Electronic supplementary information (ESI)

Trinuclear Cu(II) complexes of a chiral N₆O₃ amine

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Supporting Figure 1S. Asymmetric unit of **1** with the labelling scheme.

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Supporting Figure 2S. Asymmetric unit of **3** with chloride anion and solvent molecules, dichloromethane and water O1w and O2w molecules. The water O3w and O4w are omitted for clarity. The H atoms of water O2w, O3w and O4w molecules have been not localised. All solvated dichloromethane molecules are disordered and during refinement their parameters were restrained by SAME instructions.^{s1}

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Supporting Figure 3S. Two complex cations $[Cu_3 \mathbf{1}_{-3H}(CH_3 COO)_2]^+$ and acetate anions. The disoredred acetate $CH_3 COO^-$ anions (C212-C211-O211 and C311-C312-O311) were refined with constrained distances of 1.515 Å for the bonds C211-C212 and C311-C312.

Discussion of magnetic properties

In complex **3** the unpaired electrons of three different Cu(II) ions resides on d_{x-y}^{2-2} orbitals positioned in the square base. These orbitals interact via the bridging phenolate oxygen atoms of the pairs Cu1-Cu3 and Cu2-Cu3. On the other hand the analogous bridging in the Cu1-Cu2 pair corresponds to the interaction of the filled d_z^2 orbital of Cu1 with the partially occupied d_{x-y}^{2-2} orbital of Cu2. Similarly the bridging Cl1 atom interacts with the filled d_z^2 orbital of Cu3 and the partially occupied d_{x-y}^{2-2} orbital of Cu1.



A top view of **3** with the highlighted coordination sphere of the Cu(II) ions.

All three bonding pathways between the adjacent Cu(II) ions are also different in complex **4**. The three pairs correspond to a complex arrangement of magnetic orbitals. The unpaired electron in the square-pyramidal Cu(II) ions resides on $d_{x^{2}-y}^{2}$ orbitals positioned in the base of the pyramid. These two orbitals interact via the bridging acetate anion, and in addition one of these orbitals interact with the filled d_{z}^{2} orbital of the second square-pyramidal Cu(II) ion via the bridging phenolate oxygen atom. In the trigonal-bipyramidal Cu(II) ion the unpaired electron resides likely on the d_{z}^{2} orbital, which interacts with the filled d_{z}^{2} orbital of one of the square-pyramidal Cu(II) ions via bridging

phenolate oxygen atom. The third bridging phenolate atom connects the singly occupied $d_{x -y}^{2}$ orbital of the second square-pyramidal Cu(II) ion and the likely doubly occupied $d_{x -y}^{2}$ orbital of the trigonal-bypiramidal Cu(II) ion.



A top view of **4** with the highlighted coordination sphere of the Cu(II) ions.

To confirm the nature of the ground state of **3**, we investigated the variation of the magnetization, *M*, with respect to the field, at 2 K. The results are shown in Figure 4S, where molar magnetization *M* is expressed in N β units. As the magnetic field increases, the *M* vs. *H* curve indicates linear relation up to ~1.0 Tesla and then shows a sinusoidal variation up to 5 T with value of magnetization closely 1 N β . The magnetization curve of the title compound was reproduced by the equation 1:

$$M = g\beta SNB_{s}(x) (S = 3 \cdot S_{Cu}) (1)$$

where $B_s(x)$ is the Brillouin function and $x = g\beta SH/kT$.⁵² The M = f(H) curve is situated below the Brillouin function constructed for three independent S = 1/2 systems. Experimental values smaller than expected for isolated copper(II) evidence a antiferromagnetic coupling. On the other side, small increase of $\chi_m T$ at lowest temperature is not enough to get spontaneous magnetization at 2 K.

Figure 4S for complex **4** presents relation the M = f(H). The shape of the curve formed by the experimental points does not follow the Brillouin function constructed for three independent $S = \frac{1}{2}$ systems. Much smaller than expected for isolated copper(II) ions experimental values are indicative of antiferromagnetic interactions between copper(II) ions in trimer.



Supporting Figure 4S. Field dependence of the magnetization for complex **3** (•) and **4** (**■**). The solid line is the Brillouin function curve for three non coupled copper(II) ions ($S = 3 \times \frac{1}{2}$); dashed line is the Brillouin function for a $S = \frac{1}{2}$ state; the g – factor is taken 2.00.

Strong antiferromagnetic coupling is observed for large Cu-O-Cu bond angles and long copper-copper distances, whereas the ferromagnetic interaction is favored for small Cu-O-Cu bond angles (less than 98°) that usually imply the shorter Cu...Cu distances. ^{S3-S14} Analysis of the structural features of the **3** trinuclear system shows that with a short Cu...Cu interatomic distance (3.136 Å) and small Cu–O–Cu angle (100.17°), the Cu(1)...Cu(2) bridging system demarks from the two others, Cu(1)... Cu(3) and Cu(2)...Cu(3), which are significantly larger [Cu(1)...Cu(3) 3.210 Å, Cu(1)–O(2)–Cu(3) 106.72°, Cu(2)...Cu(3) 3.427 Å and Cu(2)–O(3)–Cu(3) 119.67°]. According to the studies on the similar systems ^{S7,S8,S12} these structural features may well consistent with a ferromagnetic coupling between Cu(1)

and Cu(2), and large antiferromagnetic couplings between Cu(1) and Cu(3) and between Cu(2) and Cu(3).

In compound **4**, the Cu-O-Cu bond angles dihedral angle equal to 123.79°. The value of -75(1) cm⁻¹ in complex **4** is lower than the values reported for hydroxo-, alkoxo- or phenoxo-bridged complexes, ⁵⁴, ⁵⁷ wherein the coordination planes are much more coplanar. The observations imply that the degree of coplanarity of the coordination equatorial planes influences the magnetic coupling between the paramagnetic ions. In additional, such behavior is consistent with the crystal structure and may arise from more trigonal character of copper(II) coordination of **4** and weaker overlap of magnetic orbitals.



Supporting Figure 5Sa. Temperature dependence of experimental χ_m (•) and $\chi_m T$ (o) vs. T for complex **3.** The solid line is the calculated curve derived from equation 1 (g = 1.55).



Supporting Figure 5Sb. Temperature dependence of experimental χ_m (•) and $\chi_m T$ (•) vs. T for complex **3.** The solid line is the calculated curve derived from equation 1 (g = 2).



Supporting Figure 6S. Temperature dependence of experimental χ_m (•) and $\chi_m T$ (0) vs. T for complex **3.** The solid line is the calculated curve derived from equation 5.

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