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FULL PAPER

Solid state polymerization causing transition to a ferromagnetic state. Crystal structures and magnetic properties of $[Cu_2(dpp)(H_2O)(dmso)Cl_4]\cdot dmso$ and $[Cu_2(dpp)Cl_4]_n$ (dpp = 2,3-bis(2-pyridyl)pyrazine)

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The preparation, crystal structures and variable-temperature magnetic susceptibility data for $[Cu_2(dpp)(H_2O)(dmso)Cl_4]\cdot dmso$ (**1a**) and $[Cu_2(dpp)Cl_4]_n$ (**2**) (dpp = 2,3-bis(2-pyridyl)pyrazine, dmso = dimethyl sulfoxide) are reported. **1a** consists of dinuclear dpp-bridged molecules with chlorine, water and dmso serving as terminal ligands. The two copper atoms are crystallographically independent, with distorted square pyramidal and trigonal bipyramidal coordination geometries, respectively. In a first approximation **2** may be described as a chain compound with out-of-plane mono-μ-chloro bridges (Cu–Cl–Cu–Cl). Only one of the crystallographically independent copper atoms participates in this chain formation. Neighbouring chains are, however, linked into zig-zag sheets through somewhat weaker, out-of-plane, di-μ-chloro interactions involving the other copper atom. Both copper atoms have square pyramidal coordination geometries, dpp coordinating in equatorial positions through both its pyridyl and pyrazine nitrogen atoms. Compound **1a** is desolvated under heating in a dynamic dinitrogen atmosphere at 130 °C, resulting in compound **1b**. Variable-temperature magnetic susceptibility measurements on **1a** (solvated state) reveal a very weak antiferromagnetic interaction between the copper(II) ions across bridging dpp ($J = -0.6(1)$ cm^{-1}). **1b** exhibits an overall ferromagnetic behaviour which is identical to that of compound **2** ($J = +6.8(1)$ cm^{-1}, $J' = +1.0(1)$ cm^{-1}, J and J' being the exchange coupling through the single and the double chloro bridge, respectively). Powder diffraction measurements on **1b** confirm that this compound is isostructural with **2**, in agreement with the magnetic results.

Introduction

Structures and magnetic properties of copper(II) complexes with mono-atomic bridges have been extensively studied during the last three decades. In the case of planar di-hydroxy bridges it has been possible to derive a magneto-structural correlation between the magnetic exchange parameter and the bond angle at the bridging oxygen.[1] Although the simple picture referred to above must be modified by taking into account variations in the metal coordination geometry and deviations from planarity in the Cu_2X_2 bridge system, relationships between structural features and magnetism are fairly well mapped out for some first-row atom mono-atomic bridges like hydroxide, alkoxide and end-on azide.[1,2] For chloro-bridged complexes, however, derivation of simple magneto-structural relationships has proved to be more difficult,[3–6] although by now a number of di-μ-chloro-bridged dinuclear [4] and chain [5] compounds, as well as mono-μ-chloro-bridged chains [6] have been fully characterized magnetically and structurally. This may be due to the large variation in structural features observed, together with the fact that chloride possesses both p and d orbitals which may participate in creating an exchange pathway.

In the context of our magneto-structural studies on polynuclear complexes with 2,3-bis(2-pyridyl)pyrazine (dpp) as bridging ligand,[7] we have isolated the copper(II) complexes of formula $[Cu_2(dpp)(H_2O)(dmso)Cl_4]\cdot dmso$ (**1a**) and $[Cu_2(dpp)Cl_4]_n$ (**2**) (dinuclear and sheetlike compounds, respectively). The former compound loses the dmso and water molecules very easily to yield the compound $[Cu_2(dpp)Cl_4]_n$ (**1b**) which is isostructural with **2**, the magnetic coupling changing from weak antiferromagnetic (**1a**) to ferromagnetic (**2**). The present work focuses on the magneto-structural results of this unprecedented solid state transformation.

Experimental

Materials

All chemicals were purchased from commercial sources and used as received.

Preparations

$[Cu_2(dpp)(H_2O)(dmso)Cl_4]\cdot dmso$ 1a and $[Cu_2(dpp)Cl_4]_n$ 1b. A mixture of 0.427 mmol (100 mg) of dpp and 0.854 mmol (146 mg) $CuCl_2\cdot 2H_2O$ was dissolved in 15 cm^3 of dmso and 3 cm^3 of water under stirring at room temperature. Evaporation at room temperature over several weeks yielded green, crystalline elongated plates of **1a**, which have been structurally characterized by X-ray crystallography (see below). The crystals are stable in dmso, but disproportionate after several days in the air, and a green powder results. TG/DSC curves for **1a** shows two fused steps of mass loss (endothermic process) starting at 80 °C and ending at 130 °C with a plateau until 200 °C. Decomposition starts at higher temperatures. The total observed weight loss between 80 and 130 °C (25.60%) corresponds to the

release of two dmso and one water molecules per formula unit (calculated value is 25.70%) to yield **1b**. The same transformation also occurs when crystals of **1a** are left to dry in air at room temperature over a couple of weeks. (Found for the desolvated species: C, 33.41; H, 1.87; N, 11.01; S, 0.26. Calc. for $C_{14}H_{10}Cl_4Cu_2N_4$: C, 33.42; H, 2.00; N, 11.14; S, 0.00%.)

$[Cu_2(dpp)Cl_4]_n$ 2. 0.76 mmol (178 mg) of dpp and 1.52 mmol (259 mg) of $CuCl_2{\cdot}2H_2O$ were added to 10 cm^3 of water and stirred at 70 °C for 30 minutes. The solution was left to evaporate at room temperature until precipitation just started. After filtration, ethanol was added, resulting in a green precipitate. The product was collected by filtration and washed with ether. (Found: C, 33.45; H, 2.10; N, 11.04; Cl, 28.22; Cu 25.27. Calc. for $C_{14}H_{10}Cl_4Cu_2N_4$: C, 33.42; H, 2.00; N, 11.14; Cl, 28.18; Cu, 25.25%.) Needle shaped, green crystals suitable for X-ray crystallographic work were obtained by very slow evaporation from a mixture of 0.50 mmol (117 mg) dpp and 1.00 mmol (170 mg) of $CuCl_2{\cdot}2H_2O$ in a 50/50 water/ethanol solution (30 cm^3).

Physical techniques

Infrared spectra were recorded with a Nicolet 800 FTIR spectrophotometer as KBr pellets in the 4000–400 cm^{-1} region. The desolvation of **1a** was performed on a sample of 19.5878 mg with a Mettler Toledo TGA/SDTA 851^e simultaneous thermobalance and differential scanning calorimeter, increasing the temperature at 5 °C min^{-1} to a maximum temperature of 200 °C in a dynamic dinitrogen atmosphere of approximately 20 cm^3 min^{-1}. The magnetic susceptibility measurements of polycrystalline samples of **1a**, **1b** and **2** were measured over the temperature range 1.9–290 K with a Quantum Design SQUID susceptometer and using an applied magnetic field of 250 G. The complex $(NH_4)_2Mn(SO_4)_2{\cdot}6H_2O$ was used as a susceptibility standard. Diamagnetic corrections of the constituent atoms were estimated from Pascal's constants and found to be -377×10^{-6} (**1a**), and -266×10^{-6} cm^3 mol^{-1} (**1b**, **2**) per two copper(II) ions.[8] A value of 60×10^{-6} cm^3 mol^{-1} was used for the temperature-independent paramagnetism of the copper(II) ion. The weighed sample of **1a** (crystals picked from the mother liquor and dried on filter paper in the open air) is introduced into the SQUID and it is purged with a helium flow without vacuum at room temperature. This procedure precludes any loss of solvent from **1a** during the measurement. The usual procedure is used for the stable samples **1b** and **2**. Powder diffraction data for compound **1b** were recorded on a Guiner-Hägg camera at ambient temperature using Cu-$K_{\alpha 1}$ radiation (λ = 1.540598 Å).

Crystallography

Single crystal studies of compounds 1a and 2. Crystal parameters and refinement results are summarized in Table 1. Diffraction data were collected using an Enraf-Nonius CAD-4 diffractometer (**1a**) and a SMART 2K CCD area detector diffractometer (**2**). For **1a** the data were corrected for linear decay as three reference reflections monitored throughout the data collection decreased by an average of 7%. Empirical absorption corrections were carried out based on ψ-scans[9a,b] and the SADABS procedure,[9c,d] respectively. The structures were solved by direct methods and refined by full-matrix least-squares refinement based on F^2 and including all reflections. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms bound to aromatic carbon were included at idealized, calculated positions while water hydrogen atoms were located in difference Fourier maps and subsequently refined according to the riding model. Hydrogen atoms belonging to the dmso molecules were included and refined as idealized, rotating CH_3.

Data reduction for **1a** was done with the XCAD program,[10] whereas data collection and integration for **2** were done with the SMART and SAINT programs.[11] Structure solutions, refinements and graphics were performed with the SHELXS-86, SHELXL-93 and XP programs.[12] Selected bond distances and angles are listed in Tables 2 and 3.

Powder diffraction data of **1b** gave a unit cell that agrees very well with that determined for compound **2** in the single crystal work. Based on the indexing of 33 lines, 15 of these being single lines, the following values were obtained (at room temperature): a = 15.223 Å, b = 15.07513 Å, c = 7.263 Å, β = 91.25°, V = 1666.3 Å^3. The figure of merits commonly used to evaluate the reliability of powder pattern indexing are M_{20} = 15 and F_{20} = 33.[13a,b]

CCDC reference numbers 164934 and 164935.

See http://www.rsc.org/suppdata/dt/b1/b103588f/ for crystallographic data in CIF or other electronic format.

Table 1 Summary of crystallographic data and structure refinement for $[Cu_2(dpp)(H_2O)(dmso)Cl_4]{\cdot}dmso$ **1a**, and $[Cu_2(dpp)Cl_4]_n$ **2**

	1a	**2**
Formula	$C_{18}H_{24}Cl_4Cu_2N_4O_3S_2$	$C_{14}H_{10}Cl_4Cu_2N_4$
M	677.41	503.14
T/K	293(2)	173
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$
a/Å	10.434(2)	15.1964(3)
b/Å	11.215(2)	15.0813(8)
c/Å	12.8942(15)	7.2346(4)
α/°	89.639(12)	
β/°	73.372(11)	91.876(3)
γ/°	66.079(13)	
U/Å^3	1311.1(3)	1657.15(13)
Z	2	4
D_c/g cm^{-3}	1.716	2.017
μ/mm^{-1}	2.2171	3.215
Reflections collected	8258	11809
Unique reflections	6001 (R_{int} = 0.0195)	3630 (R_{int} = 0.0867)
2θ maximum/°	55	54
R [$I > 2\sigma(I)$]	0.0353	0.0445
R_w [$I > 2\sigma(I)$]	0.0776	0.0676
R [all refl.]	0.0499	0.0997
R_w [all refl.]	0.0861	0.1164

Table 2 Bond lengths (Å) and angles (°) in the copper coordination sphere of $[Cu_2(dpp)(H_2O)(dmso)Cl_4]{\cdot}dmso$ **1a**, with e.s.d.s in parentheses

Cu(1)–O(1)	1.974(2)	Cu(2)–O(2)	1.969(2)
Cu(1)–N(1)	2.027(2)	Cu(2)–N(4)	1.981(2)
Cu(1)–N(2)	2.049(2)	Cu(2)–N(3)	2.187(2)
Cu(1)–Cl(1)	2.2844(9)	Cu(2)–Cl(3)	2.2861(9)
Cu(1)–Cl(2)	2.4531(9)	Cu(2)–Cl(4)	2.2962(9)
O(1)–Cu(1)–N(1)	89.94(9)	O(2)–Cu(2)–N(4)	171.01(10)
O(1)–Cu(1)–N(2)	161.73(9)	O(2)–Cu(2)–N(3)	93.59(9)
N(1)–Cu(1)–N(2)	78.90(9)	N(4)–Cu(2)–N(3)	77.50(9)
O(1)–Cu(1)–Cl(1)	91.91(7)	O(2)–Cu(2)–Cl(3)	92.63(8)
N(1)–Cu(1)–Cl(1)	157.54(7)	N(4)–Cu(2)–Cl(3)	92.62(8)
N(2)–Cu(1)–Cl(1)	93.06(7)	N(3)–Cu(2)–Cl(3)	117.79(7)
O(1)–Cu(1)–Cl(2)	97.00(8)	O(2)–Cu(2)–Cl(4)	89.80(8)
N(1)–Cu(1)–Cl(2)	95.64(7)	N(4)–Cu(2)–Cl(4)	92.19(8)
N(2)–Cu(1)–Cl(2)	98.45(7)	N(3)–Cu(2)–Cl(4)	110.52(7)
Cl(1)–Cu(1)–Cl(2)	106.33(3)	Cl(3)–Cu(2)–Cl(4)	131.35(4)

Results and discussion

Structures

$[Cu_2(dpp)(H_2O)(dmso)Cl_4]{\cdot}dmso$ (1a). The neutral, dpp-bridged dinuclear complex unit contains two crystallographically independent copper(II) atoms (Fig. 1). Cu(1) has a distorted square pyramidal coordination sphere with two dpp nitrogen atoms (Cu–N 2.027(2) and 2.049(2) Å), a dmso oxygen

Table 3 Selected bond lengths (Å) and angles (°) for $[Cu_2(dpp)Cl_4]_n$ **2** with e.s.d.s in parentheses

Cu(1)–N(1)	2.024(4)	Cu(2)–N(4)	2.024(4)
Cu(1)–N(2)	2.088(3)	Cu(2)–N(3)	2.049(3)
Cu(1)–Cl(2)	2.2425(13)	Cu(2)–Cl(3)	2.2394(13)
Cu(1)–Cl(1)	2.3043(12)	Cu(2)–Cl(4)	2.2708(12)
Cu(1)–Cl(1a)	2.5600(13)	Cu(2)–Cl(4c)	2.7726(13)
N(1)–Cu(1)–N(2)	79.31(14)	N(4)–Cu(2)–N(3)	79.53(14)
N(1)–Cu(1)–Cl(2)	170.74(10)	N(4)–Cu(2)–Cl(3)	164.42(11)
N(2)–Cu(1)–Cl(2)	91.67(11)	N(3)–Cu(2)–Cl(3)	91.08(11)
N(1)–Cu(1)–Cl(1)	93.25(10)	N(4)–Cu(2)–Cl(4)	95.43(11)
N(2)–Cu(1)–Cl(1)	154.59(11)	N(3)–Cu(2)–Cl(4)	173.76(11)
Cl(2)–Cu(1)–Cl(1)	94.08(5)	Cl(3)–Cu(2)–Cl(4)	93.01(5)
N(1)–Cu(1)–Cl(1a)	92.18(11)	N(4)–Cu(2)–Cl(4c)	91.53(11)
N(2)–Cu(1)–Cl(1a)	107.83(10)	N(3)–Cu(2)–Cl(4c)	92.47(10)
Cl(2)–Cu(1)–Cl(1a)	92.58(4)	Cl(3)–Cu(2)–Cl(4c)	101.35(5)
Cl(1)–Cu(1)–Cl(1a)	96.63(4)	Cl(4)-Cu(2)–Cl(4c)	91.34(4)
Cu(1)–Cl(1)–Cu(1b)	98.46(4)	Cu(2)–Cl(4)–Cu(2c)	88.66(4)

Symmetry transformations used to generate equivalent atoms: (a) $x, -y + 1/2, z-1/2$; (b) $x, -y + 1/2, z + 1/2$; (c) $-x + 1, -y, -z - 1$.

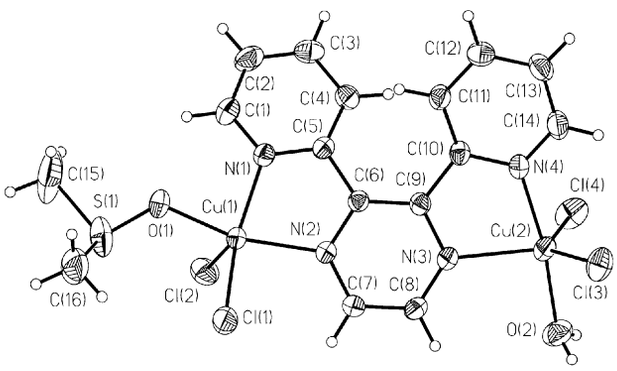

Fig. 1 The dinuclear complex $[Cu_2(dpp)(H_2O)(dmso)Cl_4]$ in **1a**. Thermal ellipsoids are plotted at the 50% probability level.

atom (Cu–O 1.974(2) Å) and a chlorine (Cu–Cl 2.2844(9) Å) in the equatorial plane; another chlorine occupying the apical position (Cu–Cl 2.4531(9) Å). Cu(2) may best be described as distorted trigonal bipyramidal with the dpp pyrazine nitrogen (Cu–N 2.187(2) Å) and two chlorine atoms (Cu–Cl 2.2861(9) and 2.2962(9) Å) forming the equatorial plane, and with dpp pyridyl nitrogen (Cu–N 1.981(2) Å) and the water oxygen (Cu–O 1.969(2) Å) coordinating in the axial positions. The mean pyrazine plane forms a dihedral angle of 31.7° with the basal plane of the square pyramidal Cu(1) and an angle of 73.5° with the equatorial plane of the trigonal bipyramidal Cu(2). The Cu(1)···Cu(2) distance across the dpp bridge is 6.917(2) Å.

Centrosymmetrically related molecules form stacks running parallel to the *b*-axis; for every second pair of molecules in the stack there are relatively short Cu···Cl distances (Cu(1)···Cl(3a) = 3.767(1) Å) opposite to the apically coordinated chlorine of the square pyramidal copper atom (Fig. 2). Within the stacks there is a certain degree of overlap between pyrazine and pyridyl rings. Distances from the pyrazine plane to individual atoms in the overlapping regions of the pyridyl rings range from 3.68 to 4.06 Å on the side where the Cu···Cl contact is present and from 3.33 to 3.56 Å on the opposite side; only the latter may indicate a certain degree of π–π interaction. The shortest intermolecular metal···metal distance occurs within the stack, Cu(1)···Cu(2a) across the weak chloro interaction being 5.653(1) Å, while the Cu(2)···Cu(2a) distance is 6.513(1) Å (Fig. 2). The shortest inter-stack copper···copper distance is Cu(1)···Cu(2) ($-x$, $1 - y$, $-z$) = 6.258(1) Å. Solvent dmso molecules link neighbouring stacks through hydrogen bonds to the coordinated water molecules, the O···O distances being 2.686(4) and 2.759(4) Å. The copper···copper distance across this contact is 7.412(1) Å.

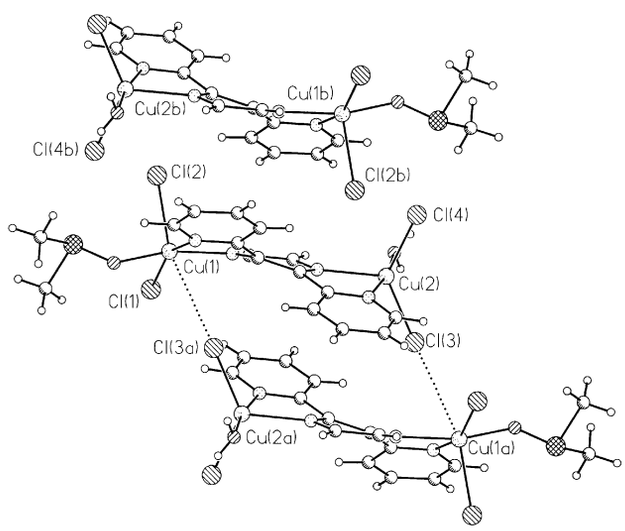

Fig. 2 Stack of dinuclear units in **1a**. The shortest intermolecular Cu···Cl contacts are indicated (Cu(1)···Cl(3a) = 3.767(1) Å). Symmetry operations: (a) $1 - x, -y, -z$; (b) $1 - x, 1 - y, -z$.

$[Cu_2(dpp)Cl_4]_n$ (2). The individual dpp-bridged $[Cu_2(dpp)Cl_4]$ entity contains two crystallographically independent copper atoms. The units are linked through strong out-of-plane mono-μ-chloro bridges into uniform chains extending along the *c*-glide plane (Fig. 3), and these chains are further connected through somewhat weaker out-of-plane di-μ-chloro bridges into zig-zag formed layers (Fig. 4). Cu(1), the copper atom which participates in the chain formation, is distorted square pyramidal with two dpp nitrogen atoms (Cu–N 2.024(4) and 2.088(3) Å) and two chlorine (Cu–Cl 2.2425(13) and 2.3043(12) Å) in equatorial positions and a chlorine in apical position (Cu–Cl 2.5600(13) Å). The apical bond and the longer of the equatorial Cu–Cl bonds are associated with the mono-μ-chloro bridge, which has a bond angle at chlorine of 98.46(4)° (Cu(1)–Cl(1)–Cu(1b)). This bridge is unique among the single-chloro bridged chains in having the shortest apical bond and the smallest bridge bond angle reported so far.[6] The zigzag Cu–Cl–Cu–Cl feature of the chain, with all copper atoms to one side and all clorine atoms to the other side is equivalent to the configuration observed in the $[Cu(pepci)Cl]_n(PF_6)_n$ chain,[6l] and differs from the other reported mono-μ-chloro bridged chains where the orientation of the bridging atom alternates.[6a–k,m,n] Cu(2), the copper atom which participates in the di-μ-chloro bridge, is also square pyramidal with two dpp nitrogen atoms (Cu–N 2.024(4) and 2.049(3) Å) and two chlorine (Cu–Cl 2.2394(13) and 2.2708(12) Å) in equatorial positions and a

chlorine in the apical position (Cu–Cl 2.7726(13) Å). Again, the longer equatorial bond and the apical bond are associated with the chloro bridge, which in this case has a bond angle at chlorine of 88.66(4)° (Cu(2)–Cl(4)–Cu(2c)). This bridging geometry is similar to geometries observed in some of the out-of-plane di-μ-chloro bridges in copper(II) dimers,[4] but the axial bond is shorter than any of those observed for corresponding bridges in the polynuclear compounds.[5]

The intrachain Cu(1)···Cu(1a) distance, across the mono-μ-chloro bridge, is 3.688(1) Å, while the Cu(2)···Cu(2c) distance across the di-μ-chloro bridge is 3.543(1)Å. Across the bridging dpp the Cu(1)···Cu(2) distance is 6.820(1) Å, which is the shortest we have observed for this bridge.[7]

The equatorial plane of Cu(1) has an appreciable tetrahedral distortion (maximum atomic deviation 0.217 Å) with the copper atom displaced by 0.170 Å towards the apical ligand; for Cu(2) the distortion is moderate (maximum atomic deviation 0.087 Å) and copper is displaced by 0.158 Å towards the apical chlorine.

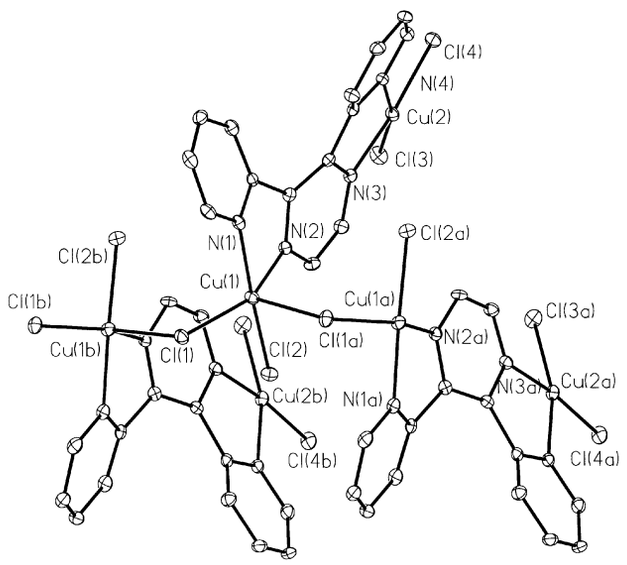

Fig. 3 Section of the $[Cu_2(dpp)Cl_4]_n$ chain in **2**. Thermal ellipsoids are plotted at the 30% probability level. Symmetry operations: (a) x, $-y + 1/2$, $z - 1/2$; (b) x, $-y + 1/2$, $z + 1/2$.

The equatorial planes of Cu(1) and Cu(2) are oriented at 30.6° to each other, and at 9.5° and 22.4°, respectively, to the mean plane of the bridging dpp. Within the chain the dihedral angle between equatorial planes of neighbouring Cu(1) atoms is 4.9°.

The bis-bidentate dpp ligand in this complex coordinates with all of its nitrogen atoms in equatorial positions of the two square pyramidal copper atoms. It is the first time this bridging mode has been observed in di- and poly-nuclear Cu(II)–dpp complexes. In previous investigations one or two of the Cu–N bonds have been found to be long, axial bonds.[7] The puckering of the pyrazine ring and the torsional angles related to the twist of the pyridyl rings are, however, within the ranges found previously.

It is difficult to envisage a specific model for the polymerization reaction from **1a** to **2**. An inspection of the crystal packing in **1a** reveals that if dmso and water molecules are removed, the remaining structure contains well separated sheets, each sheet consisting of stacks of dinuclear units. The continuity of the empty space must be assumed to permit relatively large movements of the molecules at a low energy cost, the formation of the single- and double-μ-chloro bridges of course providing the energy compensation. On conversion from **1a** to **2** the stacking pattern found in **1a** is profoundly changed, overlapping dpp units in **2** are one unit cell apart (order of 7 Å). Probably the formation of the single chloro bridge is accompanied by a displacement in different directions of alternating molecules within a stack as viewed in **1a**, this movement also facilitating the contact between stacks to form the double chloro bridges.

Infrared spectra

The IR spectra of **1b** and **2** are identical, and are rather similar to that of the free ligand, the dpp aromatic ring vibrations in the 1600–1350 cm^{-1} region being shifted to somewhat higher wavenumbers in the complexes as expected upon metal co-ordination.[7,14a] Additionally in the spectrum of **1a** a strong, sharp peak at 953 cm^{-1}, and a broader, split band at 990–1015 cm^{-1} appear. Both of these features occur at lower wavenumbers than the absorption of free dmso (1100–1055 cm^{-1} region); the peak at the lowest wavenumber may be assigned to dmso coordinated to the metal through oxygen, while the other band is due to the hydrogen bound solvent dmso.[14b]

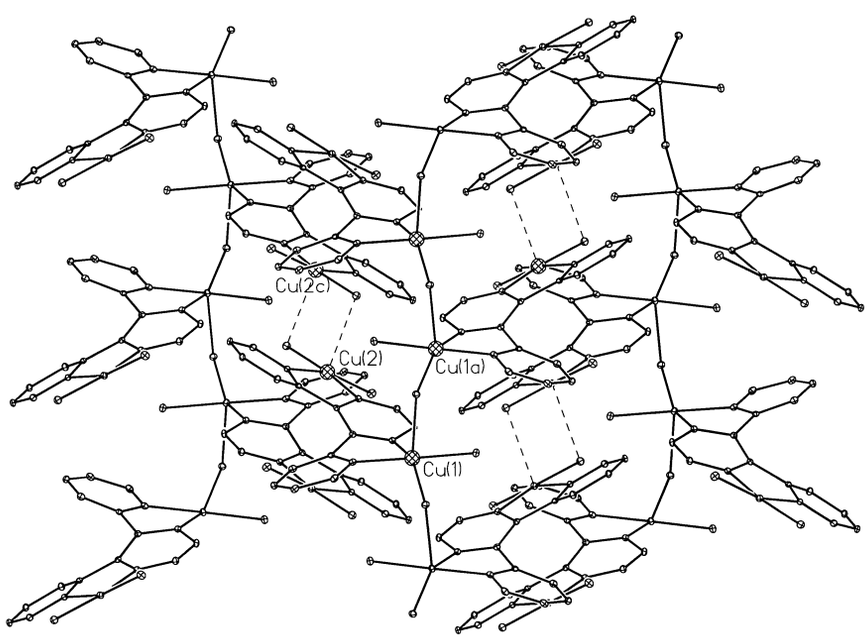

Fig. 4 Connection of $[Cu_2(dpp)Cl_4]_n$ chains into sheets.

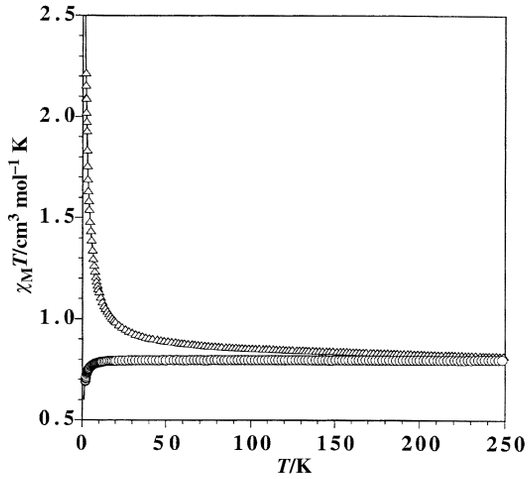

Fig. 5 $\chi_M T$ *versus* T plot for complex **1a** (○) and **2** (△). The solid lines are the best fit to the data (see text).

Magnetic properties

The magnetic properties of the complexes **1a** and **2** in the form of $\chi_M T$ *versus* T plots (χ_M being the magnetic susceptibility per two copper(II) ions) are shown in Fig. 5. The magnetic curve of **1b** is identical to that of **2**. The values of $\chi_M T$ at room temperature are 0.80 (**1a**) and 0.82 cm^3 mol^{-1} K (**2**), and they are as expected for two magnetically isolated spin doublets. These values remain practically constant when cooling down to 150 K and at lower temperatures they exhibit opposite trends: those of **1a** slightly decrease whereas those of **2** sharply increase to reach values of 0.69 (**1a**) and 2.21 (**2**) cm^3 mol^{-1} K at 1.9 K. The shape of the curves are characteristic of weak antiferromagnetic (**1a**) and overall ferromagnetic (**2**) behaviour, respectively. No susceptibility maximum was observed.

Given that compound **1a** consists of dpp-bridged copper(II) dinuclear units, we have analyzed its magnetic data through a simple Bleaney–Bowers expression,[15a] the isotropic Hamiltonian used being $\hat{H} = -J\hat{S}_1 \cdot \hat{S}_2$ where $\hat{S}_1 = \hat{S}_2 = 1/2$ (local spins) and J the intradimer exchange coupling parameter. Least-squares fit leads to the following values: $J = -0.6(1)$ cm^{-1}, $g = 2.07(1)$ and $R = 2.4 \times 10^{-6}$ (R is the agreement factor defined as $\Sigma_i[(\chi_M T)_{obs(i)} - (\chi_M T)_{calc(i)}]^2/\Sigma_i [(\chi_M T)_{obs(i)}]^2$). The small antiferromagnetic coupling constant determined for **1a** is in good qualitative agreement with the values previously found for dpp-bridged copper(II) complexes (values of J ranging from -1.4 to -0.2 cm^{-1}).[7] The magnetic orbital on Cu(2) is of the d_{z^2} type with the ternary axis defined by the dpp pyridyl nitrogen and the water oxygen. For Cu(1) the magnetic orbital is of the $d_{x^2-y^2}$ type with the two dpp nitrogen atoms in equatorial positions. The overlap between the two types of magnetic orbitals through the pyrazine fragment of bridging dpp (σ exchange pathway) is very weak (very low spin density on the pyrazine nitrogen of the Cu(2) site) and thus only a weak magnetic coupling would be expected, as observed. The occurrence of hydrogen bonding linking two centrosymmetrically related Cu(2) atoms through the coordinated water and the solvent dmso, as well as the weak intermolecular Cu(1)···Cl(3a) interaction within the stack of molecules, yield connections that could also be operative as exchange pathways at very low temperatures. This suggests that the computed antiferromagnetic coupling constant across dpp represents an upper limit.

Recalling the structure of complex **2**, we notice the occurrence of single chloro (Cl(1)) bridged chains of Cu(1) atoms which are linked to terminal Cu(2) atoms through bridging dpp units (Fig. 3). In addition the Cu(2) atoms from adjacent chains are connected through longer out-of-plane copper to chloro interactions (Cu(2)Cl(4)Cl(4c)Cu(2c) framework) leading to a zig-zag layer-like structure. The three bridging motifs are all potentially able to transmit significant exchange interactions, but there is no theoretical approach available to treat adequately such a complex system. Taking into account that the interaction through bridging dpp has been shown to be weak and antiferromagnetic, that the chloro-bridges involved in the layer-formation are appreciably longer than those involved in the chain-formation (axial Cu–Cl of 2.77 Å *versus* 2.56 Å), and that the value of χT in the low temperature range (2.21 cm^3 mol^{-1} K at 1.9 K per two copper(II) atoms) is much higher than that expected for a ferromagnetically coupled copper(II) dimer, the implication of the magnetic data is that the dominant ferromagnetic interaction occurs through the single-chloro bridged copper(II) chain. Consequently, we have in a first approach analyzed the magnetic data of **2** through the numerical expression proposed by Baker and Rushbrooke[15b] for a ferromagnetically coupled uniform chain of spin doublets: $\chi = Ng^2\beta^2/4kT\ [(1 + Ax + Bx^2 + Cx^3 + Dx^4 + Ex^5)/(1 + A'x + B'x^2 + C'x^3 + D'x^4)]^{2/3}$ where $x = |J|/kT$ and $A = 5.7979916$, $B = 16.902653$, $C = 29.376885$, $D = 29.832959$, $E = 14.036918$, $A' = 2.7979916$, $B' = 7.0086780$, $C' = 8.6538644$, $D' = 4.5743114$. A common Lande factor g for the Cu(1) and Cu(2) atoms was used, and a Curie law term was added to account for the occurrence of the pendant Cu(2) atom. The best-fit parameters obtained through this procedure are: $J = +7.4(1)$ cm^{-1}, $g = 2.08(1)$ and $R = 1.7 \times 10^{-4}$. In order to take into account the other exchange pathways, the procedure was subsequently modified by replacing T by a $T - \theta$ term in the above expression (θ being a constant). The results of the fit then are: $J = +6.0(1)$ cm^{-1}, $\theta = +0.22(1)$ K, $g = 2.08(1)$ and $R = 4.1 \times 10^{-5}$. The fit is better than for the curve calculated according to the first model. The exchange coupling through the single chloro-bridge is clearly ferromagnetic, as is the overall magnetic interaction in this system. Keeping in mind that the exchange coupling between copper(II) ions through bridging dpp is antiferromagnetic, the results of the fit strongly suggest that the interaction between Cu(2) atoms through the double-μ-chloro bridge has to be ferromagnetic and larger than the antiferromagnetic one through dpp. In order to estimate a lower limit for the interaction through the double chloro-bridge, a third fitting procedure was used in which half of a simple Bleaney–Bowers term for a copper(II) dimer was added to the ferro chain expression listed above. The following sets of parameters resulted: $J = +6.8(1)$ cm^{-1} (single chloro bridge), $J' = +1.0(1)$ cm^{-1} (double chloro bridge), $g_1 = 2.08(1)$ (catena), $g_2 = 2.06(1)$ (dinuclear) and $R = 1.5 \times 10^{-5}$. The solid line in Fig. 5 corresponds to the fit through this last model.

Magnetic interaction across out-of-plane chloro bridges are expected to be small due to the fact that the magnetic orbital of the copper(II) is mainly delocalized in the equatorial plane, and that consequently the spin density on its axial position will be very small. This is also in agreement with the experimental findings of small J-values, negative or positive.[4–6] In fact, only once has a relatively large ferromagnetic interaction been observed in a dinuclear chloro-bridged complex, but in this case one of the bridging chlorines is situated in the basal plane of both copper atoms.[4n]

Table 4 lists the available magneto-structural data on out-of-plane mono-μ-chloro bridges. It is evident that no simple relationship between J-value and structure parameters of the type found for hydroxo-bridges, is present. The bridge in compound **2** displays the strongest ferromagnetic exchange found in this series, and is characterized by having the smallest observed bond angle at the bridging chlorine as well as the shortest axial $Cu–Cl_{ax}$ bond distance. Various parameters have been considered in the pursuit of identifying systematic magneto-structural variations for chloro-bridged complexes. Although it is clear that the dependence of the bridging angle at chlorine (ϕ) is less dominating than in hydroxo complexes, simple orbital

Table 4 Structural and magnetic data for out-of-plane mono-μ-chloro-bridged copper(II) chains

Compound[a]	J/cm^{-1}	ϕ[b]/°	α[c]/°	β[d]/°	Cu–Cl_{ax}/Å	Cu···Cu/Å	ϕ/(Cu–Cl)	Ref.
$[Cu(dmso)_2Cl_2]_n$	−12.2	144.6	146.1	173.0	2.70	4.76	53.6	6*a–c*
$[Cu(imH)_2Cl_2]_n$	−4.2	117.0	166.9	174.3	2.75	4.37	42.5	6*c–e*
$[Cu(pepci)Cl]_n(PF_6)_n$	−2.8	137	156.6	170.3	2.83	4.75	48.4	6*l*
$[Cu(bipy)Cl_2]_n$	−2.3	107.5	158.5	171.5	2.67	4.01	40.3	6*h*
$[Cu(caf)(H_2O)Cl_2]_n$	+1.0	128.1	178.8	161.0	2.79	4.60	45.9	6*c,f*
$[Cu(paphy)Cl]_n(PF_6)_n{\cdot}nH_2O$	+1.3	102.0	167.6	160.1	2.81	3.92	36.3	6*n*
$[Cu(maep)Cl_2]_n$	+3.2	113.6	176.0	165.7	2.79	4.26	40.7	6*c,g*
$[Cu_2(dpp)_2Cl_4]_n$	+6.8	98.5	154.6	170.7	2.56	3.69	38.5	This work

[a] dmso = dimethyl sulfoxide; imH = imidazole; pepci = *N*-(2-pyridylethyl)pyridine-2-carbaldimine; bipy = 2,2′-bipyridine; caf = caffeine; paphy = pyridine-2-carboxaldehyde-2-pyridylhydrazone; maep = 2-(2-methylaminoethyl)pyridine. [b] Cu–Cl(bridge)–Cu bond angle. [c] *trans* L–Cu–Cl(bridge) bond angle. [d] *trans* L–Cu–Cl(terminal) or *trans* N–Cu–N bond angle.

Table 5 Structural and magnetic data for out-of-plane di-μ-chloro-bridged copper(II) dinuclear units

Compound[a]	J/cm^{-1}	ϕ[b]/°	α[c]/°	β[d]/°	Cu–Cl_{ax}/Å	Cu···Cu/Å	ϕ/(Cu–Cl)	Ref.
$[Cu(tmso)Cl_2]_2$	−16.0	88.5	145.7	165.2	3.02	3.74	29.3	4*a*
$[Cu(2\text{-}MePy)Cl_2]_2$	−7.4	100.6	177.6	173.4	3.36	4.40	29.9	4*b–d*
$[Cu(terpy)Cl]_2(PF_6)$	−5.8	89.9			2.72		33.1	4*e*
$[Cu(tmen)Cl_2]_2$	−5.6	96.8	170.8	157.5	3.15	4.09	30.7	4*f*
$[Cu(Metz)(dmf)Cl_2]_2$	−3.0	95.3			2.72		35.0	3
$[Cu(Me_2en)Cl_2]_2$	−2.2	86.1	167.7	173.6	2.73	3.46	31.5	4g
$[Cu(Et_3en)Cl_2]_2$	+0.06	94.8	174.9	145.7	2.73	3.70	34.7	4*h*
$[Cu_4(hat)_2Cl_8]_n$	+0.7	90.3	171.0	164.5	2.66	3.52	33.9	17
$[Cu_2(dpp)Cl_2]_n$[e]	+1.0	88.7	173.8	164.4	2.77	3.69	32.0	This work
$[Cu(dgm)Cl_2]_2$	+6.3	88.5	166.7		2.70	3.44	32.8	4*i–k*

[a] tmso = tetramethylene sulfoxide; 2-MePy = 2-methylpyridine; tmen = *N,N,N′N′*-tetramethylethylenediamine; Me_2en = *N,N*-dimethylethylenediamine; dmg = dimethylglyoxime; terpy = *N,N′,N″*-terpyridine; Et_3en = *N,N,N′*-triethylethylenediamine; mtz = 4-methylthiazole. [b] Cu–Cl(bridge)–Cu bond angle. [c] *trans* L–Cu–Cl(bridge) bond angle. [d] *trans* L–Cu–Cl(terminal) bond angle. [e] The data refers to the di-μ-chloro bridge, which is not involved in the chain formation, the *J*-value being a lower estimate for the interaction (see text).

considerations suggest that, other factors being equal, the smaller bond angles would favour ferromagnetic interaction. Reversal of the sign of J depending on ϕ has been predicted by theoretical calculations.[16a] A certain dependency between the ratio ϕ/R (R being the Cu–Cl_{ax} bond distance) and J has been found in the case of eclipsed out-of-plane di-μ-chloro bridges.[3] The argument for using the ratio in the search for a magneto-structural relationship is that a decrease in bond distance should be accompanied with an increase in the singlet–triplet splitting. Reviewing this ratio for the mono-μ-chloro bridged complexes (Table 4) there is no evident correlation. However, the value calculated for compound **2** lies within the region found for the other ferromagnetic compounds. Finally, distortion from a square pyramidal towards a trigonal bipyramidal copper coordination geometry is expected to increase the spin density on the bridge, and calculations on a hypothetical mono-chloro-bridged copper(II) dimer have predicted an increase of the antiferromagnetic coupling as such a distortion proceeds.[16b] In a more recent work simultaneous variation of the bridge bond angle, ϕ and the distortion towards trigonal bipyramidal geometry was considered for a mono-chloro-bridged chain, and it was concluded that the latter effect would be the more prominent.[6l]

The longer out-of-plane di-μ-chloro bridge in **2**, linking the chains into a 2D-network, may be compared to the corresponding type of bridges in dinuclear units. Our data show that the interaction across this bridge is ferromagnetic in character, and as seen from Table 5 the geometrical parameters for this bridge are fairly close to those of the other bridges with a ferromagnetic interaction. In this context it can also be mentioned that we have recently characterized another compound with a sheet structure in which a similar di-μ-chloro bridge is present, and where the interaction has been estimated to be weakly ferromagnetic.[17] The data on this compound is also included in Table 5.

Conclusion

In this work we have shown that the dinuclear dpp-bridged species $[Cu_2(dpp)(H_2O)(dmso)Cl_4]{\cdot}$dmso (**1a**) with antiferromagnetically coupled copper(II) ions, upon removal of water and dmso molecules undergoes a solid state polymerization causing a transition to a ferromagnetic state (compound **1b**). We have succeeded in synthesizing a polynuclear complex of formula $[Cu(dpp)Cl_4]_n$ (**2**) which has magnetic properties identical to those of **1b** and whose crystal structure has been determined, revealing that the formation of mono- and di-μ-chloro bridges is responsible for the ferromagnetism. Through the magnetic susceptibility data, powder diffraction, thermogravimetry, and chemical analysis it has been shown that **1b** and **2** are identical. This is an interesting example of the profound effects the desolvation process may have on structure and magnetism. A number of other examples in which dehydration leads to an increase in magnetic dimesionallity, are described in the literature.[18] The more dramatic changes observed are the conversions from antiferromagnetically coupled dinuclear or chain compounds to dehydrated compounds exhibiting spontaneous magnetization below a critical temperature.[18a–c] The detailed structures of the dehydrated phases remain unknown in these cases, however, as single crystals of these species have not been obtained.

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