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A new tetrameric Cu^{II} cluster with square topology exhibiting ferro- and antiferromagnetic magnetic pathways : which is which?†

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$[Cu_4L_2(bpy)_4(H_2O)_3](ClO_4)_4·2.5H_2O$, 1, a new tetranuclear Cu^{II} cluster showing square planar geometry, formed with aspartate bridging ligand (L) has been synthesized. The global magnetic coupling is ferromagnetic but theoretical DFT/B3LYP calculations are necessary to assign which Cu–L–Cu side is ferro or antiferromagnetically coupled.

The rational synthesis of polynuclear coordination complexes, aiming at understanding the structural and chemical factors that govern the exchange coupling between paramagnetic centers, are of continuing interest in biology, chemistry and physics.[1] Particular interest has focused on the development of single molecule magnets (SMM).[2] A variety of ligands have been employed for preparation of these clusters with the carboxylate being one of the most widely used. Aspartate is known to form versatile polymeric structures with Cu^{II}.[3] Here we provide the first report of a tetranuclear Cu^{II} complex $[Cu_4L_2(bpy)_4(H_2O)_3](ClO_4)_4·2.5H_2O$, **1**‡. Its crystal structure§ indicates that there are two centrosymmetric, $[Cu_4L_2(bpy)_4(H_2O)_3]^{4+}$ tetrameric cations in the unit cell together with perchlorate anions and solvent molecules. The two tetramers A and B have similar coordination spheres (Fig. 1 for tetramer A). In both tetramers the two independent copper atoms Cu(1) and Cu(2) have different environments.

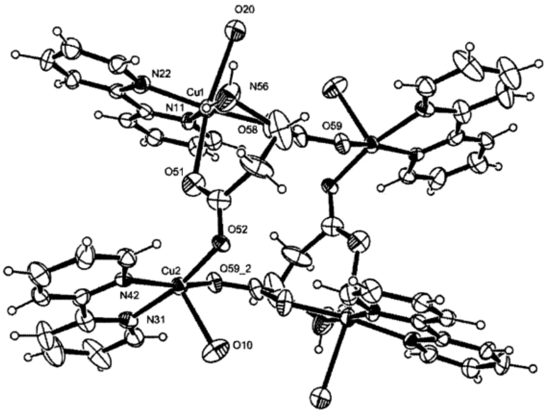

Fig. 1 ORTEP view of **1** (20% probability). Tetramer A is shown. Tetramer B has an equivalent structure. The hydrogens bonded to the water molecules O(10) and O(20) were not located and are not included. Selected bond lengths (Å), angles (°): Cu(1)–N(56) 1.925(12), Cu(1)–O(58) 1.957(9), Cu(1)–N(11) 1.956(9), Cu(1)–N(22) 2.013(9), Cu(1)–O(51) 2.324(10), Cu(2)–O(52) 1.916(8), Cu(2)–O(59)* 1.997(8), Cu(2)–N(31) 2.022(10), Cu(2)–N(42) 2.037(9), Cu(2)–O(10) 2.206(9); Cu(1)···Cu(2) 5.20(1), Cu(1)···Cu(2)* 5.17(1), Cu(1)···Cu(1)* 7.62(2), Cu(2)···Cu(2)* 7.41(2), N(56)–Cu(1)–N(11) 178.2(4), O(58)–Cu(1)–N(22) 170.0(4), O(58)–Cu(1)–O(51) 90.2(4), O(52)–Cu(2)–N(31) 169.6(4), O(59)*–Cu(2)–N(42) 160.8(3), O(59)*–Cu(2)–O(10) 96.9(3), O(52)–Cu(2)–O(10) 92.0(4). * symmetry operation designates 1−x, 1−y, 1−z.

Cu(1) forms a square pyramidal environment with O(51) in the axial position. Of the water molecules, O(10) was refined with full occupancy while O(20) was refined with 50% occupancy. This reduced occupancy, taken with the fact that the Cu(1)–O(20) bond is very long at 2.465 Å suggests that it might be more appropriate to consider Cu(1) as five-coordinate with the square pyramid environment. This is definitely the case for Cu(2): the five-coordinated pyramidal structure is completed by a water molecule, O(10), in an axial position. Main distances and angles for part A are given in Fig. 1. Each ligand therefore is bonded to three different copper atoms giving *syn-anti* L bridges, which will be described below.

The magnetic behavior of **1** was measured on a SQUID susceptometer from 300 to 2 K. $\chi_M T$ value is 1.70 cm^{3}mol^{-1}K at 300 K, first increasing and then decreasing to 1.43 cm^{3}mol^{-1}K at 2.03 K (Fig. 2). The curve of the reduced magnetization ($M/N\beta$) *vs.* H (Fig. 2 inset) lies slightly below the theoretical Brillouin curve for a ground state S = 2 and g = 2.12 (epr measurements). A very similar curve has been recently reported for $[Cu_2(mal)_2(py)_2]_2·2H_2O$, in which the J value is +5.62 cm^{-1} and J' (intermolecular) is –0.284 cm^{-1}.[4]

All intramolecular magnetic pathways in **1** are schematized in Chart 1. Structurally one distinguishes along the sides (J_1, J_2) and along the diagonal (J_3). It must be emphasised that **1** is the *first Cu$_4$ complex* with three such different carboxylato pathways reported to date. A full-diagonalization formalism through the CLUMAG program,[5] has been carried out using the Hamiltonian $H = -J_{i,j}\Sigma S_i S_j$ (Model 1). The best-fit parameters obtained are: J_1 (or J_2) = 8.38 cm^{-1}; J_2 (or J_1) = –1.27 cm^{-1}; J_3 = –0.5 cm^{-1}, g = 2.12 and R = 1.1 × 10^{-5}. J_3 corresponds to the diagonal pathway, because the coupling through four carbon atoms is either zero or

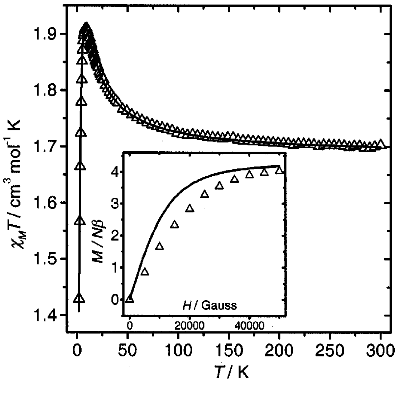

Fig. 2 A plot of $\chi_M T$ *vs.* T for **1**. The solid line represents the best fit and the points the experimental data. Inset: plot of the $M/N\beta$ *vs.* H compared with the Brillouin formula for g = 2.12 and S = 2.

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† Electronic supplementary information (ESI) available: Figure S1. See http://www.rsc.org/suppdata/cc/b4/b401061b/

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very small and antiferromagnetic.[6] But a question immediately arises: which side of the square corresponds to J_1 and which to J_2? **1** contains one side as a *syn-anti* (*basal-basal*) carboxylato bridge and the other side as a *syn-anti* (*basal-apical*) carboxylato bridge. Weak ferro- or antiferromagnetic couplings are reported for these two modes.[7] For the *basal-basal* mode the sign and magnitude of J depends on the planarity of the Cu–O–C–O–Cu skeleton as characterized by the dihedral angles between two adjacent copper planes.[7,8] It is know that at 180° the interaction is AF while close to 90° is F. In **1** these dihedral angles are 159.5 and 153.4°. For *basal-apical* coordination mode, the Addison parameter[9] (τ) of each square-pyramidal copper(II) center, represents the mixture of the magnetic x^2-y^2 and z^2 orbitals: for $\tau = 0$ (pure sp), the greatest F coupling and for $\tau = 1$ (pure tbp) the greatest AF coupling. In complex **1** τ values are 0.14 and 0.25. Indeed, J_1 and J_2 can be ferro or antiferromagnetic.

We can add to the previous model the effect of J' (intermolecular interactions) and/or the molecular Zero-Field-Splitting (D parameter) of the *hypothetical* $S = 2$ ground state (Model 2). Simulating with J' and D (considering both J_1 and J_2 ferromagnetic, which is possible) several curves with very similar shape to the experimental, have been drawn (Fig. S1†). Thus, the problem of the assignment of the J values does not have a clear solution. The only definitive feature is that J_1 and J_2 cannot be *simultaneously antiferromagnetic*.

In order to establish the right model for **1**, we have carried out DFT/B3LYP calculations[10] on Cu_i–L–Cu_j dimers of one of the tetramers to determine unequivocally the nature of the J_1, J_2, and J_3. The dimers employed to compute J_1 and J_2 are obtained by taking from the tetramer the Cu_1 and Cu_2 atoms, their bpy, the dicarboxylate ligand that connects the two copper atoms and the water molecule bound to Cu(2). The water molecule with 50% occupancy in the crystal structure bound to Cu(1) was omitted, although its inclusion would have negligible effect on the calculations. The other dicarboxylate attached to the Cu atom was simulated by an acetate (due to the similar local geometry at the Cu–L coordination point). In the case of J_3, the two dicarboxylates have been employed without truncation. We then computed the total energy of the Cu_i–L–Cu_j dimers, in their triplet and singlet states, using the B3LYP gradient-corrected density functional[11,12] and an enlarged Ahlrich's pVDZ basis set.[13,14] The broken-symmetry procedure was used to evaluate the singlet state energy. The value of the J_i parameter was obtained by direct subtraction of the energy for the triplet and broken-symmetry singlet state, without further correction. The results thus obtained for the J_1, J_2 and J_3 are 11.4, –3.8, and –1.5 cm^{-1}, respectively, reasonably close to the fit values. Without considering the exact value, it is clear that, now, we can assign the *basal-basal* pathway as the ferromagnetic and the *basal-apical* pathway as the antiferromagnetic. This allows a proper analysis of the magnetism of this system.

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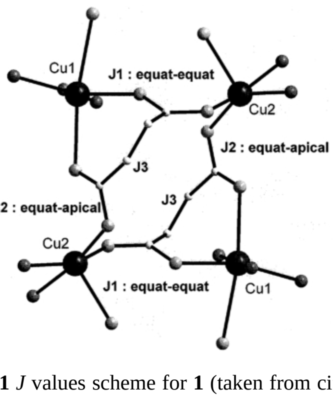

Chart 1 J values scheme for **1** (taken from cif file).

Notes and references

‡ **1**: A 30 mL methanolic solution of copper(II) perchlorate hexahydrate (5 mmol, 1.859 g) was mixed with L-aspartic acid (5 mmol, 0.665 g) and the mixture was warmed on a water-bath for 5 min. The resulting blue solution was added to the methanolic solution (10 mL) of 2,2′-bipyridine (5 mmol, 0.78 g). The dark blue solution was stirred for 15 min. The blue precipitate was filtered and washed with methanol. Single blue crystals for X-ray diffraction were obtained by slow evaporation of the aqueous solution in a refrigerator. IR (KBr pellet, cm^{-1}): 1602 $\nu_{as}(COO^-)$, 1442 $\nu_{sys}(COO^-)$ and 1093 $\nu(ClO_4^-)$.

§ *Crystal data* for **1**: $C_{48}H_{49}Cl_4Cu_4N_{10}O_{29.5}$, M_w = 1633.94, triclinic, space group $P\bar{1}$, $Z = 2$, a = 11.275(16), b = 14.520(16), c = 20.52(2) Å, α = 86.97(1), β = 77.61(1), γ = 73.43(1)°, V = 3145 $Å^3$, D_c = 1.725 g cm^{-3}, μ(Mo-Kα) = 1.6 mm^{-1}, $F(000) = 1640$, $T = 293$. 9549 independent reflections were measured with MoKα radiation using the MAR research Image Plate System. 100 frames were measured at 2° intervals with a counting time of 5 min. Data analysis was carried out with the XDS program.[15] The structure was solved using direct methods with the SHELX86 program.[16] Hydrogen atoms bonded to carbon atoms were placed in geometric positions and given thermal parameters of 1.2 times those of the atoms to which they were bonded. Hydrogen atoms bonded to oxygen atoms were not located. One of the perchlorate anions is located in two different sites and atoms were refined with occupancies of x and 1−x. An empirical absorption correction was carried out using the DIFABS program.[17] The structure was refined on F^2 using SHELXL[18] to $R1$ 0.0906, $wR2$ 0.2358 for 4875 reflections with $I > 2\sigma(I)$ respectively.

CCDC 207155. See http://www.rsc.org/suppdata/cc/b4/b401061b/ for crystallographic data in .cif or other electronic format.

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