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Communication

Spin Control in Ladderlike Hexanuclear Copper(II) Complexes with Metallacyclophane Cores

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Two new hexanuclear oxamatocopper(II) complexes **3** and **4** have been synthesized from the binuclear copper(II) complexes of the *meta*- and *para*-phenylenebis(oxamate) ligands, respectively. Complexes **3** and **4** possess an overall ladderlike structure made up of two oxamate-bridged linear trinuclear units ("rails") connected through two phenylenediamidate bridges ("rungs") between the central copper atoms to give metallacyclic cores of the *meta*- and *para*-cyclophane type, respectively. They show different ground spin states, $S = 1$ (**3**) or $S = 0$ (**4**), depending on the substitution pattern in the aromatic spacers. The triplet state molecule **3** containing two spin doublet Cu^{II}_3 units connected by two *m*-phenylenediamidate bridges represents a successful extension of the concept of "ferromagnetic coupling units" to metal complexes, which is a well-known approach toward high spin organic radicals.

Polynuclear coordination compounds of first-row transition metal ions have been actively investigated in the field of molecular magnetism, notably for the design and synthesis of high spin molecules.[1–4] In order to gain control of both the nuclearity and the topology, as well as on the ground

spin state of the polymetallic species, an alternative to serendipitous self-assembly methods is represented by the so-called "complex-as-ligand" approach.[1] Along this line, the use of binuclear rather than mononuclear complexes as ligands toward other metal ions constitutes a step further for the obtention of high nuclearity metal complexes but has received limited attention, however.[5]

In the search of rationally designed polynuclear complexes with oxamate-based ligands,[6] we recently reported the two binuclear copper(II) metallacyclophanes **1** and **2** built upon the binucleating ligands *N,N′*-1,3-phenylenebis(oxamate) (mpba) and *N,N′*-1,4-phenylenebis(oxamate) (ppba), respectively (Chart 1).[7] Complexes **1** and **2** constitute a rare example of the control of spin in metal complexes by the topology of the bridging ligand.[8,9] Thus, the two Cu^{II} ions

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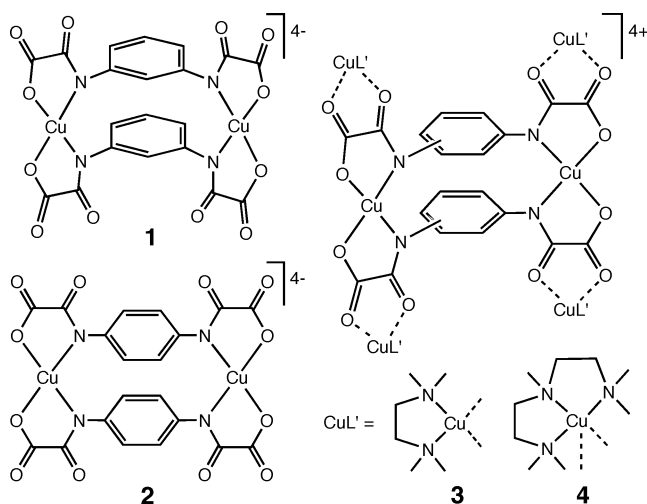‡ Departament de Química Orgànica.
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Chart 1


Figure 1. Perspective view of the noncentrosymmetric cationic hexacopper molecule of **4** with the numbering scheme of metal atoms.

of **1** are moderately ferromagnetically coupled, while those of **2** are strongly antiferromagnetically coupled, both effects resulting from a spin polarization mechanism through the π-conjugated bond system of the phenylenediamidate bridges with *meta*- and *para*-substitution patterns. Interestingly, complexes **1** and **2** are potentially tetrakis-bidentate ligands that can coordinate up to four metal ions through the free carbonyl oxygen atoms of the oxamate groups. When using metal complexes with partially blocked coordination sites to preclude polymerization, this "complex-as-ligand" approach leads to discrete high nuclearity metal complexes. This is illustrated by the two novel hexanuclear copper(II) complexes {[Cu$_2$(mpba)$_2$][Cu(tmen)]$_4$}(ClO$_4$)$_4$·6H$_2$O (**3**) and {[Cu$_2$(ppba)$_2$][Cu(pmdien)]$_4$}(ClO$_4$)$_4$ (**4**) reported herein, where *N,N,N′,N′*-tetramethylethylenediamine (tmen) and *N,N,N′,N″,N″*-pentamethyldiethylenetriamine (pmdien) are bidentate and tridentate blocking ligands, respectively (Chart 1).

Compounds **3** and **4** were obtained from reaction of sodium or lithium salts of the anionic precursors [Cu$_2$L$_2$]$^{4-}$ (L = mpba, **1**; ppba, **2**),[7] with the coordinatively unsaturated cationic complexes [CuL′]$^{2+}$ (L′ = tmen, pmdien) prepared in situ from a mixture of copper(II) perchlorate and L′ in a 1:1 stoichiometry. While crystals of **3** were not suitable for a structural determination, single crystal X-ray diffraction analysis of **4** confirmed the hexanuclear molecular structure.[10] The three crystallographically independent hexacopper(II) cations {[Cu$_2$(ppba)$_2$][Cu(pmdien)]$_4$}$^{4+}$ constituting the asymmetric unit, two centrosymmetric and one noncentrosymmetric, are structurally and stereochemically equivalent (Figure 1). They possess a ladderlike architecture of the [2 × 2]L type,[11] where the two phenylenediamidate bridges act as "rungs" between the two oxamate-bridged linear
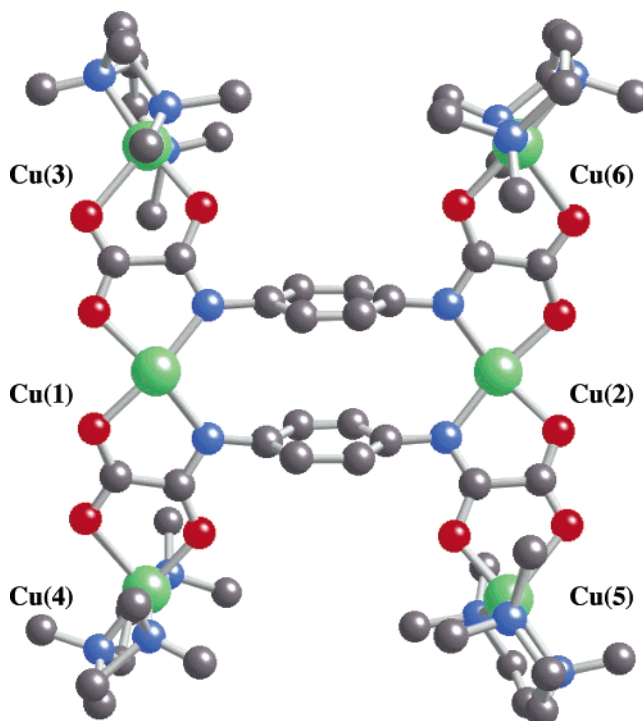
trinuclear units which then serve as "rails". The average distance between the two central copper atoms is 8.059 Å, while that between central and peripheral copper atoms is 5.340 Å.

The coordination environment of the peripheral copper atoms is best described as square pyramidal rather than trigonal bipyramidal. The geometric τ parameter is in the range 0.31−0.53 (τ = 0 and 1 for ideal square pyramidal and trigonal bipyramidal geometries, respectively).[6c] Thus, the basal plane of the square pyramid is formed by the three amine nitrogen atoms from the pmdien ligand [Cu−N = 1.864(5)−2.134(6) Å] and the carbonyl amidate oxygen atom from the oxamate bridge [Cu−O = 1.918(6)−1.968(4) Å], while the other carbonyl oxygen atom occupies the apical position [Cu−O = 2.211(6)−2.257(4) Å]. The central copper atoms have a tetragonally elongated octahedral environment formed by two amidate nitrogen atoms [Cu−N = 1.944-(7)−2.016(6) Å] and two carboxylate oxygen atoms [Cu−O = 1.923(4)−2.022(6) Å] from the oxamate groups of the ppba ligands in the basal plane, the apical positions being occupied by oxygen atoms from two weakly bound perchlorate anions [Cu−O = 2.596(5)−3.254(5) Å]. Importantly, the basal planes of the peripheral and the central copper atoms are almost perpendicular to one another [dihedral angles of 77.2(6)−88.7(6)°]. Within the dicopper metallacyclophane core unit of **4**, the two benzene rings are not eclipsed but slightly glided perpendicularly to the Cu−Cu vector. The deviations from the face-to-face alignment are smaller than in **2**, however. Thus, the copper basal planes are disposed almost perpendicularly to the phenylene planes [dihedral angles of 75.4(6)−77.8(6)°] when compared to **2** (dihedral angle of 60.6°).[7b]

(10) Crystal data for **4**: C$_{56}$H$_{100}$Cl$_4$Cu$_6$N$_{16}$O$_{28}$, M = 1968.56, triclinic, space group P1, a = 21.470(4) Å, b = 21.508(5) Å, c = 20.3051(17) Å, α = 93.678(10)°, β = 93.388(11)°, γ = 85.662(13)°, V = 9316(3) Å^3, Z = 4, T = 293 K, μ(Mo Kα) = 1.534 mm^{-1}, 27696 reflections measured, 14630 assumed as observed with I > 2σ(I). Refinement on F^2 of 1981 parameters with anisotropic thermal parameters for all non-hydrogen atoms gave R = 0.183, R$_w$ = 0.3987, and GOF = 1.031 (observed data).
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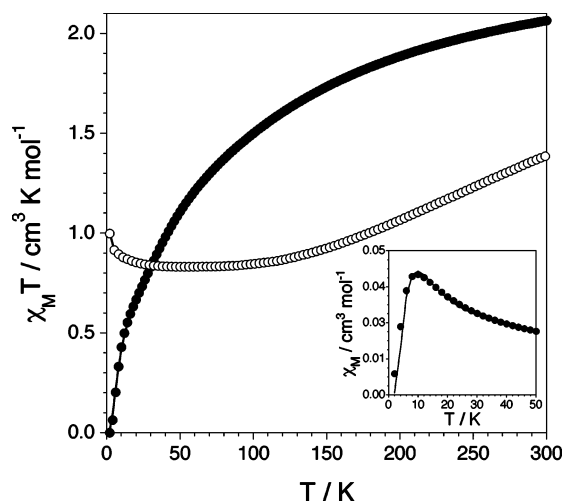
Figure 2. Thermal dependence of $\chi_M T$ of **3** (○) and **4** (●) (solid lines correspond to the best fits). The inset shows the maximum of χ_M of **4** in the low temperature region.

Table 1. Magnetic Data for **3** and **4**

compd	J (cm^{-1})^a	j (cm^{-1})^a	g^b	R^c
3	−288.3	+15.5	2.11	1.2×10^{-5}
4	−81.3	−120.6	2.09	1.0×10^{-5}

^{a} J and j are the exchange coupling parameters in the isotropic spin Hamiltonian $H = -J(S_1 \cdot S_3 + S_1 \cdot S_4 + S_2 \cdot S_5 + S_2 \cdot S_6) - j(S_1 \cdot S_2) + g\beta(S_1 + S_2 + S_3 + S_4 + S_5 + S_6)B$, with $S_1 = S_2 = S_3 = S_4 = S_5 = S_6 = {}^1/_2$. ^{b} g is the Zeeman factor. ^{c} R is the agreement factor defined as $R = \Sigma[(\chi_M T)_{exp} - (\chi_M T)_{calcd}]^2/\Sigma[(\chi_M T)_{exp}]^2$.

The magnetic properties of **3** and **4** in the form of $\chi_M T$ versus T plots (χ_M being the molar magnetic susceptibility per Cu$_6$ unit and T the temperature) are totally different (Figure 2). At room temperature, $\chi_M T$ values for both **3** and **4** are lower than that expected for six noninteracting Cu^{II} ions ($\chi_M T = 2.48$ cm^3 K mol^{-1}, with $g = 2.1$). Upon cooling, $\chi_M T$ for **3** smoothly decreases, reaches a plateau around 100 K, with $\chi_M T = 0.83$ cm^3 K mol^{-1}, and then increases below 30 K. At 1.8 K, $\chi_M T$ is equal to 1.00 cm^3 K mol^{-1}, a value that is close to that expected for a ground triplet state ($\chi_M T = 1.10$ cm^3 K mol^{-1}). Contrarily, $\chi_M T$ for **4** continuously decreases upon cooling and vanishes at 1.8 K. The maximum observed at 9.5 K in the χ_M versus T plot is characteristic of a ground singlet state (inset of Figure 2).

In the high temperature region, the magnetic behavior for **3** and **4** is reminiscent of that of two isolated Cu$^{II}_3$ linear units with an antiferromagnetic intratrimer coupling between peripheral and central Cu^{II} ions ($J = J_{13} = J_{14} = J_{25} = J_{26}$). In this case, however, $\chi_M T$ should attain a plateau at low temperatures where only the two ground doublet states of the trinuclear units are thermally populated ($\chi_M T = 0.83$ cm^3 K mol^{-1}). The deviations observed in the low temperature region for **3** and **4** are the signature of ferro- and antiferromagnetic intertrimer coupling, respectively. These magnetic couplings likely occur between the central Cu^{II} ions of each trinuclear unit ($j = J_{12}$) within the Cu$^{II}_2$ metallacyclophane core. The magnetic susceptibility data of **3** and **4** were fitted by full matrix diagonalization of the appropriate isotropic spin Hamiltonian for a Cu$^{II}_6$ molecule with a dimer-of-trimers

topology (Table 1).[12] The theoretical curves follow closely the experimental data over the whole temperature range (solid lines in Figure 2).

The $-J$ values for **3** and **4** are consistent with those reported for related oxamate-bridged linear trinuclear copper-(II) complexes.[6c] The lower $-J$ value for **4** compared to that for **3** stems from the well-known orbital reversal phenomenon caused by the substitution of bidentate tmen by tridentate pmdien as terminal ligand.[13] Thus, the attenuation of magnetic coupling through the oxamate bridges in **4** is explained by the less efficient σ-overlap between the noncoplanar d$_{xy}$ metal orbitals of the peripheral and central Cu^{II} ions (spin delocalization effect). The j values for **3** and **4** agree both in sign and magnitude with those previously found for **1** (+17 cm^{-1}) and **2** (−81 cm^{-1}), respectively.[7] This indicates that the spin polarization mechanism through the *meta*- and *para*-substituted phenylenediamidate bridges is also operative for the propagation of the exchange interaction in **3** and **4**. The higher $-j$ value for **4** compared to that for **2** likely arises from the better perpendicular arrangement of the copper basal planes with respect to the benzene planes in **4**, which leads to a larger orbital mixing between the d$_{xy}$ metal orbitals of the central Cu^{II} ions and the π-type orbitals of the aromatic bridges.[7b]

In conclusion, the binuclear copper(II) metallacyclophanes **1** and **2** act as "robust" ferro- and antiferromagnetic synthons in their corresponding hexanuclear copper(II) complexes **3** and **4**. They represent a successful extension to metal complexes of the concept of ferro- and antiferromagnetic coupling units which has been used earlier to control the spin in purely organic molecules (polyradicals) and in mixed organic−inorganic molecules (metal−polyradical complexes).[14,15] Further efforts will focus on the use of the binuclear precursor **1** to obtain heterometallic complexes with higher ground spin states and large axial anisotropy as potential single-molecule magnets exhibiting slow spin relaxation.

Supporting Information Available: Experimental preparation, analytical and spectroscopic characterization of **3** and **4**, together with X-ray crystallographic data of **4** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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