

# 1D porous framework of copper(II) showing a novel coordination mode of $\text{Ni}(\text{CN})_4^{2-}$ †

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A novel porous framework  $[\{\text{Cu}_2(\text{medpt})_2\text{Ni}(\text{CN})_4\}(\text{ClO}_4)_2 \cdot 2.5\text{H}_2\text{O}]_n$  **1**, [medpt = bis(3-aminopropyl)methylamine] is prepared where all the CN groups of  $\text{Ni}(\text{CN})_4^{2-}$  are involved in bridging; this material retains single crystallinity upon removal of water guest molecules and the dehydrated species **2** selectively binds organic molecules.

The design and synthesis of microporous inorganic materials mimicking zeolites finds widespread application in heterogeneous catalysis, adsorption, ion exchange processes, selective binding of guest molecules *etc.*<sup>1</sup> Self assembly is the most efficient approach towards elaboration and construction of such types of molecular systems. Currently, a successful example of this process is the construction of cyano bridged complexes<sup>2</sup> in which the cyanometallate anion [*e.g.*  $\text{Ag}(\text{CN})_2^-$ ,  $\text{Cu}(\text{CN})_3^{2-}$ ,  $\text{Ni}(\text{CN})_4^{2-}$ ,  $\text{M}(\text{CN})_6^{3-}$  ( $\text{M} = \text{Cr}(\text{III})$ ,  $\text{Fe}(\text{III})$  *etc.*)] behaves as the bridging moiety to build a multidimensional structure with a second coordination centre and the resulting complexes demonstrate unique properties. Usually the second coordination centres are transition metal ions since  $\sigma \rightarrow \pi$  back-bonding stabilizes the resulting complex. The rigidity and stability of such frameworks allow for shape and size selective inclusion of organic solvents, water molecules, aromatic amines,<sup>3</sup> *etc.* to fill up the void space so stabilizing the crystal structure.

The reaction of  $\text{Cu}(\text{medpt})(\text{H}_2\text{O})_2(\text{ClO}_4)_2$  [medpt = bis(3-aminopropyl)methylamine] and  $\text{K}_2\text{Ni}(\text{CN})_4 \cdot 2\text{H}_2\text{O}$  in aqueous medium leads to the formation of deep blue plates of  $\text{Cu}_2(\text{medpt})_2\text{Ni}(\text{CN})_4(\text{ClO}_4)_2 \cdot 2.5\text{H}_2\text{O}$  **1**.† The IR spectrum of compound **1** shows one sharp  $\nu_{\text{CN}}$  band at  $2150 \text{ cm}^{-1}$  which is at a higher wavenumber than that of the free  $\text{Ni}(\text{CN})_4^{2-}$  unit ( $\nu_{\text{CN}}$  band at  $2128 \text{ cm}^{-1}$ ), indicating that all the CN groups act as bridging ligands with the copper(II) centre. Although one discrete square cyano-bridged compound<sup>2c</sup> has been reported, to our knowledge, 1D square compounds where all the cyano groups are involved in bridging have not yet been reported in the literature.

The structure determination§ of **1** discloses a 1D square type open microporous material, consisting of infinite chains elongated in the direction of the crystallographic *b* axis (Fig. 1). In the polymer there are intra-chain H-bonds [ $2.94(1) \text{ \AA}$ ] between amino nitrogens [N(1), N(1'')] and the bridging water molecule O(3w), the latter interacting also with O(2w) at  $2.79(2) \text{ \AA}$ . A third crystallization water molecule O(1w) connects through hydrogen bonds the amino nitrogens N(3) of adjacent chains, in a diamond shape pattern. These inter-chain interactions of  $2.913(9)$  and  $3.021(9) \text{ \AA}$ , illustrated in Figs. 1 and 2, give rise to a 2-D structure. The water molecules, all at half occupancy, are guests in the crystalline channels and, from a topological point of view, have the ability to leave the host

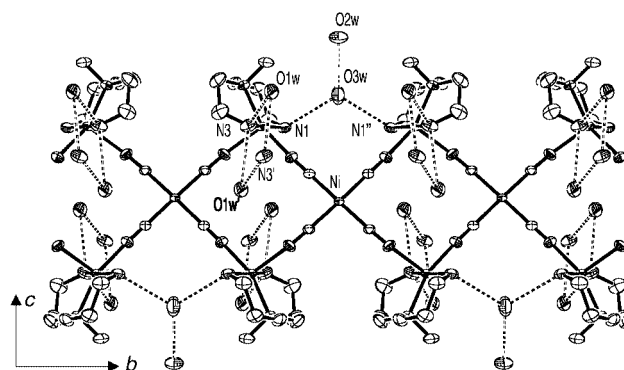


Fig. 1 ORTEP drawing of the polymeric structure of **1**, extending in the direction of crystallographic *b* axis, with guest water molecules (dotted lines indicate H-bonds;  $\text{ClO}_4^-$  anions omitted for clarity).

lattice. The dehydration process, detected by thermogravimetric analysis, occurs but leads to no deterioration of crystallinity, indicating that the structure can be envisaged as an inclusion compound and that removal of the H-bond network does not lead to destruction of the structure. A similar behaviour was described for the structure  $[\text{Ni}(\text{en})_2\text{Ni}(\text{CN})_4] \cdot 2.5\text{H}_2\text{O}$ ,<sup>4a</sup> where the role of the water molecules was interpreted using a molecular mechanics investigation. Other examples, with phenol and aniline as guest molecules accommodated among  $[\text{M}(\text{en})_2\text{Ni}(\text{CN})_4]_n$  chains ( $\text{M} = \text{Ni}$ ,  $\text{Cu}$ ,  $\text{Zn}$  or  $\text{Cd}$ ), were reported by Iwamoto *et al.*<sup>4b</sup>

The copper presents a square pyramidal coordination where the medpt ligand donors and a cyanide nitrogen occupy the basal plane, the metal being slightly displaced by  $0.27 \text{ \AA}$  from the N4 mean plane towards the apical position occupied by a cyanide ligand of a different  $\text{Ni}(\text{CN})_4^{2-}$  anion. The latter Cu–N bond distance is significantly longer [ $2.186(4) \text{ \AA}$ ] with respect to those in the basal plane [ $2.000(4)$ – $2.072(3) \text{ \AA}$ ]. The  $\text{Ni}(\text{CN})_4^{2-}$  anion, with the metal located on a symmetry plane, coordinates four adjacent copper ions. The cyanide groups show different geometries, being linear coordinated in the basal plane

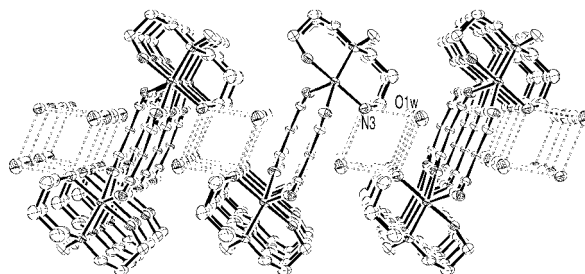


Fig. 2 Packing diagram down the *b* axis showing the diamond pattern of H-bonds linked the  $-\text{Ni}-\text{Cu}-$  polymeric chains.

† Electronic supplementary information (ESI) available: Fig. 4: ORTEP view of **2**. Fig. 5: view of **2** down the crystallographic *b* axis. Fig. 6: TG-DTA curves of **1**, **1a** and **1b**. Fig. 7: view of **1** showing the water filled channels. See <http://www.rsc.org/suppdata/cc/b1/b103823k/>

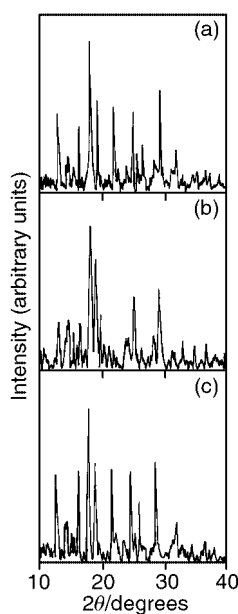
of copper, but significantly bent at the apical position of the pyramidal Cu environment [Cu–N≡C bond angles of 176.0(4) and 155.3(3)°, respectively].

Thermogravimetric analysis of a crystalline sample showed a weight loss of 5.5% at 70 °C, corresponding to the loss of the guest water occupying the channels. The remaining compound was heated to 180 °C without any additional weight decrease, indicating a robust open Cu–Ni framework. Examination of the single crystals with an optical microscope at 100 °C showed that they retained their morphology and crystallinity upon loss of the water molecules.

The X-ray structural determination of a dehydrated single crystal of **2**§ sealed in a glass capillary reveals a 1D open microporous framework and confirms the  $[\{Cu_2(\text{medpt})_2Ni(\text{CN})_4\}(\text{ClO}_4)_2]_n$  formulation. Besides a contraction in cell volume, the space group changes from  $P2_1/m$  to  $P2_1/c$ , which requires the loss of the crystallographic symmetry plane in which nickel atoms, as well as water molecules Ow2 and Ow3, were located (Fig. 1). The polymer backbone of Ni atoms is now almost collinear, and the angle and distance between the consecutive metals are 169.12(4)° and 7.109(2) Å, respectively, cf. the zigzag Ni arrangement in the hydrated species **1** where the corresponding values are 156.95(3)° and 7.460(3) Å. In addition, the conformation of the Cu(medpt) moiety appears to change slightly, and a noteworthy modification related to the dehydration process is the change in distance between nitrogens N1...N1" (5.37 Å), which for the corresponding atoms involved in H-bonding with bridging water molecules in **1**, is 4.81 Å (Fig. 1).

To examine the inclusion chemistry of this material, the synthesised microcrystalline solid was heated at 100 °C for 30 min, in order to remove the guest molecules. It is worth noting that upon reintroducing water into the pores over a period of 1 h, the XRD pattern¶ of the resulting solid is simultaneously regenerated with the peak positions and their intensities being fully coincident to those observed for the original solid, serving as evidence to the reversibility of the inclusion process (Fig. 3).

It is also interesting that the evacuated solid selectively binds MeOH (**1a**) and MeCN (**1b**)|| in the pores among the number of organic solvents tested (ethanol, benzene, carbontetrachloride, chloroform, dichloromethane *etc.*). In DMF and DMSO, the



**Fig. 3** The XRD patterns of (a) as-synthesized material,  $[\{Cu_2(\text{medpt})_2Ni(\text{CN})_4\}(\text{ClO}_4)_2 \cdot 2.5H_2O]_n$  **1**; (b) dehydrated solid,  $[\{Cu_2(\text{medpt})_2Ni(\text{CN})_4\}(\text{ClO}_4)_2]_n$  **2** and (c) regenerated solid, resulting from the reintroduction of water molecules into the channels of the dehydrated solid.

morphology of the complex breaks down. The XRD patterns of these two solids containing guest MeOH or MeCN molecules show diffraction peaks which are sharp but with slightly different positions and line widths compared to the original species containing water as guest molecules. IR spectra also corroborate the retention of morphology with MeOH or MeCN as guest molecules. Thermogravimetric analyses of **1a** and **1b** show weight losses at 130 and 170 °C, respectively, that can be attributed to the loss of *ca.* two methanol and two acetonitrile molecules per formula unit, respectively. It is also important to note that the reversibility of the inclusion process found for water guest molecules is also observed for **1a** but not **1b** for which removal of the two acetonitrile molecules per formula unit leads to instantaneous decomposition.

## Notes and references

‡ *Experimental procedure and selected data:* bis(3-aminopropyl)methylamine (medpt) (2 mmol, 0.290 g) was added dropwise to an aqueous solution (10 cm<sup>3</sup>) of Cu(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (2 mmol, 0.741 g) with constant stirring. K<sub>2</sub>[Ni(CN)<sub>4</sub>]·2H<sub>2</sub>O (1 mmol, 0.276 g) dissolved in water (5 cm<sup>3</sup>) was poured to the resulting blue solution and instantaneous deep blue precipitation occurred. The reaction mixture was stirred for 30 min and then filtered. After a few days suitable shining deep blue single crystals of **1** were obtained from the filtrate. IR: ν(N–H): 3200–3400; ν(CN): 2150; ν(ClO<sub>4</sub>): 1098–984 cm<sup>-1</sup>.

§ *Crystal data:* for **1**: C<sub>18</sub>H<sub>43</sub>Cu<sub>2</sub>NiCl<sub>2</sub>N<sub>10</sub>O<sub>10.5</sub>, *M* = 824.31, monoclinic, space group  $P2_1/m$ , *a* = 7.806(2), *b* = 14.619(7), *c* = 15.069(5) Å, β = 97.41(2)°, *V* = 1705.3(11) Å<sup>3</sup>, *Z* = 2, *D<sub>c</sub>* = 1.605 g cm<sup>-3</sup>, μ(Cu–Kα) = 4.075 mm<sup>-1</sup>, 3247 unique reflections, *R1* (*F<sub>o</sub>*) = 0.0559 for 2960 reflections with *I* > 2σ(*I*), *wR2* (*F<sub>o</sub>*<sup>2</sup>) = 0.1672.

For **2**: C<sub>18</sub>H<sub>38</sub>Cu<sub>2</sub>NiCl<sub>2</sub>N<sub>10</sub>O<sub>8</sub>, *M* = 779.27, monoclinic, space group  $P2_1/c$ , *a* = 14.410(6), *b* = 14.154(4), *c* = 16.014(5) Å, β = 91.86(2)°, *V* = 3264.5(19) Å<sup>3</sup>, *Z* = 4, *D<sub>c</sub>* = 1.586 g cm<sup>-3</sup>, μ(Mo–Kα) = 2.080 mm<sup>-1</sup>, 5018 unique reflections, *R1* (*F<sub>o</sub>*) = 0.0690 for 3110 reflections with *I* > 2σ(*I*), *wR2* (*F<sub>o</sub>*<sup>2</sup>) = 0.1983.

The structure determination was affected by the low crystallinity (2θ<sub>max</sub> = 48°), leading to geometrical data of poor accuracy, with disordered perchlorate anions being observed.

CCDC reference numbers 154468 and 163231. See <http://www.rsc.org/suppdata/cc/b1/b103823k/> for crystallographic data in CIF or other electronic format.

¶ X-Ray powder diffraction data were collected using Seifert XRD-3000P instrument, where the source of X-rays was Cu–Kα radiation.

|| For the preparation of complexes **1a** and **1b**, the parent species **1** in a micro-conical flask was heated to 100 °C for 30 min and cooled to ambient temperature whilst keeping it in a fused CaCl<sub>2</sub>-vacuum desiccator. Dry methanol (**1a**)/acetonitrile (**1b**) was then added in excess and the sample kept in the desiccator for a day.

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