 2-methylpyrazine at the required molar ratio in acetonitrile solution (T = 130 °C), all crystallise in the centrosymmetric monoclinic space group $P2_{1}/c$ and exhibit respectively single and double chains as component CuX substructures.

2-Methylpyrazine ligands bridge the (CuI)₂ rhomboid dimers through N(11)-Cu(1) and N(41)-Cu(2) bonds (Fig.1) to afford an open 4⁴ net with large 24-membered rings. Neighbouring sheets at an average distance of 6.96 Å (*b*/2) are related by 2₁ screw diad axes and stack so as to create continuous channels whose dimensions (8.74×8.54 Å cross section) are large enough to accomodate a noncoordinated 2-methylpyrazine guest molecule. As may be seen in Fig. 2a), *Einer* $\frac{1}{\infty}$ [(CuI)₂(Mepyz)] chains in direction [100] are connected by 2-methylpyrazine pillars in direction [001], which themselves belong to *Zweier* chains of the same composition. The presence of differing $\kappa^2 N1$ and



Fig. 2. a) Projection of the structure of $^{2}_{\infty}$ [CuI)₂(Mepyz)₂] **1a** with its Mepyz guests perpendicular to [010], and b) Stacking of the polymeric sheets of **1a** as viewed along [100].

 $\kappa^2 N4$ coordination modes at the independent copper atoms Cu(1) and Cu(2) is also reflected in a marked distortion of the (CuI)₂ lozenges. Longer Cu(1)-I distances of 2.659(3) and 2.737(3) Å accompany the shorter Cu(1)-N(11) and Cu(1)-N(12) bonds [2.05(1) Å]. In contrast Cu(2)-I bond lengths of 2.619(3) and 2.575(3) Å are associated with the longer Cu(2)-N distances to the 2-methylpyrazine N4 atoms [2.09(1), 2.07(2) Å]. A Cu(1)...Cu(2) separation of 2.769(3) Å is observed within the $(CuI)_2$ rings. The stacking of $^{2}_{\infty}[(CuI)_{2}(Mepyz)_{2}]$ layers in 1a is illustrated by Fig. 2b), which also shows how individual (CuI)₂ rings in neighbouring sheets interact through weak secondary I(1)...I(2) interactions. It is also apparent from this projection of the structure that the 2-methylpyrazine guest molecules are significantly displaced from the sheets of the hosting 2-dimensional coordination polymers.

1:1 CuBr and CuCl based coordination polymers of 2-methylpyrazine could only be obtained



Fig. 3. Projection of the structures of $\stackrel{2}{\sim}$ [CuX(Mepyz)] **2a** and **2b** (X=Br, Cl) with numbering for the former perpendicular to [001]. Selected bond lengths (Å) and angles (°): in **2a**, Cu(1)-Br(1) 2.591(1), Cu(1)-Br(1a) 2.507(1), N(1)-Cu(1)-N(4a) 137.3(1) in **2b**, Cu(1)-Cl(1) 2.484(1), Cu(1)-Cl(1a) 2.378(1), N(1)-Cu(1)-N(4a) 136.0(1).



Fig. 4. Projection of the structure of $\stackrel{2}{\sim}[(CuI)_2(Mepyz)]$ **3a** perpendicular to [001]. Selected bond lengths (Å): Cu(1)-I(1) 2.662(1), Cu(1)-I(1b) 2.629(1), Cu(1)-I(1c) 2.722(1), Cu(2)-I(2) 2.668(1), Cu(2)-I(2b) 2.642(1), Cu(2)-I(2c) 2.656(1).

from acetonitrile solution at higher temperature (130 °C). In contrast to **1a**, the isostructural compounds \gtrsim [CuX(Mepyz)] **2a** and **2b** (X = Br, Cl) contain infinite zigzag CuX chains as their characteristic copper(I) halide substructures. As depicted in Fig. 3, such \gtrsim [CuX] ribbons are linked through μ -N1,N4 coordinated 2-methylpyrazine spacers to afford 2-dimensional polymers with 14-membered pores. Neighbouring sheets are related through the *c* glide planes of the monoclinic space group $P2_1/c$ and stack so as to afford narrow channels in direction [001]. Particularly striking are the very wide



Fig. 5. Framework structure of $\frac{3}{20}$ [CuI(Mepip)] 4 projected perpendicular to [100]. Selected bond lengths (Å) and angles (°): Cu(1)-I(1) 2.783(2), Cu(1)-I(1a) 2.905(2), Cu(1)-N(1) 2.056(8), Cu(1)-N(4a) 2.068(9), N(1)-Cu(1)-N(4a) 135.5(3).

N(1)-Cu(1)-N(4a) angles of 137.3(1) and 136.0(1)° within the component $\frac{1}{\infty}[{Cu(Mepyz)}^+]$ ribbons of **2a** and **2b**.

2:1 coordination polymers $\stackrel{2}{\sim}[(CuX)_2(Mepyz)]$ **3a** and **3b** (X = I, Br) could be isolated for CuI and CuBr under similar reaction conditions but not for the analogous copper(I) chloride. These compounds also crystallise in the monoclinic space group $P2_1/c$ but now contain $\stackrel{1}{\longrightarrow}[CuX]$ staircase double chains,



Fig. 6. Powder diagrams (Cu-K_{α}, Bruker AXS D8 Advance): (a) of $\frac{2}{2}$ [{(CuI)₂(Mepyz)₂}·Mepyz], **1a**; (b) of $\frac{2}{2}$ [(CuI)₂(Mepyz)₂], **1b**, as obtained after removal of the guest Mepyz molecules of **1a** under vacuum.

which are depicted in Fig. 4 for **3a**. In contrast to **2a/b**, such CuX substructures in the 2:1 polymers are generated by the screw diads parallel to *y*, which therefore exhibits short repeat distances of respectively 4.228(1) and 3.996(1) Å in **3a/b**. Cu-I and Cu-Br distances within the double chains lie in the narrow ranges 2.629 - 2.722 and 2.489 - 2.540 Å.

The crystallisation of ${}^{2}_{\infty}[\{(CuI)_{2}(Mepyz)_{2}\} \cdot Me$ pyz] 1a in the chiral orthorhombic space group $P2_12_12_1$ is in accordance with our previous observations for $^{3}_{\infty}$ [CuCN(μ -Mepyz)] (space group $P2_12_12_1$) and $\frac{2}{\infty}$ [CuSCN(Mepym- $\kappa N1$)] (space group P1) [17], that asymmetrically substituted heterocyclic diazines can induce chirality into coordination polymers generated under kinetically controlled self-assembly conditions. An alternative approach to this goal is to employ a chiral bridging ligand such as R-2-methylpiperazine (Mepip), which generates a three-dimensional framework $^{3}_{\infty}$ [CuI(Mepip)] 4 with CuI in acetonitrile at room temperature. As may be seen in Fig. 5 helical $\frac{1}{\infty}$ [CuI] chains in direction [100] (space group $P2_12_12_1$) are linked together by bridging R-2-methylpiperazine molecules in 4 to afford narrow channels into which the 2-methyl substituents protrude. Alternating rather long Cu-I distances of 2.783(2) and 2.905(2) A are observed within the infinite CuI ribbons and are associated with wide N(1)-Cu(1)-N(4a) angles of $135.5(3)^{\circ}$, similar to those found in 2a/b.

Loss and Exchange of Guest Species by 1

Few examples of coordination frameworks have been described that are capable of retaining their integrity on loss or exchange of imbibed aromatic molecules [10]. More typical are reports on ion exchange or replacement of smaller solvent molecules (e. g. s H_2O , CH_3CN , DMF) in the channels of such microporous networks [15].

Yellow $\frac{2}{\infty}$ [{(CuI)₂(Mepyz)₂} · Mepyz] (1a) rapidly loses its 2-methylpyrazine guest molecules under vacuum at room temperature to afford an orange microcrystalline powder (1b), whose elemental analysis is in accordance with a formulation as [CuI(Mepyz)]. A powder diffraction pattern of (1b) [Fig. 6(b)] recorded with Cu-K_{α} radiation confirms the retention of crystallinity and contains strong Bragg reflections in the 2θ range 10 - 30° at angles closely similar to those found for **1a** [Fig. 6(a)]. On covering **1b** with benzonitrile a colour change from orange back to the original yellow can be followed over a period of days. An IR spectrum taken for the yellow powder after 7d contains characteristic absorption bands for benzonitrile (e.g. ν (CN), 2226 cm⁻¹), thereby confirming successful imbibement of this aromatic molecule. After removal of benzonitrile under vacuum, the powder diffraction pattern of the resulting yellow powder once again closely resembles that of 1b. A thermal gravimetric analysis on 1a reveals that following rapid loss its 2-methylpyrazine guests, the coordination polymer **1b** is stable up to 210 °C before endothermically losing both its bridging N-donor ligands. Our results, therefore, suggest that after removal of the Mepyz guest molecules, the host lattice of $\frac{2}{\infty}[\{(CuI)_2(Mepyz)_2\} \cdot Mepyz]$ 1a is able to reversibly imbibe benzonitrile without loss of integrity.

| Compound | 1a | 2a | 2b | 3a | 3b | 4 |
|--|---|--|--------------------------------|--------------------------------|--|--|
| Formula | C ₁₅ H ₁₈ Cu ₂ I ₂ N ₆ | C ₅ H ₆ BrCuN ₂ | C5H6ClCuN2 | $C_5H_6Cu_2I_2N_2$ | C ₅ H ₆ Br ₂ Cu ₂ N ₂ | C ₅ H ₁₀ CuIN ₂ |
| M | 663.2 | 237.6 | 193.1 | 475.0 | 381.0 | 288.6 |
| Space group | $P2_12_12_1$ | $P2_1/c$ | $P2_1/c$ | $P2_{1}/c$ | $P2_1/c$ | $P2_12_12_1$ |
| a [Å] | 8.740(3) | 4.023(1) | 3.861(1) | 15.255(5) | 15.066(3) | 7.249(2) |
| <i>b</i> [Å] | 13.920(7) | 12.940(4) | 12.887(3) | 4.228(1) | 3.996(1) | 9.090(2) |
| <i>c</i> [Å] | 17.082(5) | 12.801(4) | 12.585(3) | 16.142(4) | 15.619(3) | 12.132(3) |
| β [°] | 90 | 96.83(2) | 95.59(2) | 112.23(2) | 110.78(2) | 90 |
| $V[Å^3]$ | 2078.2(1) | 661.6(3) | 623.2(2) | 963.7(4) | 879.2(3) | 799.4(4) |
| Ζ | 4 | 4 | 4 | 4 | 4 | 4 |
| $D_{\text{calc}} [g \cdot \text{cm}^{-3}]$ | 2.120 | 2.385 | 2.058 | 3.274 | 2.879 | 2.398 |
| <i>F</i> (000) | 1256 | 456 | 384 | 856 | 712 | 544 |
| Crystal size [mm] | $0.18 \times 0.16 \times 0.12$ | $0.62 \times 0.32 \times 0.24$ | $0.66 \times 0.20 \times 0.18$ | $0.42 \times 0.18 \times 0.16$ | $0.32 \times 0.12 \times 0.02$ | $0.32 \times 0.22 \times 0.18$ |
| μ (Mo-K α)[mm ⁻¹] | 5.03 | 9.24 | 3.82 | 10.76 | 13.86 | 6.51 |
| Max./min. trans. | 0.34/0.20 | 0.31/0.23 | 0.45/0.42 | 0.79/0.21 | 0.53/0.21 | 0.37/0.19 |
| h/k/l Ranges | 0,10/0,16/0,20 | 0,5/-18,0/-17,17 | 0,5/0,16/-16,16 | -19,18/0,5/0,20 | 0,19/0,5/-20,18 | 0,9/0,11/0,15 |
| 2θrange [°] | 4 - 50 | 4 - 60 | 4 - 55 | 4 - 55 | 4 - 55 | 4 - 55 |
| Independent refls | 2097 | 1916 | 1419 | 2220 | 1992 | 1073 |
| $R_1 [I > 2\sigma(I)]$ | 0.055 | 0.032 | 0.040 | 0.037 | 0.095 | 0.040 |
| wR_2 [all data] | 0.125 | 0.074 | 0.104 | 0.106 | 0.270 | 0.107 |
| S [goodness-of-fit] | 1.024 | 1.036 | 1.214 | 1.119 | 0.957 | 1.128 |
| Min./max. res. $[e \cdot Å^{-3}]$ | 0.75/-1.30 | 0.65/-0.62 | 0.69/-1.55 | 0.85/-1.73 | 3.44/-2.16 | 1.29/-0.80 |

Table 1. Crystal and refinement data for 1 - 4.

Experimental

FTIR: KBr discs, Perkin Elmer 1760X; elemental analysis: VarioEL (Elementar Analysensystem GmbH) für C, H, and N, AAS6 vario atom absorption spectrometer (Carl Zeiss Technology) for Cu. The thermogravimetric analysis (TGA/DTA) was performed on an Exstar 6000 (Seiko Instruments), the PXRD study on a Bruker AXS D8 Advance. Syntheses of **2a**, **2b**, **3a** and **3b** were performed in sealed glass tubes using dried acetonitrile as solvent.

$\frac{2}{\infty}[\{(CuI)_2(Mepyz)_2\}\cdot Mepyz]$ (1a)

138 mg CuI (0.7 mmol) and 66 mg (0.7 mmol) 2-methylpyrazine (Mepyz) were mixed together and allowed to stand at room temperature to afford orange crystals of **1** in 91% yield (139 mg) over a period of 3 days. $C_{15}H_{18}Cu_2I_2N_6$, (M = 663.2): Calcd C 27.0, H 2.7, N 12.6%. Found C 27.3, H 2.9, N 12.9%.

$\frac{2}{\infty}$ [CuBr(Mepyz)] (2a)

192 mg CuBr (1.34 mmol) and 122 mg 2-methylpyrazine (1.34 mmol) were heated in 1.5 ml CH₃CN at 130 °C for 40 h in a sealed glass tube. Slow cooling to room temperature over 80 h afforded red needles of **2** in 66% yield (209 mg). C₅H₆BrCuN₂ (M = 237.6): Calcd C 25.3, H 2.4, N 11.8, Cu 26.7. Found C 24.9, H 2.4, N 11.8, Cu 27.2%.

$\frac{2}{\infty}$ [CuCl(Mepyz)] (**2b**)

A 56% yield (120 mg) of red crystals of **2b** was achieved under conditions similar to **2a** with 112 mg CuCl (1.1 mmol) and 103 mg 2-methylpyrazine (1.1 mmol). $C_5H_6ClCuN_2$ (M = 193.1): Calcd C 31.1, H 3.1, N 14.5, Cu 32.9. Found C 30.2, H 3.1, N 14.1, Cu 32.4%.

$\frac{2}{\infty}[(CuI)_2(Mepyz)]$ (3a)

Reaction of 191 mg CuI (1 mmol) and 68 mg 2-methylpyrazine (0.5 mmol) under conditions as for **2a** afforded yellow needles of **4** in 52% yield (123 mg). $C_5H_6Cu_2I_2N_2$ (M = 475.0): Calcd C 12.6, H 1.3, N 5.9. Found C 13.0, H 1.3, N 5.9%.

$\frac{2}{\infty}[(CuBr)_2(Mepyz)]$ (3b)

A 42% yield (206 mg) of orange crystals of **3b** was obtained by treating 373 mg CuBr (2.6 mmol) with 121 mg 2-methylpyrazine (1.3 mmol) under analogous reaction conditions to **2a**. $C_5H_6Br_2Cu_2N_2$ (M = 381.0): Calcd C 15.9, H 1.6, N 7.4. Found C 15.6, H 1.6, N 7.3%.

$\frac{3}{\infty}$ [CuI(Mepip)] (4)

191 mg CuI (1 mmol) and 98 mg R-2-methylpiperazine (Mepip) were added to 1.5 ml acetonitrile and the reaction mixture left to stand for 8 d at room temperature to afford yellow-brown crystals of 4 in 46% yield (132 mg). $C_5H_{10}CuIN_2$ (M = 288.6): Calcd C 20.8, H 3.5, N 9.7, Cu 22.0. Found C 20.1, H 4.1, N 9.0, Cu 22.1%.

X-ray structural analyses of 1 - 4

Crystal and refinement data for compounds 1 - 4 are listed in Table 1. The X-ray structural analysis for **3b** was of poor quality and this compound, which is isostructural to **3a**, is only included for comparison purposes. Unit cell constants were obtained from least-squares fits to the settings of 25 - 30 reflections centered on a Siemens P4 diffractometer. Intensity data were collected in the ω mode at 293 K. Three selected reflections were monitored for each of the compounds during the course of data collection; significant deviations in intensity were not observed. Semi-empirical absorption corrections were performed on the basis of ψ scans for 9 chosen reflections with high χ values. After structure solution with SHELXL 86, positional parameters and anisotropic temperature factors were refined against F_0^2 with SHELXL 93 [23]. Hydrogen atoms were included at calculated sites together with group isotropic temperature factors. Absolute structures of the chiral coordination polymers **1a** and **4** were assigned on the basis of their Flack parameters [24], which refined to respectively 0.05(10) and -0.03(9) [25].

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- [25] Crystallographic data for 1 4 have been deposited with the Cambridge Crystallographic Data Centre (CCDC 139859 - 139863). Copies may be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: int. Code +44(0).1223/336-033, e-mail: deposit@chemcrys.cam.ac.uk).