

# Ferromagnetic coupling in a unique Cu(II) metallacyclophane with functionalized diazamesocyclic ligands formed by Cu(II)-directed self-assembly: magneto-structural correlations for dichloro-bridged Cu(II) dinuclear complexes

Miao Du,<sup>a</sup> Ya-Mei Guo,<sup>a</sup> Xian-He Bu,<sup>\*a</sup> Joan Ribas<sup>b</sup> and Montserrat Monfort<sup>b</sup>

<sup>a</sup> Department of Chemistry, Nankai University, Tianjin 300071, P. R. China.

E-mail: buxh@nankai.edu.cn; Fax: +86-22-23502458

<sup>b</sup> Departament de Química Inorgànica, Universitat de Barcelona, Diagonal 647, 08028 Barcelona, Spain

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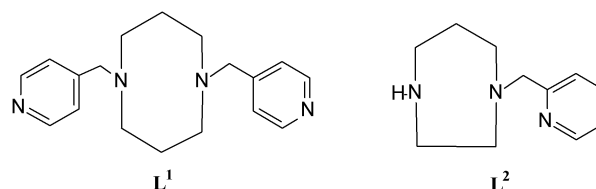
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Two new di- $\mu$ -Cl dinuclear Cu<sup>II</sup> complexes [Cu(HL<sup>1</sup>)Cl<sub>2</sub>]<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub> (**1**) and [Cu<sub>2</sub>(L<sup>2</sup>)<sub>2</sub>Cl<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> (**2**) with the pyridyl-functionalized diazamesocyclic ligands 1,5-bis(pyridin-4-ylmethyl)-1,5-diazacyclooctane (L<sup>1</sup>) and 1-(pyridin-2-ylmethyl)-1,4-diazacycloheptane (L<sup>2</sup>) have been synthesized and structurally characterized by single crystal X-ray diffraction. Complex **1** is a unique paramagnetic Cu<sup>II</sup> metallamacrocycle (*ca.* 14.1  $\times$  3.5 Å<sup>2</sup>) directly self-assembled by metal ions and the organic spacer under strongly acidic conditions. The magnetic properties of both complexes have been investigated by variable-temperature magnetic susceptibility measurements. Although complexes **1** and **2** have almost the same geometrical parameters for Cu<sup>II</sup>, their magnetic parameters vary from ferromagnetic for **1** to antiferromagnetic for **2**. The magneto-structural correlation of such complexes has been further developed.

Particular interest has been directed towards the study of dinuclear Cu<sup>II</sup> complexes to elucidate the spin coupling between paramagnetic metal centers, both from structural and theoretical points of view, especially for the monoatomic bridged (such as  $\mu$ -OH, OCH<sub>3</sub>, S and Cl) Cu<sup>II</sup> dimers, since they provide the simplest case of magnetic interaction involving only two unpaired electrons.<sup>1-4</sup> Concurrent with this has been the development of the magneto-structural correlation in the [Cu( $\mu$ -Cl)<sub>2</sub>Cu] dimeric motif, displaying a wealth of structures with a variety of Cu–Cl lengths and Cu–Cl–Cu angles depending on the coordinated ligands and also on the counterions.<sup>5-8</sup> However, no simple magneto-structural relationship relating the value of the singlet–triplet gap (*J*) to the Cu–Cl–Cu angle or Cu $\cdots$ Cu distance, for example, has been established, especially for the asymmetric [Cu( $\mu$ -Cl)<sub>2</sub>Cu] dimers. Hatfield *et al.* have shown that *J* in such compounds varies in a regular way with the quotient of the Cu–Cl–Cu bridging angle ( $\phi$ ) and the long, out-of-plane Cu–Cl bond length (*R*).<sup>9</sup>

Mesocyclic diamines, which have two nitrogen donors as bidentate chelating ligands and offer the potential for further functionalization, are the smallest members of the family of cyclic polyamines.<sup>10,11</sup> 1,5-Diazacyclooctane (DACO) and 1,4-diazacycloheptane (DACH) are the most typical diazamesocyclic ligands. The former always takes the unique “boat/chair” configuration when coordinated to metal ions, while the latter can take on different forms. In our efforts to systematically investigate the control of the structures and magnetic properties as well as the coordination chemistry of diazamesocyclic ligands by modifying their backbone, we have reported a variety of Cu<sup>II</sup> complexes with different coordination modes and magnetic properties by altering the donor pendants.<sup>12-14</sup> In this contribution, we report the syntheses and crystal structures of two chloro-bridged Cu<sup>II</sup> dimers

[Cu(HL<sup>1</sup>)Cl<sub>2</sub>]<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub> (**1**) and [Cu<sub>2</sub>(L<sup>2</sup>)<sub>2</sub>Cl<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> (**2**) with new pyridyl-functionalized diazamesocyclic ligands, 1,5-bis(pyridin-4-ylmethyl)-1,5-diazacyclooctane (L<sup>1</sup>) and 1-(pyridin-2-ylmethyl)-1,4-diazacycloheptane (L<sup>2</sup>). To our knowledge, **1** is the first structurally characterized water-soluble Cu<sup>II</sup> macrometallacycle assembled in strong acidity conditions. It is interesting that although **1** and **2** have almost the same quotient values of  $\phi/R$ , their magnetic parameters differ from ferromagnetic to antiferromagnetic. This means that Hatfield’s rule seems to be less general in this case, and other factors should also be taken into consideration. The magneto-structural correlation of such complexes has been further developed.



## Results and discussion

### Syntheses and general characterization

The doubly substituted ligand L<sup>1</sup> was prepared by using an excess of 4-chloromethylpyridine, and an excess of DACH was used to obtain the monoalkylated product L<sup>2</sup>. Acid-free ligands were obtained as oils so they were converted into the HCl salts to get purified crystalline solids. The yields for both ligands were over 50% and all the analytical data were in good agreement with the theoretical requirements.

The syntheses of the complexes **1** and **2** were achieved by the reactions of the protonated ligand ( $L^1 \cdot 4HCl$ ) or the corresponding acid-free ligand ( $L^2$ , neutralized with KOH aqueous solution prior to complexation) with  $Cu(ClO_4)_2 \cdot 6H_2O$ . The IR spectra for both complexes show absorption bands resulting from the skeletal vibrations of the aromatic rings in the 1400–1600  $cm^{-1}$  region. For **1**, there is a weak but sharp band at 3066  $cm^{-1}$  due to the N–H stretching of the protonated ligand.<sup>15</sup> The bands of  $ClO_4^-$  appear at  $\sim 1100$  and 623  $cm^{-1}$  for **1**, and an interesting feature of the spectrum of **2** is the occurrence of highly split  $\nu_{Cl-O}$  stretches of the  $ClO_4^-$  ions at  $\sim 1100$   $cm^{-1}$ , which provides good evidence of their involvement in the formation of hydrogen bonds.

### Description of crystal structures

In complex **1**, a  $[Cu(HL^1)Cl_2]_2^{2+}$  cation unit and two  $ClO_4^-$  ions were found to exist due to the mono-protonation of the ligand  $L^1$ . In the complex cation [Fig. 1(a)], resulting from the pairing of two mononuclear units related by a crystallographic center of symmetry, the two  $Cu^{II}$  ions are bridged equivalently by two  $Cl^-$  anions in a very weak coordination with a Cu–Cl length of 2.918(3) Å. Each  $Cu^{II}$  is penta-coordinated, in an approximately ideal square pyramid polyhedron reflected by the  $\tau$  value (0.01 here) defined by Addison *et al.* ( $\tau = 0$  for an ideal square pyramid and 1 for an ideal trigonal bipyramid)<sup>16</sup> and deviates by only 0.107 Å from the basal plane defined by N(1)–N(4)–Cl(1)–Cl(2) towards the apical Cl(2A). The axial Cu–Cl bond length is significantly longer than that of the Cu–Cl bond in the basal plane (Table 1). Also, it is longer than the normal values in similar dimeric complexes with  $C_{4v}$  coordination geometry of  $Cu^{II}$ .<sup>13</sup> The Cu–Cl–Cu bridging angle is 94.7(6)° and the intramolecular  $Cu \cdots Cu$  separation is 3.856 Å. The shortest intermolecular  $Cu \cdots Cu$  distance is 8.916 Å and the DACH ring takes the normal “boat/chair” configuration.<sup>12</sup> **1** is a unique dinuclear water-soluble  $Cu^{II}$  metalamacrocycle (*ca.*  $14.1 \times 3.5$  Å<sup>2</sup>) directly self-assembled by  $Cu^{II}$  and the new organic spacer  $L^1$ , and is also a nice example for

**Table 1** Selected bond distances (Å) and angles (°) for complexes **1** and **2**

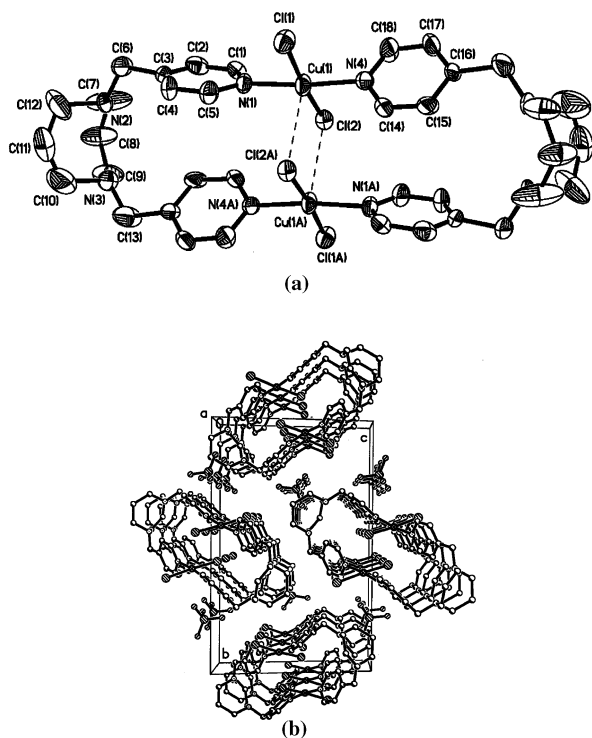
Complex <b>1</b>			
Cu(1)–N(1)	2.023(6)	Cu(1)–N(4)	1.995(6)
Cu(1)–Cl(1)	2.266(3)	Cu(1)–Cl(2)	2.292(2)
Cu(1)–Cl(2A)	2.918(3)		
Cl(1)–Cu(1)–Cl(2)	174.27(9)	N(4)–Cu(1)–N(1)	173.5(3)
N(4)–Cu(1)–Cl(1)	89.2(2)	N(1)–Cu(1)–Cl(1)	90.4(2)
N(4)–Cu(1)–Cl(2)	87.8(2)	N(1)–Cu(1)–Cl(2)	92.0(2)
Cu(1)–Cl(2)–Cu(1A)	94.7(6)		
Complex <b>2</b>			
Cu(1)–N(1)	2.020(7)	Cu(1)–N(2)	1.991(7)
Cu(1)–N(3)	1.996(7)	Cu(1)–Cl(1)	2.624(2)
Cu(1)–Cl(2)	2.273(3)	Cu(2)–N(4)	1.986(7)
Cu(2)–N(6)	2.001(6)	Cu(2)–N(5)	2.022(7)
Cu(2)–Cl(1)	2.279(2)	Cu(2)–Cl(2)	2.656(3)
N(2)–Cu(1)–N(3)	158.9(3)	N(1)–Cu(1)–Cl(2)	166.9(2)
N(2)–Cu(1)–N(1)	79.8(3)	N(3)–Cu(1)–N(1)	82.3(3)
N(2)–Cu(1)–Cl(2)	96.3(3)	N(3)–Cu(1)–Cl(2)	98.6(2)
N(4)–Cu(2)–N(6)	155.5(3)	N(4)–Cu(2)–N(5)	79.1(3)
N(6)–Cu(2)–N(5)	82.4(3)	N(4)–Cu(2)–Cl(1)	97.6(2)
N(6)–Cu(2)–Cl(1)	97.8(2)	N(5)–Cu(2)–Cl(1)	169.8(2)
Cu(1)–Cl(1)–Cu(2)	86.76(8)	Cu(1)–Cl(2)–Cu(2)	86.11(8)

the “symmetry interaction” model to construct metal-based supramolecules with special topology.<sup>17</sup> Another interesting point is the stacking pattern of this assembly in the solid state because the cation parts of the metallamacrocycle are stacked along the *a* axis about 5.9 Å apart, resulting in long, channel-like cavities [Fig. 1(b)]. This interesting arrangement may find application in solid-state catalysis, especially in cases where the exact dimensions of the absorbing channels are of importance.<sup>18</sup>

Complex **2** consists of a dichloro-bridged  $[Cu_2(L^2)_2Cl_2]^{2+}$  dimeric unit and two  $ClO_4^-$  ions. Both  $Cu^{II}$  centers are also penta-coordinated, in a distorted square pyramid geometry with  $\tau$  values of 0.13 for Cu(1) and 0.24 for Cu(2). Cu(1) is 0.234 Å above the mean basal plane defined by N(1)–N(2)–N(3)–Cl(2) toward the apical Cl(1), and Cu(2) is 0.191 Å above the N(4)–N(5)–N(6)–Cl(1) mean plane toward Cl(2). The Cu–Cl bond lengths in the axial position are significantly longer than those in the basal plane (Table 1) and the Cu–Cl–Cu bridging angles are 86.76(8) and 86.11(8)°. The intramolecular  $Cu \cdots Cu$  separation is 3.376 Å, and the shortest intermolecular  $Cu \cdots Cu$  length in the unit cell is 7.772 Å. The DACH ring takes the normal boat configuration. One feature of this structure is that each  $[Cu_2(L^2)_2Cl_2]^{2+}$  unit carries one  $ClO_4^-$  hydrogen-bonded to the non-substituted nitrogen atoms of the diazamesocycle to form a macrocycle-like ring system including a N–H $\cdots$ O $\cdots$ H–N bridge (Fig. 2), reflected by the highly split bands for  $ClO_4^-$  in the IR spectrum.

### Electronic and EPR spectra

The UV-Vis spectrum of complex **1** (light green) in water solution shows a quite weak absorption maximum at 804 nm, which indicates that the coordination geometry changes to the planar form.<sup>19</sup> For **2** (dark blue), a broad and intense band centered at 645 nm was found in methanol solution, and this spectral feature is typical of penta-coordinated  $Cu^{II}$  complexes with distorted square-pyramidal geometry, which generally exhibits a band in the 550–660 nm range ( $d_{xz}$ ,  $d_{yz} \rightarrow d_{x^2-y^2}$ ).<sup>20</sup> The relative higher  $\lambda_{max}$  value suggests the coordination geometry of  $Cu^{II}$  in **2** is distorted from square-pyramidal (toward trigonal bipyramid),<sup>20</sup> which is consistent with the degree of distortion found in the X-ray structural analysis. In addition, the electronic spectra of both complexes display characteristic absorptions at 200–300 nm assigned to ligand  $\pi \rightarrow \pi^*$  transitions.



**Fig. 1** (a) ORTEP structure of  $[Cu_2(HL^1)Cl_2]^{2+}$  unit in complex **1** with 50% probability thermal ellipsoids. (b) Stacking diagram of **1** in the unit cell showing the channel-like cavities along the *a* direction.

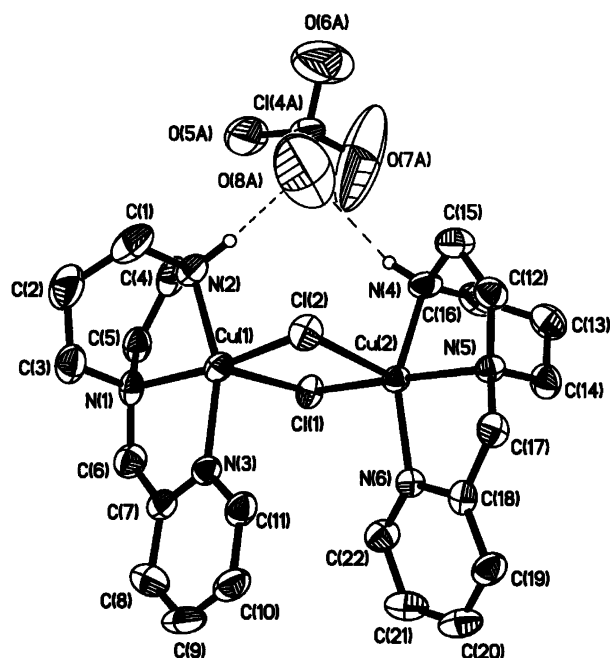


Fig. 2 ORTEP structure of the  $\{[\text{Cu}_2(\text{L}^1)_2\text{Cl}_2](\text{ClO}_4)^+\}$  ring system showing the hydrogen bonds in complex **2** with 50% probability thermal ellipsoids.

The X-band EPR spectra of both complexes were registered in the solid state at different temperatures (from room temperature to 4 K). For **1**, at all the temperatures, the spectra show isotropic bands with  $g_{\text{av}} = 2.14$ . The triplet did not appear even at the lowest temperature and it is normal for these kinds of ferromagnetic  $\text{Cu}^{\text{II}}$  complexes, probably owing to exchange narrowing. No absorption is observed at half-field ( $\Delta m_s = 2$ ,  $g = 4$ ) indicating a small zero-field splitting effect.<sup>21</sup> For **2**, at all temperatures there is a typical pattern from axial distortion with  $g_{\parallel} = 2.15$  and  $g_{\perp} = 2.06$ , and there is only a small variation with the temperature. This pattern is typical for a square-pyramidal geometry, with the unpaired electron mainly located in the  $d_{x^2-y^2}$  orbital.

### Magnetic properties

The magnetic properties of **1** and **2** in the form of  $\chi_{\text{M}}T$  vs.  $T$  plots are shown in Fig. 3 ( $\chi_{\text{M}}$  is the magnetic susceptibility per two  $\text{Cu}^{\text{II}}$  ions). For **1**, the value of  $\chi_{\text{M}}T$  at room temperature is  $0.85 \text{ cm}^3 \text{ K mol}^{-1}$ , continuously increasing to a maximum of  $1.06 \text{ cm}^3 \text{ K mol}^{-1}$  at 5.6 K. It then decreases to  $1.01 \text{ cm}^3 \text{ K mol}^{-1}$  at 2 K. This shape of the curve is typical of a moderate ferromagnetic interaction between  $\text{Cu}^{\text{II}}$  ions. The decrease at lower temperatures is due to intermolecular interactions and/or zero-field splitting effects. For **2**, the value of  $\chi_{\text{M}}T$  at 298 K is  $0.84 \text{ cm}^3 \text{ K mol}^{-1}$ , corresponding to two independent uncoupled  $\text{Cu}^{\text{II}}$  ions. The  $\chi_{\text{M}}T$  value decreases monotonically down to 2 K, attaining a value of  $0.53 \text{ cm}^3 \text{ K mol}^{-1}$ . This feature is characteristic of the presence of a weak intramolecular antiferromagnetic interaction between  $\text{Cu}^{\text{II}}$  ions. Very good fits can be obtained through a simple Bleaney–Bowers expression for a  $\text{Cu}^{\text{II}}$  dimer using the hamiltonian  $\hat{H} = -J\hat{S}_1 \cdot \hat{S}_2$ ,<sup>22</sup> and the best-fit parameters are  $J = 10.70 \text{ cm}^{-1}$ ,  $J' = -0.26 \text{ cm}^{-1}$ ,  $g = 2.12$  and  $R = 3.9 \times 10^{-6}$  for **1**, and  $J = -1.95 \text{ cm}^{-1}$ ,  $g = 2.11$  and  $R = 2.2 \times 10^{-5}$  for **2** (all symbols have their usual meanings). For **1**, a new parameter  $J'$  indicating intermolecular interactions must be introduced in the formula, according to the theory reported by Kahn,<sup>3</sup> in order to take into account the decrease of  $\chi_{\text{M}}T$  at very low temperature.

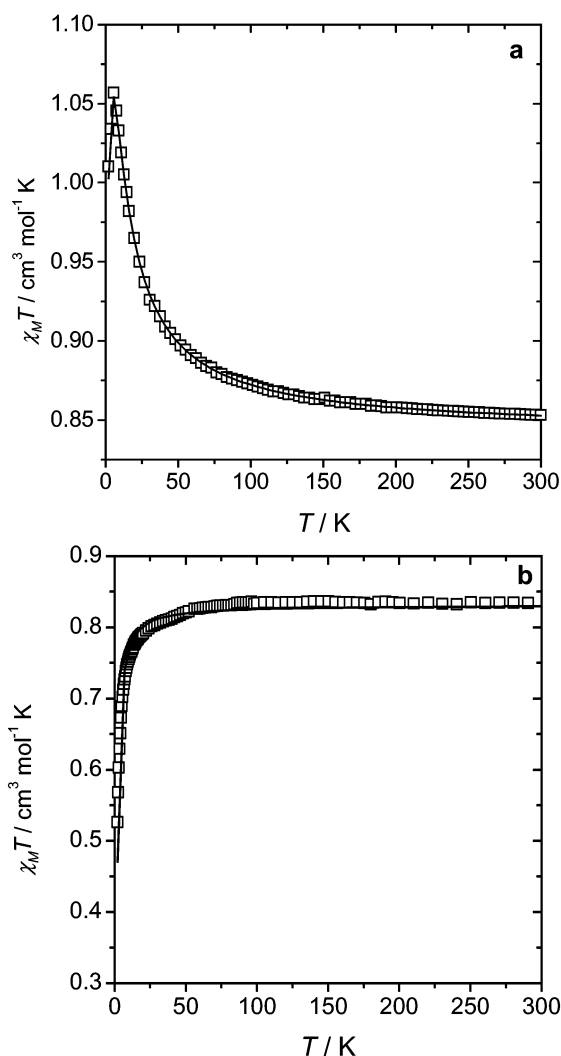


Fig. 3 Magnetic coupling diagram of (a) **1**; (b) **2**. The solid lines represent the best fit from the Bleaney–Bowers expression.

A number of investigations have been carried out concerning the magneto-structural correlation and different magnetic behaviors have been found in chloro-bridged  $\text{Cu}^{\text{II}}$  dimers.<sup>5–9,13,14,23–28</sup> To date, three types<sup>5</sup> of pyramidal arrangements in  $[\text{Cu}(\mu\text{-Cl})_2\text{Cu}]$  units are found in the literature. The two complexes studied in this paper belong to the same type (I): square pyramids sharing one base-to-apex edge but with parallel basal planes [Scheme 1(a)]. Such  $\text{Cu}^{\text{II}}$  dimers have been well studied, with the aim to correlate their structures and magnetic properties, but no simple magneto-structural relationship relating the value of  $J$  to the  $\text{Cu}-\text{Cl}-\text{Cu}$  angle or  $\text{Cu} \cdots \text{Cu}$  distance, for example, has been established. Hatfield *et al.*<sup>9</sup> have shown that the singlet–triplet gap in such compounds varies in a regular way with the quotient  $\phi/R$  as described above. It was found that for values of this quotient lower than 32.6 and higher than 34.8, the exchange interaction is antiferromagnetic. For values falling between these limits it is ferromagnetic. In the case of **1** and **2** having similar cores, the magnetic properties are widely divergent. **1** is ferromagnetic while **2** being antiferromagnetic although the parameter  $\phi/R$  is almost the same [32.43 for **1** and 32.74 (average) for **2**]. This indicates that Hatfield's rule seems to be less general for our new case, and other structural factors should be taken into consideration.

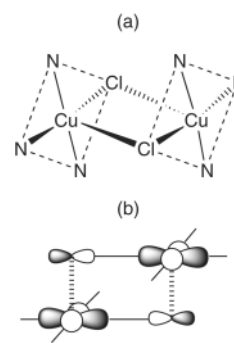
Actually, in the case of complexes **1** and **2**, the values of the quotient  $\phi/R$  are near 32.6, and thus near the limit between ferro and antiferromagnetic interactions. The main difference

(and the origin of the magnetic behavior) is the characteristics of the magnetic orbitals: in **2** the geometry of Cu<sup>II</sup> is not a perfect square-pyramid, thus the magnetic orbital is a mixture of  $d_{x^2-y^2}$  and  $d_{z^2}$ , mainly located in the equatorial plane ( $d_{x^2-y^2}$ ) but with non-zero spin density on its axial position. This feature (participation of the  $d_{z^2}$  orbital) creates a small overlap between the two Cu<sup>II</sup> magnetic orbitals, giving the antiferromagnetic coupling. On the contrary, in **1**, the geometry of Cu<sup>II</sup> is almost a perfect square-pyramid. Thus, the magnetic orbital is purely  $d_{x^2-y^2}$ , without any (or with only negligible) delocalization in  $d_{z^2}$ . Consequently, there is no overlap between magnetic orbitals and the behavior must be ferromagnetic [Scheme 1(b)].

Another important point, according to the literature, is the dihedral angle between two Cl–Cu–Cl planes (planarity or deviation of the planarity for Cl–Cu–Cl–Cu). The bending of the dihedral angle  $\delta$  causes a shortening of the Cu...Cu distance. A very crude mono-electronic reasoning would lead one to expect an enhancement of bonding and antibonding character of single occupied MOs, leading to an increase of the antiferromagnetic coupling. However, variational *ab initio* MO calculations have shown that these bent structures display ferromagnetic properties.<sup>29</sup> Moreover, the relationship between the S–T gap and the  $\delta$  angle shows that the non-planarity of the bridge increases the ferromagnetic coupling. The experimental  $\delta$  value is 9.4° for **2**, thus enhancing the ferromagnetic contribution between both Cu<sup>II</sup> atoms and, logically, diminishing the global antiferromagnetic coupling. For **1**, however, the  $\delta$  value is zero, increasing the antiferromagnetic component in the global ferromagnetic coupling. From the magnetic parameters of several such Cu<sup>II</sup> dimers (type I),<sup>23–28,30–35</sup> as listed in Table 2, we can also see that the magnetic coupling is, as expected, relatively small (either ferro- or antiferromagnetic) due to the near orthogonality of the magnetic orbitals as illustrated in Scheme 1(b).

## Conclusions

Two novel di- $\mu$ -chloride Cu<sup>II</sup> dimers with new diazamesocyclic ligands functionalized by pyridine pendants have been rationally designed and synthesized, and their structures elucidated by X-ray analyses. Complex **1**, obtained from direct self-assembly by the metal ion and organic spacer, constitutes a rare example of a paramagnetic dinuclear metallacycle.<sup>36</sup> The crucial structural parameter  $\phi/R$  for complexes **1** and **2** (having the same geometric arrangement) are almost the same, however, their magnetic couplings are different. This indicates that the superexchange pathway of such complexes depends on various orbitals, and therefore, different structural dimers must be studied separately. More appropriate examples, like **1**



**Scheme 1** (a) The type of pyramidal arrangements (I) in  $[\text{Cu}(\mu\text{-Cl})_2\text{Cu}]$  units for complexes **1** and **2**. (b) Schematic representation of the magnetic orbitals of **1**.

and **2**, are needed in order to explore this magneto-structural correlation. Furthermore, Cu<sup>II</sup> ions have weakly coordinated axial chloride anions in both complexes that may be replaced by other donor molecules or ions (such as azide, thiocyanate and cyanate, *etc.*) to form the corresponding Cu<sup>II</sup> dimers, which is under way in our laboratory.

## Experimental

### Materials and general methods

All the reagents and solvents for syntheses and analyses were of analytical grade. FT-IR spectra (KBr pellets) were taken on a FT-IR 170SX (Nicolet) spectrometer and electronic absorption spectra on a Hitachi UV-3010 spectrometer. Carbon, hydrogen, and nitrogen analyses were performed on a Perkin–Elmer 240C analyzer. <sup>1</sup>H NMR spectra were recorded on a Bruker AC-P 400 spectrometer (400 MHz) at 25 °C with tetramethylsilane as the internal reference. ESR spectra were recorded on powder samples at X-band frequency with a Bruker 300E automatic spectrometer, varying the temperature between 4 and 300 K.

### Magnetic measurements

Magnetic measurements were carried out in the Servei de Magnetoquímica (Universitat de Barcelona) on polycrystalline samples (30 mg) with a Quantum Design MPMS SQUID susceptometer operating at a magnetic field of 0.1 T between 2 and 300 K. The diamagnetic corrections were evaluated from Pascal's constants.

**Table 2** Structural and magnetic data of some out-of-plane di- $\mu$ -chloro-bridged Cu<sup>II</sup> complexes

Compound <sup>a</sup>	$J/\text{cm}^{-1}$	$\phi_{\text{Cu-Cl-Cu}}/^\circ$	$R_{\text{Cu-Cl}}/\text{\AA}$	$\phi/R/\text{\AA}$	$d_{\text{Cu...Cu}}/\text{\AA}$	Ref.
$[\text{Cu}(\text{tms})\text{Cl}_2]_2$	–16	88.5	3.02	29.30	3.74	30
$[\text{Cu}(\text{2-Mepy})\text{Cl}_2]_2$	–7.4	100.6	3.36	29.94	4.40	31
$[\text{Cu}(\text{terpy})\text{Cl}_2](\text{PF}_6)_2$	–5.8	89.9	2.72	33.05	—	32
$[\text{Cu}(\text{tmen})\text{Cl}_2]_2$	–5.6	96.8	3.15	30.73	4.09	33
$[\text{Cu}(\text{Metz})(\text{dmf})\text{Cl}_2]_2$	–3.0	95.3	2.72	35.03	—	9
$[\text{Cu}(\text{Me}_2\text{en})\text{Cl}_2]_2$	–2.2	86.1	2.73	31.53	3.46	34
$[\text{Cu}(\text{Et}_3\text{en})\text{Cl}_2]_2$	+0.06	94.8	2.73	34.72	3.70	35
$[\text{Cu}(\text{dmg})\text{Cl}_2]_2$	+6.3	88.0	2.70	32.59	3.44	15
Complex <b>1</b>	10.70	94.7	2.92	32.43	3.86	* <sup>b</sup>
Complex <b>2</b>	–1.95	86.44	2.64	32.77	3.37	** <sup>b</sup>

<sup>a</sup> Abbreviations: tms = tetramethylsulfoxide, 2-Mepy = 2-Methylpyridine, terpy =  $N,N',N''$ -terpyridine, tmen =  $N,N,N',N'$ -tetramethylethylenediamine, Metz = 4-methylthiazole, Me<sub>2</sub>en =  $N,N$ -dimethylethylenediamine, Et<sub>3</sub>en =  $N,N,N'$ -triethylethylenediamine, dmg = dimethylglyoxime, bpy = 2,2'-bipyridine. <sup>b</sup> This work.

**1,5-Bis(pyridin-4-ylmethyl)-1,5-diazacyclooctane tetrahydrochloride trihydrate ( $L^1 \cdot 4HCl \cdot 3H_2O$ ).** A solution of DACO $\cdot 2HBr$  (1.42 g, 5.3 mmol) and KOH (0.90 g, 13.2 mmol) in anhydrous ethanol (50 mL) was vigorously stirred for *ca.* 4 h and then filtered at room temperature. 4-Chloromethylpyridine (1.84 g, 11.2 mmol) was added to the filtrate with stirring. The stirring was continued for 3 days at room temperature, and small portions of solid KOH were added to keep the pH value of the mixture at *ca.* 9 during this period. Then the mixture was filtered. After rotary evaporation of the solvent, the residue was dissolved in water (15 mL) and extracted with  $CH_2Cl_2$  (100 mL  $\times$  5). The combined  $CH_2Cl_2$  phases were dried over anhydrous  $MgSO_4$ . The organic solvent was removed by rotary evaporation and the residue was dissolved in anhydrous EtOH. Concentrated hydrochloric acid was added to the ethanol solution and the white solid was obtained by filtration. Yield: 1.54 g (60% based on DACO).  $^1H$  NMR ( $D_2O$ ):  $\delta$  2.21–2.40 (m, 2H), 3.52 (t,  $J$  = 5.2 Hz, 8H), 4.68 (s, 4H), 8.9 (d,  $J$  = 6.4 Hz, 4H), 8.3 (d,  $J$  = 6.4 Hz, 4H). IR (KBr pellet,  $cm^{-1}$ ): 3465vs, 3403b, 3064s, 1641s, 1600s, 1511s, 1482s, 1464s, 1452s, 1427s, 1370w, 1319m, 1232s, 1090m, 999m, 940m, 867m, 812s. Anal. calcd for  $C_{18}H_{24}N_4 \cdot 4HCl \cdot 3H_2O$ : C, 43.56; H, 6.91; N, 11.29%. Found: C, 43.76; H, 6.68; N, 11.51%.

**1-(Pyridin-2-ylmethyl)-1,4-diazacycloheptane dihydrochloride tetrahydrate ( $L^2 \cdot 2HCl \cdot 4H_2O$ ).** To a solution of DACH (0.57 g, 5.6 mmol) in anhydrous ethanol (100 mL), 2-(chloromethyl)pyridine hydrochloride (0.47 g, 2.9 mmol) was added with vigorous stirring at reflux for *ca.* 2 h. The stirring was continued for about 4 days at room temperature, and small portions of solid KOH were added during this time. After filtration of the mixture, the solvent was removed by rotary evaporation. Then the residue was dissolved in water (15 mL) and extracted with  $CH_2Cl_2$  (100 mL  $\times$  5). The combined organic phases were dried over anhydrous  $MgSO_4$ . The solvent was removed and the residue was purified by silica gel column chromatography ( $CH_2Cl_2$ – $CH_3OH$ – $NH_3 \cdot H_2O$  = 10 : 10 : 1). The free ligand was further purified by conversion to the HCl salt to obtain white solid material. Yield: 0.50 g [52% based on 2-(chloromethyl)pyridine hydrochloride].  $^1H$  NMR ( $D_2O$ ):  $\delta$  2.15–2.34 (m, 2H), 3.39 (t,  $J$  = 5.2 Hz, 2H), 3.46 (t,  $J$  = 5.2 Hz, 2H), 3.60 (s, 4H), 4.52 (s, 2H), 7.75 (t,  $J$  = 6.2 Hz, 1H), 7.80 (d,  $J$  = 7.6 Hz, 1H), 8.24 (t,  $J$  = 7.6 Hz, 1H), 8.70 (d,  $J$  = 4.8 Hz, 1H). IR (KBr pellet,  $cm^{-1}$ ): 3448vs, 3392vs, 3358vs, 2996s, 2693vs, 1642s, 1620s, 1605m, 1547m, 1469s, 1447s, 1435m, 1387m, 1376m, 1298w, 1232m, 1160m, 1111s, 1102m, 1050m, 1016m, 994m, 948m, 775s. Anal. calcd for  $C_{11}H_{17}N_3 \cdot 2HCl \cdot 4H_2O$ : C, 39.29; H, 8.09; N, 12.50%. Found: C, 39.56; H, 8.03; N, 12.19%.

**$[Cu(HL^1)Cl_2]_2(ClO_4)_2$  1.** The ligand  $L^1 \cdot 4HCl \cdot H_2O$  (0.10 g, 0.2 mmol) was dissolved in methanol (20 mL) and to it  $Cu(ClO_4)_2 \cdot 6H_2O$  (0.08 g, 0.2 mmol) dissolved in methanol–acetone (15 mL) was added dropwise with stirring for 2 h at pH  $\sim$  2. Then the solution was filtered and the light green precipitate was collected. Single crystals suitable for X-ray analysis were obtained by recrystallization of the precipitate from methanol. Yield: 64 mg (58%). IR (KBr pellet,  $cm^{-1}$ ): 3066m, 1641s, 1597m, 1506s, 1487m, 1466m, 1454m, 1145s, 1090vs, 623vs. Anal. calcd for  $C_{36}H_{50}N_8Cl_6Cu_2O_8$ : C, 40.69; H, 4.74; N, 10.55%. Found: C, 40.90; H, 5.08; N, 10.20%.

**$[Cu_2(L^2)_2Cl_2](ClO_4)_2$  2.** Complex 2 was obtained by mixing equimolar amounts of  $Cu(ClO_4)_2 \cdot 6H_2O$  (0.04 g, 0.1 mmol) and  $L^2 \cdot 2HCl \cdot 4H_2O$  (0.03 g, 0.1 mmol) in ethanol (40 mL) with stirring. The pH of the mixture was adjusted to *ca.* 6–7 with

**Table 3** Summary of crystal data for  $[Cu(HL^1)Cl_2]_2(ClO_4)_2$  (1) and  $[Cu_2(L^2)_2Cl_2](ClO_4)_2$  (2)

	1	2
Formula	$C_{36}H_{50}Cl_6Cu_2N_8O_8$	$C_{22}H_{34}Cl_4Cu_2N_6O_8$
FW	1062.62	779.43
$T/K$	293(2)	293(2)
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$
$a/\text{\AA}$	8.916(3)	11.860(4)
$b/\text{\AA}$	19.774(5)	8.114(3)
$c/\text{\AA}$	13.027(4)	32.848(10)
$\beta/^\circ$	106.411(6)	90.908(6)
$u/\text{\AA}^3$	2203.1(11)	3160.6(17)
$Z$	2	4
$\mu/cm^{-1}$	13.88	17.37
Unique reflect.	3850	5528
Obsd reflect.	1456	2463
$R^a$	0.0661	0.0611
$wR^b$	0.1285	0.1362

$$^a R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|. \quad ^b wR = [\Sigma (w(F_o^2 - F_c^2)^2) / \Sigma w(F_o^2)]^{1/2}.$$

dilute KOH aqueous solution. Then the blue solution was filtered and left to stand at room temperature. Single crystals suitable for X-ray analysis were obtained by slow evaporation of the solvent. Yield: 41 mg (70%). IR (KBr pellet,  $cm^{-1}$ ): 1609s, 1571m, 1475s, 1467s, 1448s, 1433s, 1145s, 1111vs, 1090vs, 1053s, 624s. Anal. calcd for  $C_{22}H_{34}N_6Cl_4Cu_2O_8$ : C, 33.90; H, 4.40; N, 10.78%. Found: C, 33.55; H, 4.35; N, 10.87%.

**Caution!** Although no problems were encountered in this study, transition metal perchlorate complexes are potentially explosive and should be handled with proper precautions.

## X-Ray diffraction

Single crystal X-ray diffraction studies were performed on a Bruker Smart 1000 CCD diffractometer with Mo-K $\alpha$  radiation ( $\lambda$  = 0.71073  $\text{\AA}$ ). The structures were solved by direct methods and semi-empirical absorption corrections were applied. The non-hydrogen atoms were located by direct phase determination and full-matrix least-squares refinement on  $F^2$ . Hydrogen atoms were generated theoretically and refined isotropically. Further details of the structural analyses are summarized in Table 3.

CCDC reference numbers 182815 and 182816. See <http://www.rsc.org/suppdata/nj/b1/b110465a/> for crystallographic data in CIF or other electronic format.

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