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A three-dimensional zeolite-like organic–inorganic hybrid material constructed from $\{CuMo_2O_8N\}_n$ double helical chains linked *via* $[Cu(4,4'\text{-bpy})]_n$ fragments†

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The three-dimensional microporous $[Cu_2Mo_2O_8(4,4'\text{-bpy})]_n \cdot 3nH_2O$ 1 contains $\{CuMo_2O_8N\}$ double helical chains, which are built up from $\{Cu^{II}O_4N\}$ square pyramids linked by $\{Mo^{VI}O_4\}$ tetrahedra and further connected to each other by 4,4′-bpy coordinated $\{Cu^{II}O_5N\}$; the study of the physical properties of 1 demonstrates it is a paramagnetic semi-conductor and a zeolite material; the specific channeling cavities in 1 have potential adsorption activities, indicating that 1 might be an attractive functional microporous solid material.

The synthesis and characterization of 2D or 3D materials are currently of significant interest, of which the main focus is for new functional materials ranging from zeolite-like microporous polymers to biomaterials,[1,2] not only because of their intriguing architectures, but also of their tremendous potential applications in a wide number of fields.[2–6] The number of host frameworks of such materials which can facilitate the removal/adsorption of guest molecules has rapidly grown.

Among the large amount of reported work the rational synthesis of organic–inorganic compounds containing double-helical arrays is of particular interest.[7–10] It is well known that five-coordinate copper(II) often adopts a distorted square pyramidal geometry which can be used for the synthesis of chiral or double helical structures.[11] Herein, we report the hydrothermal synthesis, single crystal X-ray structure and preliminary studies of some properties of $[Cu_2Mo_2O_8(4,4'\text{-bpy})]_n \cdot 3nH_2O$ **1** (4,4′-bpy = 4,4′-bipyridine).

Green crystals of **1** were obtained from the hydrothermal reaction of $CuSO_4 \cdot 5H_2O$, $Na_2MoO_4 \cdot 2H_2O$, 4,4′-bpy·$2H_2O$ and HNO_3 in an aqueous solution heated at 166 °C for five days.‡ A single crystal X-ray diffraction study§ reveals that compound **1** consists of a three-dimensional covalently bonded microporous framework built up from $\{CuO_5N\}$ octahedra, $\{CuO_4N\}$ square pyramids, $\{MoO_4\}$ tetrahedra and 4,4′-bpy. The $\{CuO_4N\}$ square pyramids link $\{MoO_4\}$ tetrahedra *via* corner-sharing to form double helical chains. In these double helices, each five-coordinated copper atom is coordinated by four oxygen atoms (Cu–O 1.956(6)–2.274(7) Å), from four different $\{MoO_4\}$ tetrahedra (Mo–O 1.744(6)–1.807(6) Å), and by a nitrogen atom from 4,4′-bpy (Cu–N 2.014(8) Å). Interestingly, these $\{CuO_4N\}$ and $\{MoO_4\}$ are connected to each other alternately *via* corner-sharing to produce right- and left-handed helical $\{CuMoO_4N\}_n$ chains, which are further entangled together to produce the double helical chain (Fig. 1). Another crystallographically independent copper atom, residing in a distorted octahedral environment, is coordinated by five oxygen atoms (Cu–O 1.960(6)–2.409(7) Å) from five different $\{MoO_4\}$ tetrahedra (Mo–O 1.774(7)–1.807(6) Å) and a nitrogen atom (Cu–N 1.984(8) Å) from 4,4′-bpy. These octahedrally co-ordinated copper(II) centers in pairs link the double helices *via* corner-sharing to produce a $\{Cu_2Mo_2O_8N_2\}_n$ layer (Fig. 2).

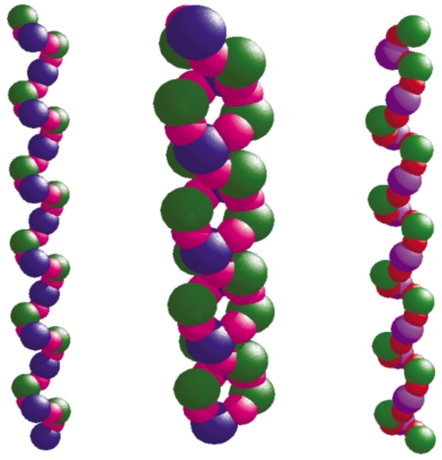
(a) (b) (c)

Fig. 1 Space-filling plots of the left-handed (a), right-handed (c) (for clarity, only the Cu–O–Mo–O– backbone is shown) and the double helix (b) (Mo, green; Cu, blue and purple; O red).

Adjacent $\{Cu_2Mo_2O_8N_2\}_n$ layers are connected by 4,4′-bpy ligands, linking up differently coordinated copper centers to generate a 3D structure with some channels (6.656 × 11.100 Å), which are clathrated by water molecular guests. As shown in Fig. 3, these guests link to each other (O···O 2.754–2.805 Å) and to the oxygen atoms of the MoO_4 tetrahedra (O···O 2.845–2.904 Å) in a zigzag pattern through complicated hydrogen bonding.

The powder magnetic susceptibility of compound **1** has been studied. The variation of the molar magnetic susceptibility χ_M

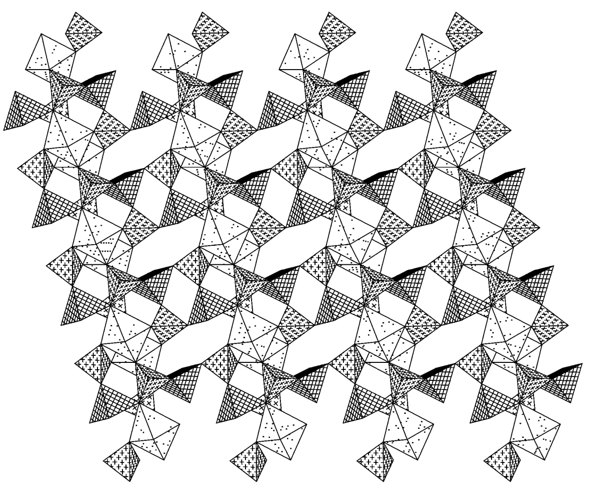

Fig. 2 Polyhedral representation of the $\{Cu_2Mo_2O_8N_2\}$ layer ($\{Mo^{VI}O_4\}$: cross hatched tetrahedra; $\{Cu^{II}O_4N\}$: dark hatched square pyramids; $\{Cu^{II}O_5N\}$: dotted octahedra).

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† Electronic supplementary information (ESI) available: Fig. S1: $\chi_M T$ *vs.* *T* and χ_M *vs.* *T* plots for compound **1**. See http//www.rsc.org/suppdata/cc/b1/b108704e/

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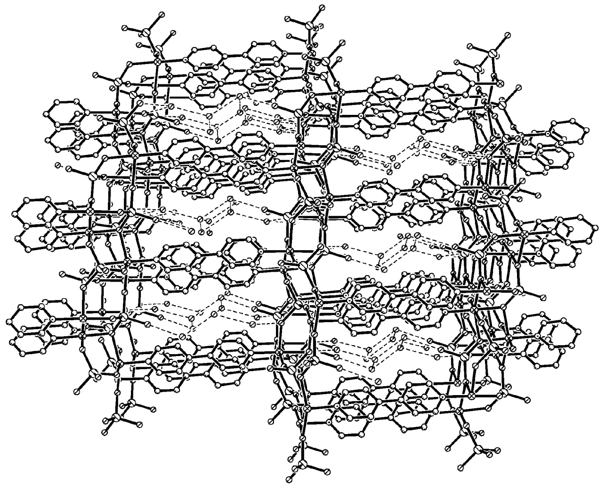

Fig. 3 Side view of the packing of **1**, showing the three-dimensional framework and the channels that are occupied by water molecular guests.

was investigated for compound **1** in the temperature range 5.0–300 K in a 10 kG applied field. At 299.32 K, the $\chi_M T$ value is 1.731 emu K mol^{-1} per tetramer, which is almost consistent with the spin only value for four uncoupled Cu^{II} ions. Upon cooling to 5.0 K, the $\chi_M T$ values decrease gradually to 0.218 emu K mol^{-1}, suggesting that compound **1** is antiferromagnetic. The magnetic susceptibility data were quantitatively analyzed by treating it as an interacting tetramer, with the exchange through the 4,4′-bpy and {MoO$_4$} tetrahedra bridges as an inter-tetramer molecular field.[12] In this case J_1 and J_2 are the intra-tetramer exchange constants (through the oxygen atom bridge), J' is the inter-tetramer coupling constant (transferred by 4,4′-bpy and {MoO$_4$} tetrahedra), z the interaction number of interacting neighbors, while TIP is the temperature-independent paramagnetism. Least-square fitting of all experimental data leads to J_1, J_2, zJ', g and TIP values of −28.39 cm^{-1}, −20.67 cm^{-1}, −5.46 cm^{-1}, 2.028 and 0.0229 with the agreement factor $R = 2.1 \times 10^{-4}$, which demonstrate the existence of antiferromagnetic interactions among the copper(II) centers of tetramer unit and adjacent tetramer units.

The EPR spectrum of polycrystalline **1** at room temperature gives $g_\| = 2.170$, $g_\perp = 2.057$ and hyperfine constant $A_\| = 85.56$ G, which are in accord with expected values for copper(II) ions with square-pyramidal geometries and $d_{x^2-y^2}$ electronic configurations.[13] There is a further signal with $g = 2.101$, indicating that the coordination geometry of another Cu^{II} center is octahedral. Similarly, at 77 K, we obtained $g_\| = 2.166$, $g_\perp = 2.056$, $A_\| = 83.33$ G and $g = 2.103$, which are almost the same as the results at room temperature.

Determination of the conductivity for **1** (powder sample from ground crystals) gives its electrical conductivity of 3.36×10^{-7} S cm^{-1} at 300 K, which increases as the temperature rises, indicating that **1** is a semiconductor. By examining its structure, the semiconducting property of **1** should be attributed to its characteristic structural feature of the conjunction array of copper(II) and molybdenum(VI) centers, which also demonstrate the existance of interactions among themselves.

The overall neutral three-dimensional framework of **1** clearly shows the presence of large channels that are occupied by water molecular guests. These guest molecules can potentially be removed to generate nanoporous solids while the framework skeleton is retained which is confirmed by thermogravimetric analysis (TGA) and XRPD. When fine powder samples (lattice water molecules removed from the channels) were soaked in acetonitrile for two days at room temperature noticeable absorption of acetonitrile molecules occurred, as characterized by EI–MS spectra. The EI–MS show parent peaks at m/z 41, 40, 26 and 15, which clearly demonstrated that CH_3CN molecules were incorporated into the cavities in dehydrated **1**. Based on above discussions, complex **1** might be a suitable microporous solid for molecular adsorption and heterogeneous catalysis.

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Notes and references

‡ A mixture of $Na_2MoO_4 \cdot 2H_2O$ (0.10 g, 0.41 mmol), $CuSO_4 \cdot 5H_2O$ (0.10 g, 0.40 mmol), 4,4′-bpy·2H$_2$O (0.05 g, 0.26 mmol) and HNO_3 (63 wt%) (0.1 ml, 1.5 mmol) in H_2O (18 ml) was heated at 166 °C for five days in a sealed 30 ml Teflon-Lined stainless steel vessels under autogeneous pressure. After the reaction mixture was slowly cooled to room temperature green crystals were produced (yield 78.3%, based on Cu). Anal. Calc. for **1**: C, 18.28; H, 2.15; N, 4.26. Found: C, 18.17; H, 2.17; N, 4.23%. IR (solid KBr pellet /cm^{-1}): 1647s, 1614s, 1558m, 1537m, 1495s, 1414s, 1335m, 1225s, 1076s, 930s, 887s, 893m, 820m, 796m, 737s, 646m, 544m.

§ *Crystal data* for **1**: $C_{10}H_{14}Cu_2Mo_2N_2O_{11}$, $M_r = 657.19$, triclinic, space group $P\bar{1}$, $a = 7.4488(2)$, $b = 9.2576(1)$, $c = 13.9332(4)$ Å, $\alpha = 71.992(2)$, $\beta = 89.745(2)$, $\gamma = 73.640(2)°$, $U = 873.14(4)$ Å^3, $Z = 2$, $D_c = 2.500$ g cm^{-3}, $\mu = 3.867$ mm^{-1}, $F(000) = 636$, crystal size = $0.20 \times 0.06 \times 0.04$ mm. Final $R1 = 0.0555$, $wR2 = 0.1159$ and $S = 0.998$ for 2137 reflections with $F_o > 4\sigma(F_o)$ and 266 parameters and $R1 = 0.0922$, $wR2 = 0.1328$ for all 3052 data. CCDC reference number 164885. See http://www.rsc.org/suppdata/cc/b1/b108704e/ for crystallographic data in CIF or other electronic format.

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