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## Ferro- and antiferro-magnetic coupling in a chlorido-bridged, tetranuclear Cu(II) complex

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### Abstract

A bispidine-style ligand involving four pyridine-N and three aliphatic-N donor atoms forms a bimetallic species with CuCl<sub>2</sub> in which all seven N-donors are bound and which aggregates in the crystal through double chloride-bridging to give a tetranuclear unit. The magnetism of this solid can be interpreted in terms of a relatively weak antiferromagnetic coupling between the two Cu(II) centres of the dinuclear subunits and strong ferromagnetic coupling of the Cu(II) centres in different dinuclear units involved in the bis-chlorido bridge. In solution, the assembly decays into the dinuclear subunits and, in agreement with the solid state studies, the interaction between the corresponding Cu<sup>II</sup> centres is shown to be primarily due to dipole-dipole coupling.

## Introduction

The bispidine platform has proven to be extremely useful for the generation of multidentate ligands, in particular ditopic species suited to the formation of both homo- and hetero-dinuclear complexes in which specific coordination geometries are enforced.<sup>1</sup> In the case of Cu(II), the separation of the metal ions in these dinuclear species can be such as to provide useful models of copper oxidase enzymes, especially of intermediate species involving oxygen coordination.<sup>2</sup> Here, intramolecular bridging of the metal centres by the exogenous (oxygen-derived) ligand may be observed but it is also known that an exogenous ligand, cyanide ion, for example,<sup>3</sup> can cause intermolecular bridging and thus lead to the formation of higher aggregates, potentially with interesting magnetic properties. The magnetic properties of ligand-bridged Cu(II) centres in general have in fact been of interest for a very long time<sup>4</sup> and their characteristics are known to be sensitive to subtle variations in the co-ligand structure for a given bridge,<sup>5</sup> with chloride ion being an especially prominent bridging species.<sup>5,6</sup> Bispidine-derived oligonuclear complexes are of particular interest in this respect due to the specific and rigid structure of the adamantane-derived ligand backbone.<sup>3</sup> We report herein the characterisation of the complex of a dinucleating bispidine derivative **L** (Figure 1) with copper(II) chloride in which chloride bridging in the solid state leads to the presence of centrosymmetric tetranuclear units in which there are inequivalent inner and outer magnetic centres.

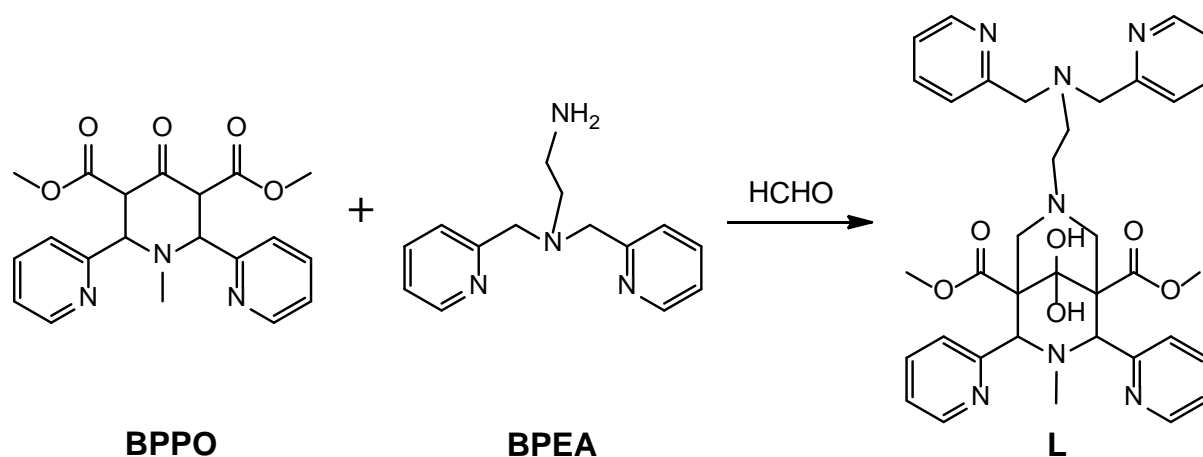


Figure 1 Synthesis of the bispidine derivative **L** used in the present work, shown in its carbonyl-hydrate form, from bis(pyridyl)piperidone (BPPPO) and bis(pyridyl)diamine (BPEA) precursors.

## Experimental

### 1. Syntheses

All reagents were purchased from Aldrich and used without further purification. Chromatography was conducted in glass columns under gravity flow with SP-Sephadex C25 (Na<sup>+</sup> form) ion exchange resin. Electronic absorption spectra were recorded on a SCINCO S-2100 diode array spectrophotometer and elemental analyses were obtained using a Chemtronics TEA-3000 analyser.

*N*<sup>1</sup>,*N*<sup>1</sup>-bis(pyridin-2-ylmethyl)ethane-1,2-diamine (BPEA)<sup>7</sup> and bis(pyridyl)piperidone (BPPO)<sup>8</sup> (Figure 1) were prepared by published procedures. BPEA (2.42 g, 10 mmol) and aqueous formaldehyde (37%, 1.9 mL, 23 mmol) were added to a suspension of BPPO (4.57 g, 13 mmol) in the 1:1 THF/methanol (50 mL). The mixture was heated at 70 °C for 24 h with stirring under a nitrogen atmosphere. The solvent was removed under reduced pressure to give a black-coloured syrup, which was suspended in methanol (20 mL) and CuCl<sub>2</sub>·2H<sub>2</sub>O (3.75 g, 22 mmol in 50 mL methanol) added. The solvent was removed under reduced pressure and the residue dissolved in water (200 mL) then absorbed onto SP-Sephadex C25 and eluted with aqueous NaCl solution (0.3 mol L<sup>-1</sup>). Three fast-moving minor bands were removed and discarded before the fourth major blue fraction was collected. It was evaporated to dryness under reduced pressure and extracted several times into ethanol to leave NaCl behind, then evaporated again to give a green powder. Yield, 1.6 g. The complex was dissolved in a minimum volume of methanol and this solution slowly evaporated at ambient temperature after addition of LiClO<sub>4</sub> to give the crystals used for the structure determination. Anal. Calc. for C<sub>72</sub>H<sub>86</sub>Cl<sub>8</sub>Cu<sub>4</sub>N<sub>14</sub>O<sub>30</sub>: C, 39.94; H, 4.00; N, 9.06. Found: C 40.1, H 4.11, N 8.87 %. Visible spectrum (in water) :  $\lambda_{\max}$  635 nm,  $\epsilon_{\max}$  152 M<sup>-1</sup> cm<sup>-1</sup>.

### 2. Crystallography

Crystallographic data were collected at 150(2) K on a Nonius Kappa-CCD area-detector diffractometer<sup>9</sup> using graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). The crystal was introduced into a glass capillary with a protecting "Paratone-N" oil (Hampton Research) coating. The unit cell parameters were determined from ten frames, then refined on all data. The data (combinations of  $\varphi$ - and  $\omega$ -scans with a minimum redundancy of 4 for 90% of the reflections) were processed with HKL2000.<sup>10</sup>

Absorption effects were corrected empirically with the program SCALEPACK.<sup>10</sup> The structure was solved by direct methods and refined by full-matrix least-squares on  $F^2$  with SHELXTL.<sup>11</sup> All non-hydrogen atoms were refined with anisotropic displacement parameters. One perchlorate ion (containing Cl4) is disordered over two positions sharing two oxygen atoms, while another one (Cl5) has a twofold rotation axis of symmetry. The hydrogen atoms bound to oxygen atoms were found on a Fourier-difference map and the carbon-bound hydrogen atoms were introduced at calculated positions; all were treated as riding atoms with an isotropic displacement parameter equal to 1.2 times that of the parent atom (1.5 for CH<sub>3</sub>).

Crystal data for [Cu<sub>4</sub>L<sub>2</sub>Cl<sub>4</sub>](ClO<sub>4</sub>)<sub>4</sub>.2H<sub>2</sub>O: C<sub>72</sub>H<sub>86</sub>Cl<sub>8</sub>Cu<sub>4</sub>N<sub>14</sub>O<sub>30</sub>,  $M = 2165.31$ , monoclinic, space group  $C2/c$ ,  $a = 23.3110(15)$ ,  $b = 8.0645(4)$ ,  $c = 44.562(3)$  Å,  $\beta = 92.994(6)^\circ$ ,  $V = 8365.9(9)$  Å<sup>3</sup>,  $Z = 4$ . Refinement of 594 parameters on 7875 independent reflections out of 71127 measured reflections ( $R_{\text{int}} = 0.106$ ) led to  $R1 = 0.068$ ,  $wR2 = 0.196$ ,  $\Delta\rho_{\text{min}} = -0.71$ ,  $\Delta\rho_{\text{max}} = 1.17$  e Å<sup>-3</sup>. Full information can be obtained free of charge from the Cambridge Crystallographic Data Centre *via* [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif) by citing CCDC 979553.

### 3. EPR and magnetic susceptibility measurements

Continuous-wave X-band EPR spectra (ca. 9 GHz) were recorded on a Bruker Biospin ELEXSYS E500 spectrometer with a Super High Q cavity. A flow-through cryostat in conjunction with a Eurotherm (B-VT-2000) variable-temperature controller was used to provide liquid nitrogen temperatures. The microwave frequency and magnetic field were calibrated with a Bruker frequency counter and an ER041XK Teslameter. The simulated and experimental spectra were visualized with Bruker's Xepr software suite. The mono- and dinuclear complexes were simulated with the computer simulation software package XSophe.<sup>12</sup>

Magnetic measurements were carried out on a MPMS-XL 5T (Quantum Design) SQUID magnetometer. Samples were powdered and pressed in PTFE tape to avoid field-induced orientation. Data were corrected for diamagnetism of the sample holder, and Pascal's constants were used for diamagnetic corrections of the sample.<sup>13</sup> For the simulation of the susceptibility plot, the program julX was used.<sup>14</sup> The Hamiltonian used was:

$$H = -2 \sum_{i=1}^{ns-1} \sum_{j=i+1}^{ns} J_{ij} \vec{S}_i \cdot \vec{S}_j + \sum_{i=1}^{ns} D_i \left[ S_{z,i}^2 - \frac{1}{3} S_i(S_i + 1) + \frac{E_i}{D_i} (S_{x,i}^2 - S_{y,i}^2) \right] + \sum_{i=1}^{ns} g\beta \vec{S}_i \cdot \vec{B}$$

## Results and discussion

### *Synthesis*

The versatility of the bispidine pathway to multidentate ligand fabrication<sup>1</sup> is further illustrated by the present work, although the basic chemistry itself is, of course, familiar. Formation of the Cu(II) complex and its chromatography on a cation exchange column provides a convenient means of purifying the viscous and involatile crude ligand reaction product.

### *Crystallography*

The crystal lattice of  $[\text{Cu}_4\text{L}_2\text{Cl}_4](\text{ClO}_4)_4 \cdot 2\text{H}_2\text{O}$  can be regarded as comprising sheets of centrosymmetric tetranuclear cations,  $[\text{Cu}_4\text{L}_2\text{Cl}_4]^{4+}$  (Figure 2; Table 1), separated by sheets of perchlorate anions and water molecules, these sheets lying parallel to the *bc* plane. This separation of the cation sheets is such as to ensure that there are no Cu...Cu contacts  $\leq 10$  Å between sheets, and although there are inter-cation contacts spanning the anion-water sheets mediated by CH...O interactions of the bispidine ester groups, they are associated with a minimum Cu...Cu distance just slightly  $>13$  Å. Thus, we assume that any intermolecular magnetic coupling would be limited to that within the cation sheets. Within a sheet, each Cu of a tetranuclear cation is separated by *b* (= 8.064 Å) from the equivalent Cu of another and each terminal Cu is separated by 10.780 Å from the terminal Cu atoms of two adjacent tetranuclear cations, this separation being shorter than that between the terminal Cu atoms (12.823 Å) of a given tetranuclear cation. Of course, it is expected that direct bridging of Cu centres by a ligand should give rise to a short separation and thus to the strongest coupling. As is commonly the case with Cu(II) complexes, there is some degree of arbitrariness in defining the coordination sphere of the metal. For each Cu1 atom, there are six donor atoms in proximity in an approximately octahedral (meridional  $\text{N}_3\text{Cl}_3$ ) array, although the very long Cu1...Cl2 separation of 3.213 Å indicates that the system is subject to a major Jahn-Teller distortion. The central (Cu1)(Cl1)(Cu1<sup>i</sup>)(Cl1<sup>i</sup>) rhomb, in which Cu1-Cl1 = Cu1<sup>i</sup>-Cl1<sup>i</sup> = 2.2514(14) and Cu1-Cl1<sup>i</sup> = Cu1<sup>i</sup>-Cl1 = 2.8255(14) Å, is strictly planar with a Cu1...Cu1 distance of 3.4919(12) Å, geometrical characteristics which may, on the basis of

comparison with known, simpler systems,<sup>6</sup> be associated with antiferromagnetic coupling of the Cu(II) centres (and an antiparallel arrangement of  $d_{z^2}$  orbitals in the approximation that Cu1(N1N2N3Cl1) can be regarded as a square-planar unit). For each Cu2 atom, there are but five donor atoms in proximity, with the relatively long Cu2-N4 distance (2.333(4) Å) justifying the description of the Cu2(N4N5N6N7Cl2) unit as a square pyramid with N4 in the axial position. While the square planar units incorporating Cu1 and Cu1' lie in parallel planes, this is not the case for the square planar units involving Cu1 and Cu2 (bridged by Cl2) (or Cu1<sup>i</sup> and Cu2<sup>i</sup>, bridged by Cl2<sup>i</sup>), a situation which, in simpler systems,<sup>5</sup> has been associated with ferromagnetic coupling of the metal centres, although the Cu1...Cu2 separation in the present complex is rather long (4.7881(9) Å). Considering the ligand **L** alone, it behaves as an exclusively N-donor, heptadentate species towards Cu(II) and is able to bind two such metal ions in quite close proximity, although the flexibility in the link between the N<sub>4</sub> and N<sub>1</sub> donor sites presumably means that the juxtapositioning of the complexed units could be sensitive to the nature of other ligands (here, chloride) involved.

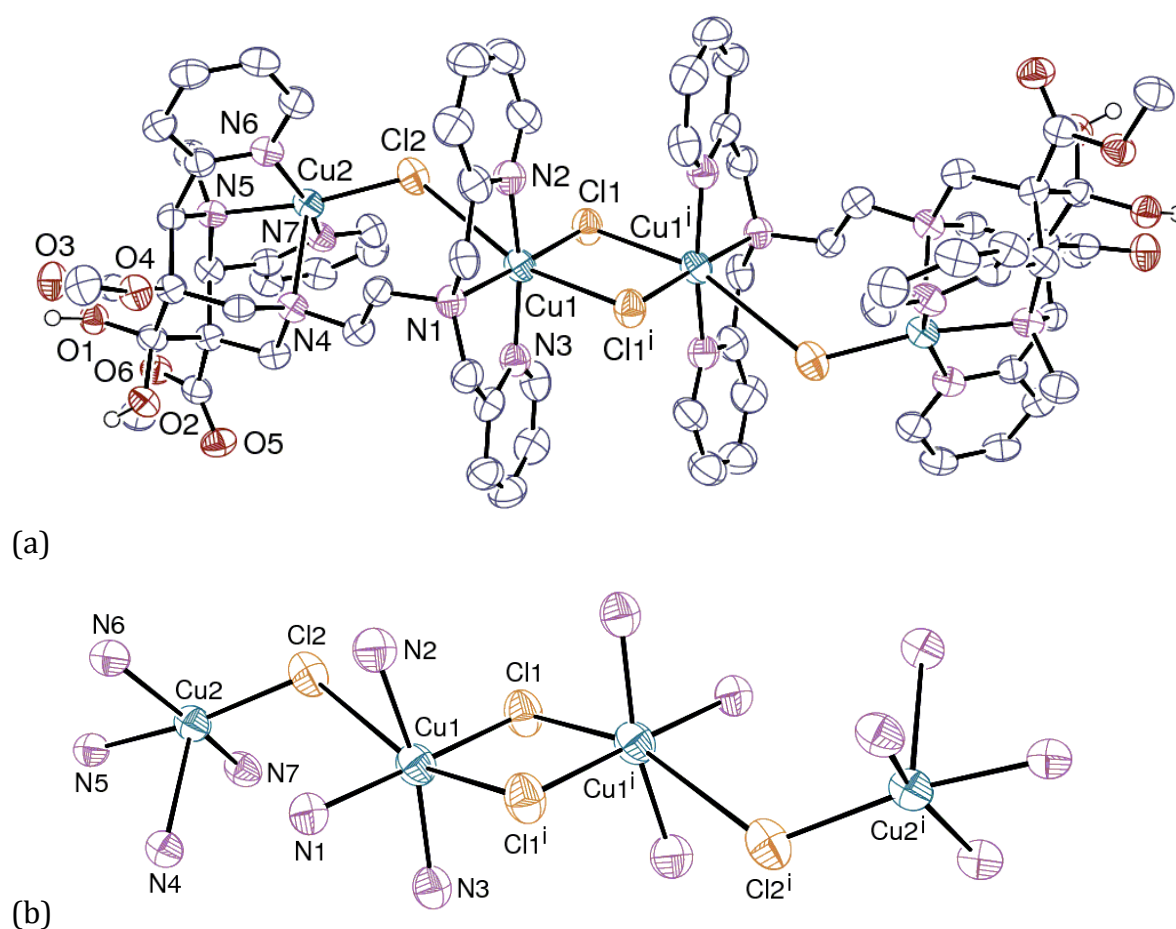


Figure 2 (a) View of the centrosymmetric, cationic complex  $[\text{Cu}_4\text{L}_2\text{Cl}_4]^{4+}$ . Carbon-bound hydrogen atoms are omitted and displacement ellipsoids are drawn at the 50% probability level. Symmetry code:  $i = 1/2 - x, 3/2 - y, -z$ . (b) View of the tetranuclear metal/donor atom array.

**Table 1 Metal and donor atom geometry in  $[\text{Cu}_4\text{L}_2\text{Cl}_4](\text{ClO}_4)_4 \cdot 2\text{H}_2\text{O}$**

Cu1-N1	2.038(4) Å	Cu2-N4	2.333(4) Å
Cu1-N2	1.996(5) Å	Cu2-N5	2.031(4) Å
Cu1-N3	1.985(5) Å	Cu2-N6	2.005(4) Å
Cu1-Cl1	2.2514(14) Å	Cu2-N7	1.990(4) Å
Cu1-Cl1 <sup>i</sup>	2.8255(14) Å	Cu2-Cl2	2.2097(14) Å
Cu1-Cl2	3.2131(15) Å	Cu2...Cu1	4.7889(9) Å
Cu1...Cu1 <sup>i</sup>	3.4919(12) Å		

Euler angles between plane 1 and plane 2:

Cu1...Cu2 4.788 Å  $\alpha = 48.57^\circ, \beta = 75.25^\circ, \gamma = 0.00^\circ$

Cu1-Cl1-Cu1<sup>i</sup> 86.13° Cu2-Cl2-Cu1 122.93°

Symmetry code:  $i = 1/2 - x, 3/2 - y, -z$ .

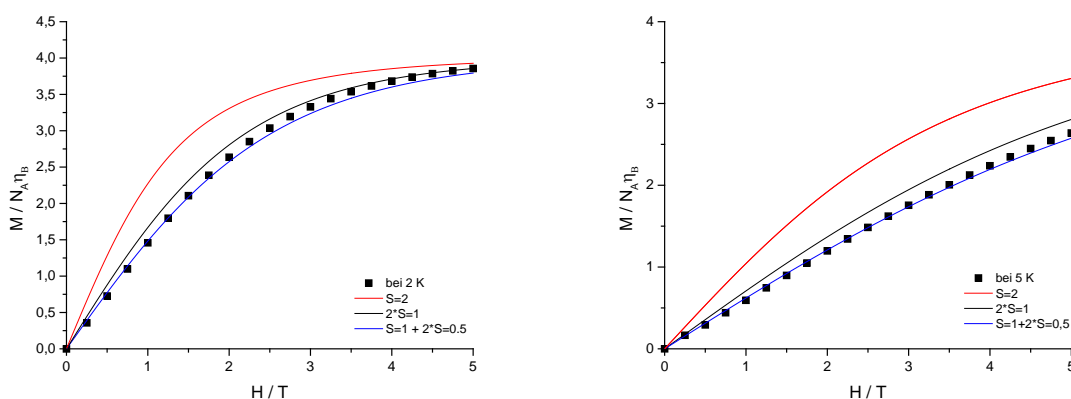
### **Magnetism**

The magnetic susceptibility of powdered crystals was measured at 500 Oe in the range of 2 to 300 K. At room temperature the  $\chi T$  value is  $1.40 \text{ cm}^3 \text{ K mol}^{-1}$ , which corresponds to four uncoupled Cu(II) centres with  $S = 0.5$  each. The maximum susceptibility is reached at 5 K with a  $\chi T$  value of  $1.91 \text{ cm}^3 \text{ K mol}^{-1}$ . This fits a system of two ferromagnetically coupled Cu(II) ions ( $S_{\text{total}}=1$ ) and two additional uncoupled Cu(II) centres ( $2 \times S = 0.5$ ). This is also what one can expect from the molecular structure of the tetrakis-copper(II) complex with angles between the two central Cu(II) ions and the two bridging chlorides (Cl1 and Cl1<sup>i</sup>) of close to  $90^\circ$ , i.e., this is a geometric arrangement known to lead to ferromagnetic coupling.<sup>15</sup> The decrease of  $\chi T$  below 5 K indicates an antiferromagnetic coupling pathway between the inner to the outer Cu(II) ions at these temperatures. This is supported by a qualitative fit of the data which suggests that the coupling between the weakly coupled outer copper(II) centres (Cu1 and Cu2) is  $J_1 = -0.1 \text{ cm}^{-1}$ , and the stronger coupled central pair of Cu(II) ions have  $J_2 = 5 \text{ cm}^{-1}$  (see Supporting



Information). Note that only a relatively small amount of the crystalline sample used for crystallography was available, and all experiments were done with this sample for consistency of the data. The scattering observed in the susceptibility data is due to the small quantity of material available and, therefore, these data have only been interpreted qualitatively.

The magnetization was measured at 2 K and 5 K at fields between 0 to 5 T (Figure 3). For each temperature three Brillouin functions are plotted, and those with a ferromagnetically coupled inner pair and two uncoupled outer Cu(II) ions (blue curves), *i.e.* those which qualitatively agree with the above interpretation, fit the experimental data reasonably well.



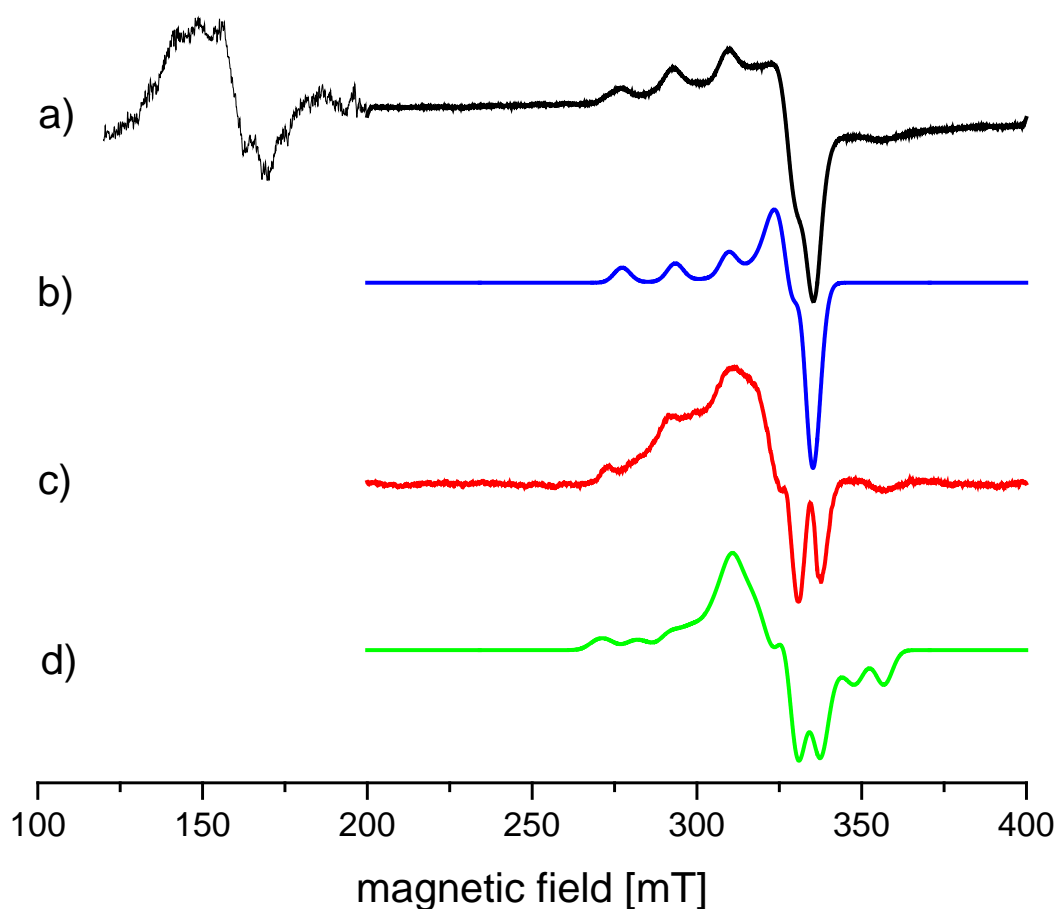
**Figure 3:** Magnetisation vs. field at 2 K (left) and 5 K (right); three curves are plotted together with the experimental data (black squares), *i.e.* for systems with either a total spin of 2 (for ferromagnetically coupled Cu(II) centres, red line), or two uncoupled centres with a spin of 1 each (black line), or one ferromagnetically coupled pair of Cu(II) centres with a total spin of 1 plus two other Cu(II) centres with a spin of 0.5 each (blue line).

### EPR Spectroscopy

EPR spectra were measured from solid samples (powder) and from frozen solutions. Powder spectra were measured at room temperature, those from glasses (1 mM solutions in MeOH) at 110 K. Due to magnetic interactions between the tetranuclear units in the crystal lattice, the solid state spectra were, as expected, rather unstructured (see Supporting Information). In MeOH, which was used as the solvent for the frozen solution spectra, dissociation of the axial chloride ligands Cl1<sup>i</sup> may lead to dinuclear species with partially differing structures if the tenuous interaction Cu1-Cl2 is also

replaced by one with solvent. Indeed, the experimental spectra are typical for mononuclear Cu(II) complexes (Figure 4).

The simulation of this spectrum, shown in Figure 4b reveals spin Hamiltonian parameters typical for a mononuclear axial Cu(II) site. However, comparison of the experimental and simulated spectra reveals that there are additional features, and these are visualized in Figure 4c which is a difference spectrum involving the experimental and simulated traces. Indeed, there are also very weak signals at half-field, typical for forbidden  $\Delta m_j = \pm 2$  transitions of dinuclear Cu(II) complexes (Figure 4a; this part of the spectrum is plotted with a larger amplitude). The simulation of dipole-dipole coupled spectra of dicopper(II) complexes may be used for solution structural assignments.<sup>16,17</sup> The simulation of the  $\Delta m_j = \pm 1$  transitions (Figure 4 d; structural parameters together with the spin Hamiltonian parameter are given in the Figure caption. See also Table 2) indicates that there is some structural rearrangement of the dinuclear subunits, and this may be due to dissociation of the chlorido bridges. We therefore conclude, that there are (at least) two conformations of the dinuclear subunits, with different orientations (and distances) of the two Cu<sup>II</sup> centres (Cu1 and Cu2), one leading to weak dipole-dipole coupling, and one to an uncoupled system (or a situation governed by “magic angles”).<sup>18</sup>



**Figure 4:** a) EPR spectrum measured in MeOH (1mM) at 110 K (black line), b) simulated spectrum (blue line): 9.43671 GHz;  $g_x = 2.044$ ,  $g_y = 2.068$ ,  $g_z = 2.238$ ;  $A_x = 16.1$ ,  $A_y = 17.2$ ,  $A_z = 168.8$  [ $10^{-4}$  cm $^{-1}$ ], Differential spectrum of a) and b) (red line) and EPR simulation spectra of a coupling between the Cu1 and Cu2 centres (green line): 9.43671 GHz; Cu1:  $g_x = 2.034$ ,  $g_y = 2.056$ ,  $g_z = 2.262$ ;  $A_x = 15$ ,  $A_y = 15$ ,  $A_z = 115$ ; Cu2:  $g_x = 1.922$ ,  $g_y = 2.112$ ,  $g_z = 2.237$ ;  $A_x = 6$ ,  $A_y = 6$ ,  $A_z = 112$  [ $10^{-4}$  cm $^{-1}$ ].

## Conclusions

The N<sub>7</sub>-donor ligand **L** characterized in the present work, while providing chelating sites which can strongly bind two Cu(II) centres, at the same time leaves open access to coordination sites which enable a simple bridging ligand like chloride ion to cause the formation of extended magnetic aggregates. The ligand superstructure is, however, effective in limiting Cu...Cl interactions within the dinuclear unit involving one ligand to

much weaker antiferromagnetic interactions than the ferromagnetic interactions resulting from chloride bridging between dinuclear units.

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A binuclear complex of copper(II) chloride with a heptadentate bispidine-like ligand undergoes dimerisation in the solid state involving chloride bridging and leading to both ferro- and antiferro-magnetic coupling of the Cu(II) centres.

