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Synthesis and structural characterisation of a novel polynuclear copper ribbon-like network. A study of its magnetic properties between 4 and 300 K

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ABSTRACT

A new route to $\{Cu_2(\kappa^1\text{-pyNH}_2)_2(\mu\text{-OMe})_2Cl_2\}_n$ (pyNH$_2$ = 2-aminopyridine) (**3**) is reported. Structural characterisation reveals the presence of methoxide and chloride bridging units within the complex which support close copper–copper bonding interactions resulting in interesting magnetic properties. The variable-temperature (4–300 K) magnetic susceptibility data of the complex were interpreted with the dimer law using the molecular field approximation. The results obtained indicate a weak antiferromagnetic ($zJ' = -15$ cm^{-1}) inter-chain interaction through the chloro-bridge. A relatively strong antiferromagnetic interaction, transmitted through the oxygen-bridge, with an exchange coupling of $2J = -305$ cm^{-1}, which dominates the magnetic properties of the title complex.

1. Introduction

A number of copper complexes with [Cu(OMe)Cl]$_2$ [1] or similar [2] cores that contain close Cu–Cu interactions have previously been reported and have been shown to possess interesting magnetic properties. As part of our ongoing interest in hydrogen bonding interactions within metal complexes, we have engaged in the study of some copper complexes which contain ligands that contain hydrogen bonding motifs. The rationale of this approach is to study the structural differences of compounds containing additional pendant hydrogen bonding groups. In this paper we present the structural characterisation of a copper complex, containing amine functional group which hydrogen bonds and links to adjacent chains. The addition of a hydrogen bonding functional group alters the structure of the compound with respect to similar compounds which do not have the ability to undergo hydrogen bonding.

2. Results and discussion

Breneman previously reported the preparation of a one dimensional ribbon-like structure with dimeric copper(II) [Cu$_2$Cl$_2$(C$_5$H$_5$N)$_2$(μ-OCH$_3$)$_2$] (**1**) repeat units and a [Cu(OMe)Cl]$_2$ core (Fig. 1) [1a]. This complex featured an intra-dimer Cu–Cu dis-

tance of 3.037 Å bridged by methoxy groups and showed strong antiferromagnetic coupling between 80 and 280 K. Extended chains were formed by chloride bridges and the chains were also linked by π-stacking interactions between the pyridine rings.
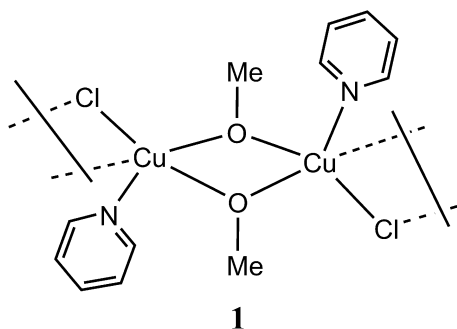
Sterns also prepared a similar compound based on 2-methylpyridine **2** [1b,1c]. This structure also forms extended chains via chloride bridging, however, there does not appear to be any π-stacking perhaps due to the greater steric effect of the methyl group blocking rotation of the pyridine ring to an appropriate angle to allow such interaction.

We postulated that the incorporation of amine groups on the pyridine ring would provide stronger inter-chain interactions and so prepared the analogous compound with 2-aminopyridine. The copper complex [(2-aminopyridine)Cl(OMe)Cu(II)]$_n$ **3** was prepared in two steps firstly by the addition of one equivalent of 2-aminopyridine to a solution of CuCl$_2$ in methanol. This mixture was left stirring for five minutes and one equivalent of NaOMe was subsequently added (Scheme 1). A dark-green solid precipitated immediately from the reaction mixture. The product was obtained in high yield by filtration and washing with methanol and diethyl ether.[1] This solid was characterised as **3** on the basis of
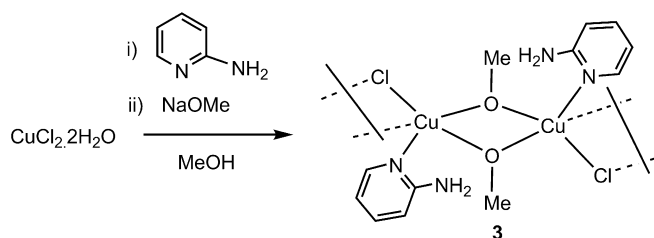
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Fig. 1. Cu₂Cl₂(C₅H₅N)₂(OMe₃)₂ dimer **1** reported by Breneman.

Scheme 1. The synthesis of **3**.

Fig. 2. The extended structure of **3**.

Fig. 3. Packing diagram of **3**.

elemental analysis, IR spectroscopy[2] and an X-ray determination.[3] The insolubility of the compound precluded any solution characterisation. An alternative route to complex **3** has been reported by Brzóska et al. [3].
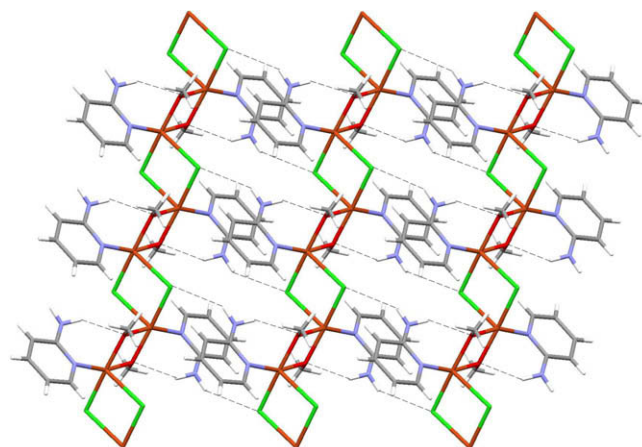
Single crystals were obtained via slow diffusion of the methanol solution of NaOMe into a solution containing 2-aminopyridine and CuCl₂ · 2H₂O. The X-ray analysis of **3** showed that the structure (see Figs. 2 and 3) contained a extended ribbon-like ladder structure containing a [Cu(OMe)Cl]₂ core with an alternating methoxide and chloride bridging motif similar to compounds **1** and **2**. The extended chains show similar characteristics to both compounds **1** and **2**. Each copper consists of a distorted square based pyramidal geometry. Each amino group forms one intramolecular hydrogen bond to the oxygen atom of the bridging methanol and one intermolecular hydrogen bond to a bridging chloride in an adjacent chain. A further intramolecular hydrogen bond is observed between a methoxide hydrogen and adjacent chlorine atom (Table 1 and Fig. 2).

Table 2 shows a comparison of selected distances and angles in compounds **1–3**. The table shows that the [Cu(OMe)Cl]₂ core in compounds **1–3** are very similar.
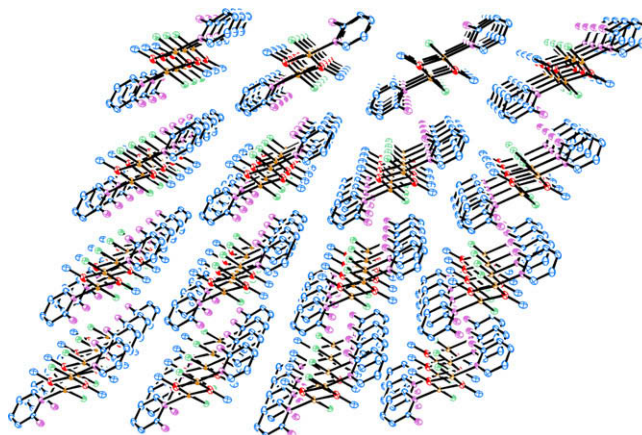
In order to determine whether the extended ribbon type structure is also observed in powder samples of (**3**) X-ray powder diffraction was carried out. Powder patterns for bulk microcrystalline samples of **3** were consistent with the presence of no phase other than that identified in the single crystal experiment (see Supplementary material).

Table 1
Hydrogen-bond geometry (Å) for the title compound.

D–H⋯A	D–H	H⋯A	D⋯A	D–H⋯A
N(2)–H(2A)⋯O(1)[a]	0.89	2.28	3.051	145.00
N(2)–H(2B)⋯C1(1)[b]	0.89	2.80	3.539	142.00
C(6)–H(6A)⋯Cl(1)	0.96	2.78	3.434	126.00

Symmetry codes: (a) $[-x, 2-y, -z]$, (b) $[-x, 1-y, -z]$.

Table 2
Comparison of the main interatomic bond distances and angles of **1**, **2** and **3**.

	R = H (**1**)	R = Me (**2**)	R = NH₂ (**3**)
Cu–O	1.932(4)	1.91(1)	1.935(3)
Cu–O	1.940(6)	1.94(1)	1.971(3)
Cu–Cl	2.279(3)	2.265(4)	2.2995(10)
Cu–Cl	2.820(3)	2.944(4)	2.841
Cu–N	2.012(5)	2.01(1)	1.990(3)
Cu–Cu	3.037(2)	3.025(3)	3.0601(10)
Cu–Cu	3.736(3)	3.800	3.757(1)
Cu–Cl–Cu	93.62(8)	98.8(2)	93.33
Cu–O–Cu	103.2(1)	103.3(5)	103.13(12)
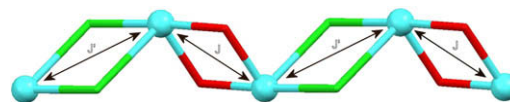
Fig. 4. Magnetic exchange parameters along the chains inferred from the structure, see text for details.

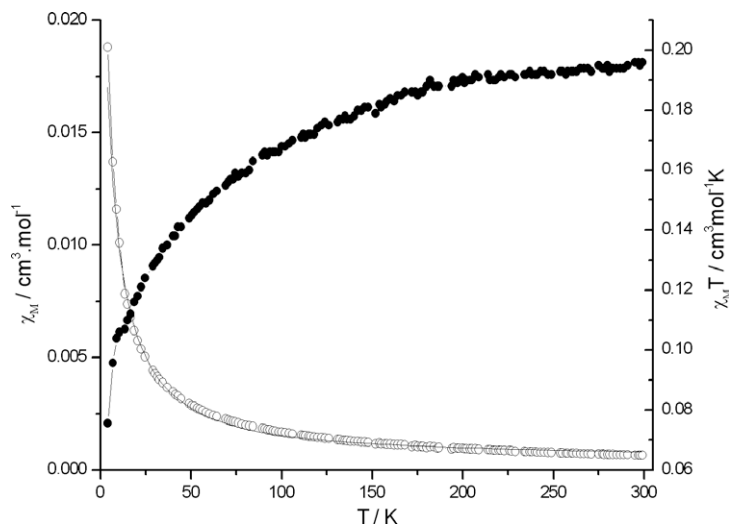**Fig. 5.** χ_M (- ○ -) and $\chi_M T$ (- ● -) vs. T plots for the **3**. The solid line shows the best-fit theoretical curve.

2.1. Magnetic studies

Variable-temperature magnetic susceptibility measurements were performed on polycrystalline samples in the 4–300 K range (Fig. 4). The plots of $\chi_M T$ and χ_M versus T are given in Fig. 5. The molar susceptibility value χ_M (6.54×10^{-4} cm^3 mol^{-1} at room temperature) increases with decreasing temperature, reaching a maximum of 18.8×10^{-3} cm^3 mol^{-1} at 4 K. The $\chi_M T$ curve exhibits a continuous decrease upon cooling, with $\chi_M T = 0.196$ cm^3 mol^{-1} K ($\mu_{eff} = 1.25\mu_B$) at room temperature and a value of 0.0755 cm^3 mol^{-1} K ($\mu_{eff} = 0.777\mu_B$) at 4 K. The continuous decreasing in the $\chi_M T$ values clearly indicates the existence of anti-ferromagnetic interactions in the title compound.

We can envisage three possibilities when these magnetic properties are considered. The first possibility was to assume that the magnetic coupling mediated by the chloride bridge is negligible and that the magnetic properties arise solely from the copper(II) methoxide dimer [1a]. We used the simple Bleaney–Bowers expression to fit the magnetic data. In this case however, the resulting data fit was poor at low temperature.

The second possibility takes the molecular field approximation into account. The crystal structure of the compound suggests that two kinds of coupling parameters must be considered to interpret the magnetic properties, according to the Fig. 4; where J and J' are the constants for exchange coupling via the oxygen bridge in the dimeric unit and the chloro bridge in the chain, respectively (Fig. 4). Experimental data from 300 K down to 4 K have been fitted with the dimer law with a molecular field correction in order to account for interdimer interactions of the complex. Therefore, for two exchange coupled copper(II) ions the Bleaney–Bowers equation (1) was used with a molecular field correction (2) [4–7][4]:

$$\chi_{Cu} = \frac{Ng^2\mu_B^2}{3kT}\left[1+\frac{1}{3}\exp(-2J/kT)\right]^{-1}(1-x_p) + \frac{Ng^2\mu_B^2}{4kT}x_p + TIP \quad (1)$$

$$\chi^{exp} = \frac{\chi_{Cu}}{1-(2zJ'/Ng^2\mu_B^2)\chi_{Cu}} \quad (2)$$

where χ^{exp} is the measured magnetic susceptibility, z is the number of nearest-neighbouring dimers (in this case $z = 2$) and J' accounts

Table 3
Relevant magneto-structural parameters for binuclear Cu(II) complexes containing hydroxo/alkoxo-bridged.

Complex	Cu–Cu	Cu–O–Cu (°)	⟨Cu–O⟩	$-2J$ (cm^{-1})[*]	Reference
1	3.037	103.2	1.936	1030[a]	[1a]
2	3.025	103.3	1.925		[1b]
3	3.037	103.13	1.932	305[b]	this work
4	3.041	100.4	1.980	186.5[c]	[12]
5	2.941	99.3	1.930	68.1[d]	[13]
6	3.147	100.4	2.045	226.8[e]	[14]
7	2.9015	97.96	1.923	7.2[e]	[15]

[*] Magnetic susceptibility was measured between (K): [a]80–280, [b]4–300, [c]25–300, [d]5–266, [e]5–300.
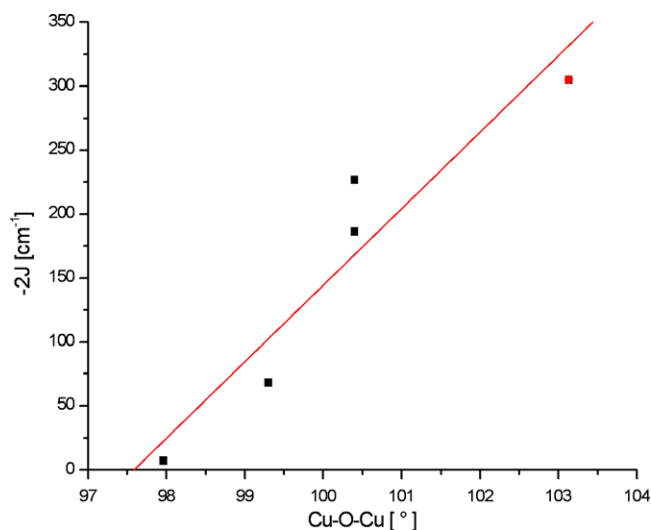

Fig. 6. A plot of Cu–O–Cu angles vs. the exchange interactions (J); squares (black) are literature data listed in Table 2 and circle (red) is from this work; the solid line is drawn only as a guide. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

for the presence of magnetic interactions between neighbouring dimers. x_p is the fraction of a monomeric impurity, A temperature independent paramagnetism (*TIP*) of 60×10^{-6} cm^3 mol^{-1} per Cu(II) ion has been used. Within the frame of this approximation,

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[4] Magnetization measurements of polycrystalline samples were carried out with a Quantum Design model MPMS computer-controlled SQUID magnetometer at a magnetic field of 1 T over the temperature range 4–300 K. Diamagnetic corrections were made using Pascal's constants [8].
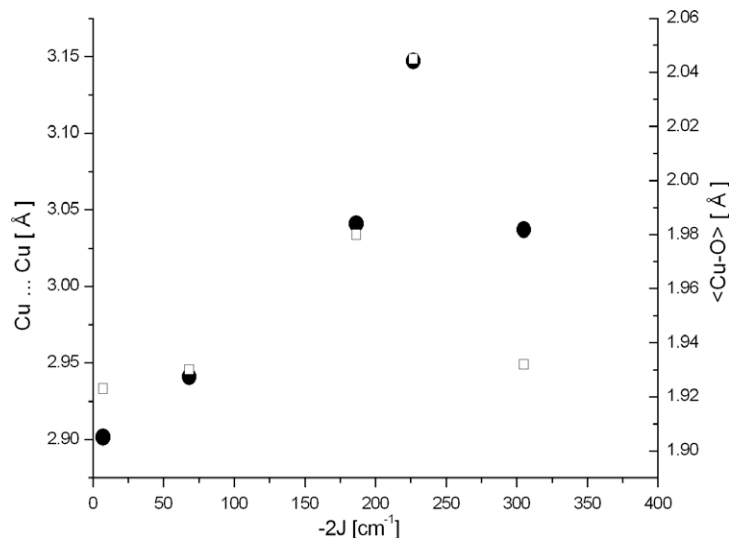
Fig. 7. A plot of ⟨Cu—O⟩ (squares) and Cu⋯Cu distance (circles) vs. the exchange interactions (J).

with the interaction Hamiltonian $H = -2JS_1 \cdot S_2$, the magnetic data fit the model very well to this model (Fig. 5). The best-fit parameters obtained by least squares fit through Eq. (2) are as follows: $2J = -305$ cm^{-1}, $zJ' = -15$ cm^{-1}, $g = 2.09$, $x_p = 2.92\%$ with $R^2 = 0.99675$.

The third possibility is that weak magnetic interaction can be mediated by the chloride bridge and the magnetic behaviour of the compound can be explained by the alternating antiferromagnetic Heisenberg chain model [8]. The results of the fit, in this case proved unsatisfactory. The least squares fitting did not converge and theoretical results have not been reliable.

Magnetostructural correlations for dinuclear transition metal complexes have been known for a long time [9]. Binuclear copper(II) complexes have several structural features to affect the strength of exchange coupling interactions, such as the dihedral angle between the two coordination planes, the planarity of the bonds around the bridging oxygen atom, the length of the copper–oxygen bridging bonds, and the Cu–O–Cu bridging angle. The most widely accepted factor correlating structure and magnetism is the Cu–O–Cu bridging angle. Hodgson and co-workers established the linear correlation between the Cu–O–Cu bridging angle (φ) and singlet–triplet exchange parameter ($2J$) within Cu_2O_2 ring of dihydroxo-bridged copper(II) complexes ($2J = 74.53\varphi + 7270$ cm^{-1}) [10]. From this correlation it is concluded that when the Cu–O–Cu angle is larger than 97.55°, the overall magnetic behaviour is antiferromagnetic and for smaller values a ferromagnetic coupling is observed. These correlations have been extended and theoretically justified in the literature [11]. The magnetic measurements reveal a calculated singlet–triplet energy gap of $2J = -305$ cm^{-1}. This value differs with the predicted value of $2J = -416$ cm^{-1} from the above classical formula [10] which may originate from the chloride bridge may provide an additional pathway for superexchange. Selected magneto-structural data of the dihydroxo-bridged binuclear copper(II) are summarized in Table 3 [12–15] and a correlation diagram between $-2J$ and φ is presented in Fig. 6. The solid line drawn as a guide shows a correlation between J and Cu–O–Cu angles. This guide indicates that an increase of the Cu–O–Cu bridging angle parallels an increase of the anti-ferromagnetic exchange integral. Plots of $-2J$ versus Cu⋯Cu and the ⟨Cu—O⟩ distance are shown in Fig. 7. It is clear that there is no simple correlation of the ⟨Cu—O⟩ and Cu⋯Cu distance with the strength of the exchange interaction.

3. Conclusion

In summary, the synthesis and structural characterisation of a novel polynuclear copper(II) ribbon-like network has been presented together with an investigation into its magnetic properties. A weak antiferromagnetic interaction is observed through the chloride bridge and a strong antiferromagnetic interaction is observed through the oxygen bridge.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2009.03.037.

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