

# Synthesis, crystal structure, thermal behaviour and magnetic properties of a novel one-dimensional copper(II) complex containing neutral and deprotonated 3-hydroxypyridine ligands†

Oscar Castillo, Antonio Luque,\* Sonia Iglesias, Pablo Vitoria and Pascual Román

Departamento de Química Inorgánica, Universidad del País Vasco, Apartado 644, E-48080, Bilbao, Spain. E-mail: qipluara@lg.ehu.es

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The compound  $\{[\text{Cu}(\mu\text{-}3\text{-pyO-N,O})(3\text{-pyO})(3\text{-pyOH})(\text{H}_2\text{O})] \cdot 2 \text{H}_2\text{O}\}_n$  ( $3\text{-pyO}^-$  = pyridin-3-onato anion,  $\text{C}_5\text{H}_4\text{NO}^-$ ;  $3\text{-pyOH}$  = 3-hydroxypyridine,  $\text{C}_5\text{H}_5\text{NO}$ ), has been prepared, its crystal structure determined and its thermal and magnetic properties characterised. The structure is made up of infinite one-dimensional chains running along the  $b$  axis of copper(II) atoms linked by bridging N,O-bidentate pyridin-3-onato ligands with a  $\text{Cu} \cdots \text{Cu}$  distance of 7.030(2) Å. The copper(II) atom is in a distorted square-pyramidal environment with the basal plane formed by the nitrogen and the oxygen atoms of two bridging pyridin-3-onato ligands and the pyridinic nitrogen atoms of two terminal aromatic ligands in a *trans* arrangement. The apical position is filled by the oxygen atom from a water molecule. One of the two terminal aromatic ligands is a neutral 3-hydroxypyridine. Polymeric chains are held together by means of a three-dimensional network of  $\text{O}_w\text{-H} \cdots \text{O}^-$  and  $\text{O-H} \cdots \text{O}^-$  hydrogen bonding interactions in which there are channels parallel to the  $a$  axis that host solvated  $\text{H}_2\text{O}$  molecules. These water molecules are connected to the polymeric chains by means of hydrogen bonds. In the thermal degradation of the title compound, free and co-ordinated water molecules are released in two overlapping endothermic processes between 40 and 90 °C. Magnetic measurements show an antiferromagnetic interaction between the metallic centres with a  $J$  (triplet-singlet gap) value of  $-16.4 \text{ cm}^{-1}$ .

In the past few years, the design of polymeric compounds in which metal centres are linked by organic molecules has been an active area of research owing to the fact that these systems offer an enormous potential in areas such as selective absorption,<sup>1</sup> catalysis,<sup>2</sup> molecular magnetism<sup>3</sup> and bioinorganic chemistry.<sup>4</sup> The generation of this type of molecular architectures rests on the combination of several factors like the co-ordination geometry of metals, the performance of the ligands and the reaction conditions. In relation to the ligands, the use of bidentate organic ligands with a remarkable ability to mediate electronic effects between paramagnetic metal ions not only allows one to obtain systems with very interesting magnetostructural correlations but also some of them may serve as bioinorganic models because co-ordination compounds of first-row transition metals are known to participate in multiple biological processes involving acid-base and redox reactions.<sup>5</sup> In this sense, complexes of hydroxypyridine and its derivatives have been determined to exhibit a broad spectrum of physiological effects on the activity functions of both animal and plants organisms,<sup>6</sup> and have also been used to model the binding of platinum to DNA and to characterise in more detail “platinum blues”.<sup>7</sup>

Despite such widespread interest, a scarce number of co-ordination compounds of hydroxypyridine ligands have been structurally characterised so far<sup>8–10</sup> and the majority of them contain 2-hydroxypyridine or its tautomer, the lactam 2-pyridone.<sup>11</sup> As a contribution to this field, we report herein the synthesis, structure and the thermal and magnetic characterisation of a new hydroxypyridine containing copper(II)

complex that is, to our knowledge, the first one-dimensional (1D) copper(II) complex with an anionic pyridin-3-onato bridge. Recently, the two-dimensional compound  $[\text{Cu}(3\text{-pyOH})(\text{O}_2\text{CCF}_3)_2]_n$ <sup>8</sup> has been reported in which copper centres are bridged by neutral 3-hydroxypyridine ligands acting as N,O-bidentate ligands with a  $\text{Cu-O}$  bond distance of 2.63 Å.

## Experimental

### Reagents and physical measurements

All reagents were purchased from Fluka and Aldrich, and were used without further purification. Microanalyses of carbon, nitrogen and hydrogen were performed on a Perkin-Elmer CHN-2400 analyser. The atomic absorption technique was used to determine the amount of copper in the compound. The infrared spectra (KBr pellets) were recorded on a Nicolet 740 FT-IR spectrometer in the  $4000\text{--}400 \text{ cm}^{-1}$  spectral region. Thermogravimetric studies were performed using 8–15 mg samples in a Setaram Tag 24 S16 instrument under a  $50 \text{ mL min}^{-1}$  flow of synthetic air; the temperature was ramped from 20 to 600 °C at a rate of  $1^\circ\text{C min}^{-1}$ . Magnetic susceptibility measurements were performed on polycrystalline samples of the compound with a Quantum Design SQUID susceptometer covering the temperature range 5–300 K and using an applied magnetic field  $H = 1 \text{ T}$ . The susceptometer was calibrated with  $(\text{NH}_4)_2\text{Mn}(\text{SO}_4)_2 \cdot 12 \text{ H}_2\text{O}$ . The experimental susceptibility data were corrected for the diamagnetism estimated from Pascal's tables,<sup>12</sup> the temperature-independent paramagnetism ( $60 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$  per  $\text{Cu}^{\text{II}}$ ), and magnetisation of the sample holder. X-ray powder diffraction patterns of the compound and the thermal dehydration products were recorded with a Philips PW 1710 instrument equipped with graphite-monochromated  $\text{Cu-K}_\alpha$  radiation.

† Electronic supplementary information (ESI) available: X-ray powder diffraction patterns of **1** at 373 and 443 K. Thermal variation of the magnetic susceptibility for the thermal residue at 373 K. See <http://www.rsc.org/suppdata/nj/b0/b004072j/>

## Synthesis

$[\{\text{Cu}(\mu\text{-}3\text{-pyO-N,O})(3\text{-pyO})(3\text{-pyOH})(\text{H}_2\text{O})\} \cdot 2\text{H}_2\text{O}]_n$  (**1**). To a stirred aqueous solution (30 ml, pH = 8.0) containing 3-hydroxypyridine (0.200 g, 2.10 mmol) and potassium carbonate (0.079 g, 0.57 mmol) was added dropwise 5 ml of an aqueous solution of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  (0.100 g, 0.43 mmol). A green polycrystalline powder, in almost quantitative yield, appeared in a few minutes, which was collected by filtration, washed with diethyl ether and dried in air for 2 h. Anal. Found: C, 44.87; H, 4.80; N, 10.61; Cu, 15.90. Calcd. for  $\text{C}_{15}\text{H}_{19}\text{CuN}_3\text{O}_6$ : C, 44.94; H, 4.78; N, 10.48; Cu, 15.85%. Main IR features ( $\text{cm}^{-1}$ , KBr pellet): 3425s [ $\nu(\text{O-H})$ ]; 3080s, 2955w, 2840w [ $\nu(\text{C-H})$ ]; 1645w [ $\delta(\text{O-H})$ ]; 1565s, 1485s, 1415m, 1385w [ $\nu_{\text{as}}(\text{C=N}) + \nu_{\text{as}}(\text{C=C})$ ]; 1295s, 1255m [ $\nu(\text{C-O})$ ]; 1165m [ $\delta(\text{C-H})$ ]; 1020s [ $\nu_{\text{s}}(\text{C=N}) + \nu_{\text{s}}(\text{C=C})$ ]; 845m [ $\delta(\text{O-H})$ ]; 700m, 650m, 575m [ $\delta(\text{C-H})$ ]. The pH value of the mother liquor was 7.4. Yield: 90–95% (based on copper).

X-ray suitable single crystals of **1** were obtained using a less concentrated copper salt solution (0.18 mmol, 5 ml). The resulting black green solution was filtered (pH = 7.4) and after two days, dark-green prismatic crystals were harvested by slow evaporation of the solvent at room temperature. Yield: 70–75% (based on copper). The X-ray powder pattern of the single crystals and of the polycrystalline sample matched the calculated pattern generated from the single-crystal structure data.<sup>13</sup> Taking into account the above cited biological role of the hydroxypyridine molecules, it is interesting to note that the title compound was obtained from an aqueous solution with a pH value (7.4) near to the physiological one.<sup>14</sup>

## Crystallographic data collection and structure determination

Diffraction data on a prismatic crystal of dimensions  $0.15 \times 0.10 \times 0.05$  mm were collected at 293 K with an Enraf-Nonius CAD4 automatic four-circle diffractometer using graphite-monochromated  $\text{Mo-K}\alpha$  radiation ( $\lambda = 0.71069$  Å) and the  $\omega - 2\theta$  scan mode. Unit cell parameters and orientation matrix were determined by least-squares treatment of the setting angles of 25 reflections in the range  $7 < \theta < 12^\circ$ . Crystal data, experimental conditions and structural refinement parameters are presented in Table 1. Two standard reflections were monitored every hour, but no intensity variations were observed. Data reduction was done with the XCAD program.<sup>15</sup> No absorption correction was applied; only Lorentz and polarisation effects were taken into account. The structure was solved by direct methods using the SIR 92 program.<sup>16</sup> Full-matrix least-squares refinements were performed on  $F^2$  including all reflections and using SHELXL93.<sup>17</sup> Scattering factors for neutral atoms and anomalous dispersion were taken from ref. 18. Non-hydrogen atoms were anisotropically refined. All hydrogen atoms were found from difference maps and isotropically refined except for those attached to the crystallisation water molecules, which were included as isotropic fixed contributors. All calculations were

performed using the WinGX crystallographic software package.<sup>19</sup>

CCDC reference number 440/200. See: <http://www.rsc.org/suppdata/nj/b0/b004072j/> for crystallographic file in .cif format.

## Results and discussion

### Description of the structure

The crystal structure of complex **1** consists of crystallisation water molecules and polymeric neutral  $[\text{Cu}(\mu\text{-}3\text{-pyO-N,O})(3\text{-pyO})(3\text{-pyOH})(\text{H}_2\text{O})]_n$  chains in which the metal atoms are bridged sequentially by N,O-bidentate pyridin-3-onato ligands. Fig. 1 shows a perspective view of the polymeric chain with the atom-labelling scheme. Main interatomic bond distances and angles are listed in Table 2. The copper(II) ion is in a distorted square-pyramidal environment. The basal plane is formed by the *endo*-nitrogen atoms [N11 and N21] of two aromatic ligands (average Cu–N: 2.02 Å) in a *trans* arrangement, the pyridinic nitrogen atom of a pyridin-3-onato bridge [Cu–N31: 2.037(2) Å] and the deprotonated exocyclic oxygen atom of the next anionic bridge [Cu–O37: 1.979(2) Å]. The 4 + 1 co-ordination sphere of the copper atom is completed by an apical oxygen atom from a water molecule with a Cu–O bond of 2.210(2) Å. The basal plane is not perfectly planar and there are tetrahedral displacements from the mean plane ranging from 0.04–0.01 Å. The copper atom is displaced from the mean basal plane towards the apical site by 0.07 Å. The intrachain Cu...Cu distance across the pyridin-3-onato bridge is 7.030(2) Å. This value is somewhat shorter than that (7.27 Å) published for the 2D polynuclear complex  $[\text{Cu}(3\text{-pyOH})(\text{O}_2\text{CCF}_3)_2]_n$ <sup>8</sup> in which copper centres are joined by neutral 3-hydroxypyridine bridges and the Cu–O bond (2.63 Å) is only partially formed. The polymeric chains run along the *b* axis of the unit cell, and show a corrugated arrangement with

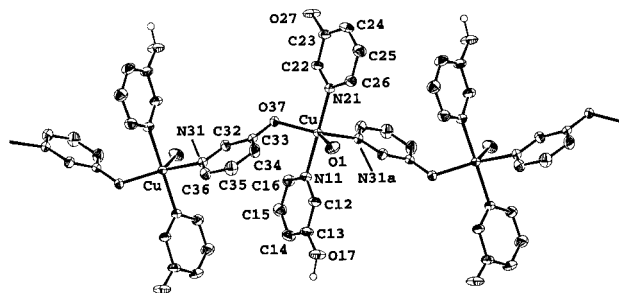


Fig. 1 A fragment of the polymeric  $[\text{Cu}(\mu\text{-}3\text{-pyO-N,O})(3\text{-pyO})(3\text{-pyOH})(\text{H}_2\text{O})]_n$  chain (ellipsoids at 50% probability level) showing the atom labelling.

Table 1 Crystallographic data for compound **1**

|                          |  |                                       |                |
|--------------------------|--|---------------------------------------|----------------|
| Formula                  | $\text{C}_{15}\text{H}_{19}\text{CuN}_3\text{O}_6$ | Z                                     | 4              |
| <i>M</i>                 | 400.87   | <i>T</i> /K                           | 293(2)         |
| Crystal system           | Monoclinic   | $\mu/\text{mm}^{-1}$                  | 1.3            |
| Space group              | $P2_1/c$ (No. 14)                                  | Unique data                           | 4932           |
| <i>a</i> /Å              | 8.992(2)   | Observed data [ $I \geq 2\sigma(I)$ ] | 3395           |
| <i>b</i> /Å              | 13.718(1)  | $R_1, wR_2^a$                         | 0.0373, 0.0909 |
| <i>c</i> /Å              | 14.130(3)  |                                       |                |
| $\beta/^\circ$           | 103.87(2)  |                                       |                |
| <i>U</i> /Å <sup>3</sup> | 1692.1(5)  |                                       |                |

<sup>a</sup> The structure was refined on  $F_o^2$  using all data, the value of  $R_1$  is given for comparison with older refinements based on  $F_o$  with a typical threshold of  $F \geq 4\sigma(F)$ ,  $R_1 = [\sum \|F_o\| - |\sum F_c|] / \sum \|F_o\|$ ;  $wR_2 = \{\sum [w(F_o^2 - F_c^2)^2] / \sum w(F_o^2)^2\}^{1/2}$  where  $w = 1/[\sigma^2(F_o^2) + (0.0527P)^2]$  and  $P = (F_o^2 + 2F_c^2)/3$ .

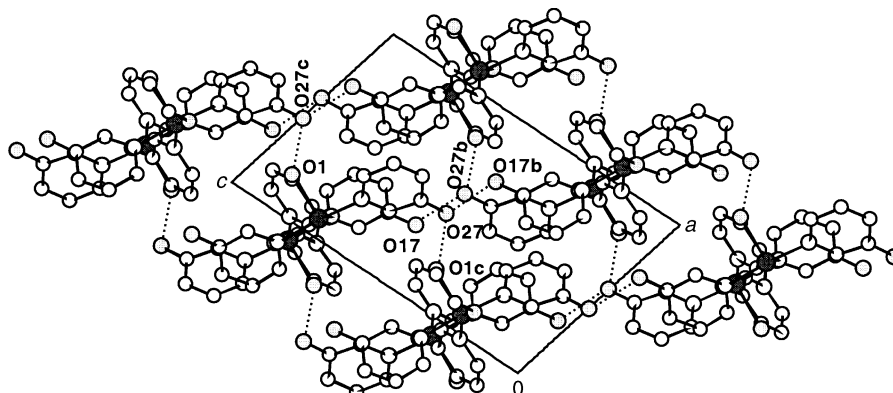
**Table 2** Selected bond distances (Å), angles (°) and hydrogen contacts (Å, °) for compound **1**. Symmetry code: (a)  $-x, y - 1/2, -z + 3/2$ ; (b)  $x - 1, -y + 1/2, z + 1/2$ ; (c)  $x, -y + 1/2, z + 1/2$ ; (d)  $-x, -y + 1, -z + 1$ ; (e)  $-x, y + 1/2, -z + 3/2$

|                           |                         |                         |                        |         |
|---------------------------|-------------------------|-------------------------|------------------------|---------|
| Cu(II) environment        |                         |                         |                        |         |
| Cu–O1                     | 2.210(2)                | Cu–N21                  | 2.021(2)               |         |
| Cu–O37                    | 1.979(2)                | Cu–N31a                 | 2.037(2)               |         |
| Cu–N11                    | 2.027(2)                | Cu···Cu                 | 7.030(2)               |         |
| O1–Cu–O37                 | 111.44(8)               | O37–Cu–N21              | 90.87(7)               |         |
| O1–Cu–N11                 | 94.04(8)                | O37–Cu–N31a             | 150.40(7)              |         |
| O1–Cu–N21                 | 90.52(8)                | N11–Cu–N21              | 175.28(8)              |         |
| O1–Cu–N31a                | 98.16(8)                | N11–Cu–N31a             | 88.93(7)               |         |
| O37–Cu–N11                | 88.60(7)                | N21–Cu–N31a             | 89.23(7)               |         |
| Organic ligands           |                         |                         |                        |         |
|                           | neutral ( <i>X</i> = 1) | anionic ( <i>X</i> = 2) | bridge ( <i>X</i> = 3) |         |
| NX1–CX2                   | 1.336(3)                | 1.335(3)                | 1.340(3)               |         |
| NX1–CX6                   | 1.339(3)                | 1.340(3)                | 1.338(3)               |         |
| CX2–CX3                   | 1.389(3)                | 1.403(3)                | 1.401(3)               |         |
| CX3–OX7                   | 1.335(3)                | 1.315(3)                | 1.327(3)               |         |
| CX3–CX4                   | 1.399(3)                | 1.396(4)                | 1.395(3)               |         |
| CX4–CX5                   | 1.370(4)                | 1.374(4)                | 1.379(4)               |         |
| CX5–CX6                   | 1.381(3)                | 1.380(3)                | 1.381(3)               |         |
| CX2–NX1–CX6               | 118.4(2)                | 118.5(2)                | 119.0(2)               |         |
| NX1–CX2–CX3               | 123.5(2)                | 124.1(2)                | 123.8(2)               |         |
| CX2–CX3–OX7               | 117.5(2)                | 120.4(2)                | 120.9(2)               |         |
| CX4–CX3–OX7               | 124.7(2)                | 123.6(2)                | 123.1(2)               |         |
| CX2–CX3–CX4               | 117.8(2)                | 116.1(2)                | 116.0(2)               |         |
| CX3–CX4–CX5               | 118.2(2)                | 119.7(2)                | 120.2(2)               |         |
| CX4–CX5–CX6               | 120.8(2)                | 120.3(2)                | 119.9(2)               |         |
| NX1–CX6–CX5               | 121.4(2)                | 121.3(2)                | 121.2(2)               |         |
| Hydrogen bonding contacts |                         |                         |                        |         |
| D–H···A                   | D–H                     | H···A                   | D···A                  | D–H···A |
| O17–H171···O27b           | 1.04(6)                 | 1.41(6)                 | 2.446(3)               | 176(5)  |
| O1–H11···O27c             | 0.73(3)                 | 1.90(3)                 | 2.623(3)               | 178(4)  |
| O1–H12···O2c              | 0.80(4)                 | 1.99(4)                 | 2.783(3)               | 177(4)  |
| O2–H21···O37              | 0.98                    | 1.80                    | 2.764(3)               | 165     |
| O2–H22···O2d              | 0.86                    | 1.97                    | 2.743(3)               | 148     |
| O3–H31···O2               | 0.84                    | 1.95                    | 2.745(4)               | 158     |
| O3–H32···O17e             | 0.98                    | 1.91                    | 2.880(4)               | 169     |

a Cu···Cu···Cu angle of 154.7° between three successive Cu ions along the chain. The dihedral angle between the basal planes of the co-ordination polyhedra of two adjacent copper atoms is 7.6° while the bridging ligand's mean plane is almost perpendicular to them (*ca.* 80°). The aromatic rings of the two terminal ligands are tilted only 9°, and the dihedral angles with the bridging ligand are 54 and 129°, respectively. Co-ordinated water molecules and the pyridinic rings of the bridges alternatively reside on opposite sides of the row of copper atoms. The organic ligands are planar, and the carbon–carbon and carbon–nitrogen bonds within these ligands are as expected.<sup>8,9</sup> The carbon–oxygen bond distances are in the range 1.31–1.34 Å, with the shorter one being

associated to the exocyclic deprotonated oxygen atom of the terminal anionic ligand.

The polymeric chains are connected through an extensive network of hydrogen bonds (Fig. 2). In particular, one may notice that chains related by a two-fold screw axis are linked by means of ionic O–H···O<sup>−</sup> hydrogen bonds [O···O: 2.446(3) Å] involving the oxygen atoms of both neutral and anionic terminal ligands. These extraordinarily short hydrogen bonds form sheets of chains parallel to the (101) plane in which the shortest interchain Cu···Cu distance is 12.716 Å. These sheets are cross-linked along the *c* axis by also negatively charged O<sub>w</sub>–H···O<sup>−</sup> hydrogen bonds between the axially co-ordinated water molecules and the oxygen atom of



**Fig. 2** A view of the hydrogen bonds (dotted lines) linking the polymeric chains.

the anionic terminal ligand. The shortest Cu...Cu between two neighbour chains belonging to different sheets is 7.098(2) Å. This three-dimensional framework assembled through hydrogen bonds shows microchannels in the centre and the edges of the unit cell along the *a* axis. The void volume per unit cell is 226 Å<sup>3</sup> (14%) as estimated by PLATON.<sup>20</sup> These cavities are filled by unco-ordinated water molecules (Fig. 3). The oxygen atoms of the co-ordinated water molecules, the bridge ligand and the terminal neutral 3-hydroxypyridine base form the outer walls of the large cavities and thus the solvated water molecules are joined to the framework by hydrogen bonds. Hydrogen bonding interactions between solvent molecules also occur along the channels. Table 2 collects all relevant hydrogen bonding parameters. It is interesting to note that the assignment of the neutral pyridine ligand, based on the localisation of the position of the proton, is further substantiated by the particular pattern of the hydrogen bonding interactions. Distances associated with the deprotonated oxygen atom of the anionic ligand are shorter than that found for the oxygen atom of the hydroxyl group, in accordance with the different degree of basicity. No face-to-face or edge-to-face interactions between the aromatic rings have been found in the crystal structure.

### Magnetic and thermal properties

Variable-temperature magnetic susceptibility measurements were performed on polycrystalline samples in the 5–300 K range. The plots of  $\chi_M T$  and  $\chi_M$  vs. *T* are given in Fig. 4. The molar susceptibility value  $\chi_M$  ( $1.54 \times 10^{-3}$  cm<sup>3</sup> mol<sup>-1</sup> at room temperature) increases with decreasing temperature, reaching a maximum of  $10.9 \times 10^{-3}$  cm<sup>3</sup> mol<sup>-1</sup> at 15 K and then rapidly decreases. The  $\chi_M T$  curve exhibits a continuous decrease upon cooling, with  $\chi_M T = 0.388$  cm<sup>3</sup> mol<sup>-1</sup> K ( $\mu_{\text{eff}} = 1.76 \mu_B$ ) at room temperature, which is close to the spin-only value for one non-interacting d<sup>9</sup> copper(II) ion and a value of 0.046 cm<sup>3</sup> mol<sup>-1</sup> K at 5 K. The continuous decreasing in the  $\chi_M T$  values and the maximum observed in the thermal variation of the molar susceptibility clearly indicate the existence of antiferromagnetic interactions in the title compound. Considering the structural features, the experimental

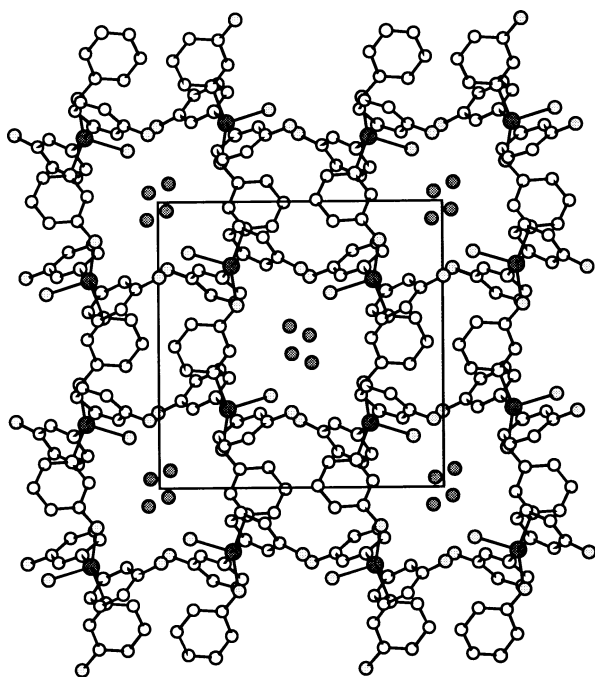


Fig. 3 Projection along the [100] direction of the unit cell of **1** showing the crystallisation water molecules in the microchannels (the *b* axis is vertical, and the *c* axis is horizontal).

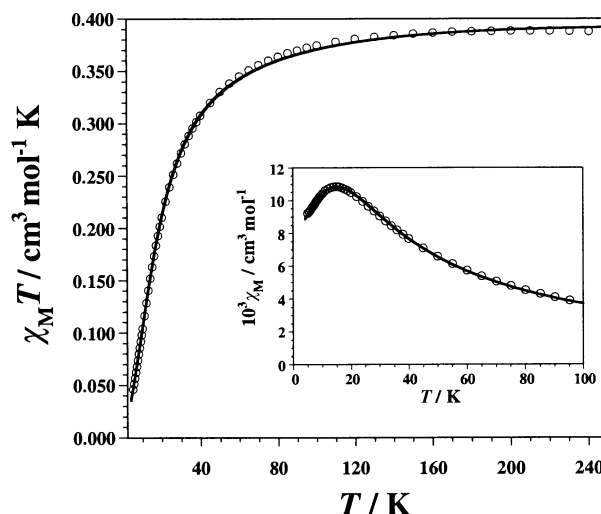


Fig. 4 Thermal variations of the magnetic susceptibility ( $\chi_m$ ) and the product  $\chi_m T$  for compound **1**. Solid curves represent the best fit to the theoretical model.

data were least-squares fitted with a numerical expression proposed for an antiferromagnetic copper(II) uniform chain<sup>21</sup> that leads to  $J$  (triplet-singlet gap) =  $-16.4$  cm<sup>-1</sup>,  $g = 2.15$ ,  $\rho = 0.4\%$  and  $R = 4.5 \times 10^{-5}$ . The percentage of monomeric impurities per mol of copper atom (assuming that the molecular weight of the impurity is the same as that of the investigated compound) is given by  $\rho$  and  $R$  is the agreement factor defined as  $\sum_i [(\chi_M)_{\text{obs}}(i) - (\chi_M)_{\text{calc}}(i)]^2 / \sum_i [(\chi_M)_{\text{obs}}(i)]^2$ . Attempts to evaluate the possible interchain interactions by means of a  $J'$  parameter treated in the molecular field approximation lead to extremely low values without a significant improvement of the fit. As far as we are aware, the two-dimensional compound  $[\text{Cu}(\text{3-pyOH})(\text{O}_2\text{CCF}_3)_2]$ <sup>8</sup> is the only polynuclear first-row transition metal complex containing a bridging 3-hydroxypyridine ligand that has been magneto-structurally characterised to date. In this compound a weak ferromagnetic coupling is observed. The different magnetic behaviour of the two compounds may be understood in terms of the nature of the orbital involved in the exchange interactions, together with the arrangement of the bridging ligand. In the present compound the unpaired electron of the copper(II) ion is essentially described by a magnetic orbital built from the  $d_{x^2-y^2}$  metallic orbital and localised mainly in the basal plane. The pyridin-3-onato bridge binds to the two coplanar basal planes located at two Cu<sup>II</sup> centres and thus an interaction of the two magnetic orbitals *via* a  $\sigma$  pathway is achieved. The small observed antiferromagnetic coupling may be explained by the long Cu...Cu pathway through the bridge and by the almost perpendicular arrangement of the bridging ligand with respect to the basal planes. Ligand  $\pi$  orbitals are essentially orthogonal to the  $d_{x^2-y^2}$  orbital and consequently the  $\pi$  super-exchange pathway, which may contribute to the antiferromagnetic coupling, becomes impossible. This ligand arrangement is also observed in the compound  $[\text{Cu}(\text{3-pyOH})(\text{O}_2\text{CCF}_3)_2]$  but in it the 3-pyOH bridge occupies axial and equatorial positions in two consecutive co-ordination polyhedra; thus, it binds to  $d_{z^2}$  and  $d_{x^2-y^2}$  orbitals located at two Cu<sup>II</sup> centres, respectively, such that the interaction of the two  $d_{x^2-y^2}$  magnetic orbitals *via* a  $\sigma$  pathway also becomes impossible.

The decomposition steps of compound **1** were obtained from its TG and DTA curves in air atmosphere (Fig. 5). The thermal degradation starts in the 40–90 °C temperature range with a loss of weight corresponding to two lattice water molecules and one aqua ligand per empirical formula (expt. 13.2%; calcd. 13.5%). This process appears in the DTA curve

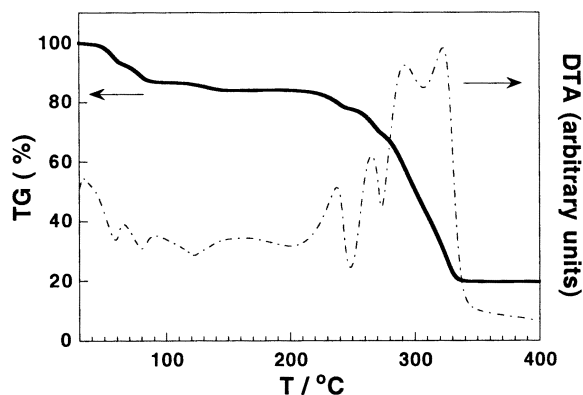


Fig. 5 Thermogravimetric (TG) and DTA curves for compound 1.

as two overlapped endotherms with a  $\Delta H$  of  $35 \text{ kJ mol}^{-1}$ . The temperature range for the release of the water molecules, and especially that corresponding to the loss of the co-ordinated water molecule, are at the lower limit found for this type of water molecules, probably owing to their localisation in the crystal structure. According to Petit and Coquerel<sup>22</sup> the mechanism of dehydration is dependent on topological and energetic considerations, so that it is favoured by the accessibility of water molecules to the tunnels existing in the crystal structure and by the low liberation of energy. Solvated molecules are located in the middle of the channels and co-ordinated water molecules point toward the microchannels; they thus have an easy access to the tunnels. The totally dehydrated compound remains stable up to  $110^\circ\text{C}$  and a second endothermic ( $T_{\text{max}} = 125^\circ\text{C}$ ,  $\Delta H = 88 \text{ kJ mol}^{-1}$ ) weight loss is observed from  $110$  to  $145^\circ\text{C}$ , corresponding to the loss of one OH group per formula unit (expt. 4.1%; calcd. 4.2%). The loss of the OH group is confirmed by the change in the IR bands in the  $3500\text{--}3000 \text{ cm}^{-1}$  range. A similar dehydroxylation process is observed between  $120$  and  $160^\circ\text{C}$  during the thermal degradation of the compound  $[\text{Co}(\text{N}_3)_2(3\text{-pyOH})_4]$ .<sup>23</sup> The resulting black product is stable up to  $200^\circ\text{C}$  above which temperature are seen four successive exothermic processes, without stable residues, to yield copper(II) oxide as a final black powdery product above  $350^\circ\text{C}$  (expt. 80.4%, calcd. 80.2%).

With the aim to obtain some information on the structural properties of the stable residues, we have recorded X-ray powder diffraction spectra at  $100$  and  $170^\circ\text{C}$  (see Electronic Supplementation Information). Diffraction profiles show a significant peak broadening, which indicates a significant loss of crystallinity during the two first thermal degradation processes, especially in the release of the OH group, and thus unfortunately no clear indications of structural changes could be deduced. The overall magnetic behaviour of the residue obtained after the loss of the water molecules apparently corresponds to a polymeric system with an antiferromagnetic coupling between the metal centres. At room temperature, the residue has a  $\chi_{\text{M}}T$  value of  $0.390 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ , which is in accord with the spin-only value in the absence of any exchange interaction. Upon cooling, the value decreases very slowly to a value of  $0.338 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$  at  $80 \text{ K}$  and then decreases rapidly to  $0.012 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$  at  $5 \text{ K}$ . The  $\chi_{\text{M}}$  value increases (from  $1.31 \times 10^{-3} \text{ cm}^3 \text{ mol}^{-1}$  at room temperature) upon cooling, reaching a maximum at  $20 \text{ K}$  ( $8.17 \times 10^{-3} \text{ cm}^3 \text{ mol}^{-1}$ ) and then the curve drops sharply upon further cooling. The magnetic data of the dehydroxylated product show that this stable black residue is diamagnetic over the whole temperature range. This fact seems to indicate that the

dehydroxylation step must be tied to a more complex process that reduces copper(II) to copper(I).

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