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A very bulky carboxylic perchlorotriphenylmethyl radical as a novel ligand for transition metal complexes. A new spin frustrated metal system

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Reaction of a carboxylic perchlorotriphenylmethyl radical with $Cu_2(O_2CCH_3)_4 \cdot 2H_2O$ using different molar ratios yields two different transition metal complexes with strong intramolecular antiferromagnetic interactions, which in the case of complex 2 follows a butterfly spin frustrated model.

A great deal of work in molecular magnetism has focused on the so-called metal-radical approach that combines paramagnetic metal ions and pure organic radicals as ligating sites.[1] The electronic open-shell character of such organic ligands is particularly appealing since they are expected to interact with transition metal ions enhancing the strength of magnetic interactions. At the same time, the magnetic dimensionality of the molecular material will increase in comparison with systems made up from paramagnetic metal ions and diamagnetic coordinating ligands. However, even though a large number of metal-radical systems have been studied, the variety of radical-based ligands used up to now is fairly limited. The most extensively used family is that of nitroxide-based radicals,[2] although a few other examples have also been reported.[3–5] We describe herein, for the first time, the use of perchlorotriphenylmethyl radicals to obtain complexes with paramagnetic metal ions. Among others, the main advantages of these radicals are their astonishing thermal and chemical stability and their stereochemical characteristics, with a helical (chiral) surrounding of the radical center by very bulky substituents. Here we report the first complexes of the perchlorinated monocarboxylic triphenylmethyl radical (PTMMC)[6] with transition metals exhibiting non-conventional structural motifs and exotic magnetic behaviors. In addition, their crystal packing exhibits microporous frameworks originated by the preference to locate closely the very bulky perchlorotriphenylmethyl groups maximizing the Cl···Cl interactions between molecules.

Reaction of 1 eq. of $Cu_2(O_2CCH_3)_4 \cdot 2H_2O$ with 4 eq. of PTMMC in a mixture of EtOH and H_2O at room temperature gave a high yield (89%) of a crystalline sample characterized as the complex $[Cu(PTMMC)_2(H_2O)_3] \cdot 6H_2O \cdot 2EtOH$ (**1**).† Surprisingly, complex **1** does not adopt the paddle-wheel motif with four bidentate carboxylate ligands joining two Cu(II) ions, characteristic of most of the copper acetate clusters. Instead, its structure consists of one Cu(II) ion that adopts a square pyramidal coordination polyhedron formed by two monodentate carboxylic groups and three water ligands (Fig. 1(a)). This conformation is further stabilized by strong intermolecular hydrogen bonds between non-coordinative O atoms of both carboxylate groups of PTMMC ligands and coordinated water molecules and solvent water and ethanol molecules.

The tendency to form mononuclear Cu(II) clusters instead of binuclear ones is attributed to the extreme steric demand of the PTMMC ligands.[7] Indeed, due to the great steric hindrance of the chlorine atoms located at the *ortho* positions of the carboxylate group, the rotation angles (φ_{rot}) of the polychlorinated phenyl rings relative to the COO^- moieties are 87 and 89°. Such structural arrangement is expected to disrupt the formation of a binuclear complex with a paddle-wheel disposition of the four PTMMC ligands around the two Cu(II) units, simply due to the direct confrontation of bulky chlorine atoms of neighbouring (*syn*) PTM units. This result prompted us to control the stoichiometry of metal-radical complex by modification of the molar ratio of PTMMC in its reaction with $Cu_2(O_2CCH_3)_4 \cdot 2H_2O$. The objective was to obtain a mixed dimeric complex with PTMMC and acetate groups. Indeed, slow addition of PTMMC over an excess of $Cu_2(O_2CCH_3)_4 \cdot 2H_2O$ yielded (19%) a crystalline sample of complex $[Cu_2(PTMMC)_2(O_2CCH_3)_2(H_2O)_2] \cdot 4EtOH$ (**2**).† Complex **2** shows a paddle-wheel dinuclear Cu(II) structure, where each Cu metal ion has four O atoms of different carboxylate groups in the equatorial positions and a water molecule at the apex, completing the square pyramidal coordination geometry (Fig. 1b).

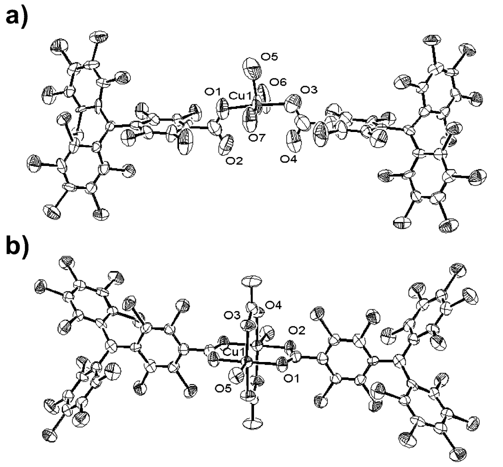

Fig. 1 ORTEP views of (a) $[Cu(PTMMC)_2(H_2O)_3]$ (**1**) (asymmetric unit) and (b) $[Cu_2(PTMMC)_2(O_2CH_3)_2(H_2O)_2]$ (**2**).

Interestingly, the crystal of complex **2** is built up by the paddle-wheel supramolecules, in such a way as to form microchannels. A view down the [001] direction reveals an

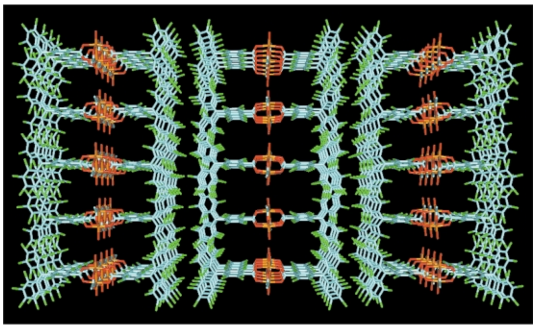

Fig. 2 View down the [001] direction of the square micropores in complex **2**.

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arrangement of square microchannels stabilized by 12 chlorine–chorine contacts ranging from 3.2 to 3.5 Å (Fig. 2). Thus, two confronted supramolecules of complex **2** along the [001] direction creates a rectangular synthon, which is partially divided in two nearly square micropores by the water ligands of both molecules. The diameter of such micropores are 7.5 and 8.0 Å, with an effective size of 4.2 × 4.5 Å when van der Waals radii are considered. The cavities are filled with two ethanol molecules, strongly bonded through hydrogen bonds with water and acetate ligands of molecule **2**. Similar microchannels in the [010] direction with a diameter of 8.4 and 8.1 Å (effective size 5.1 × 4.6 Å) are also formed in complex **1**. The channels are filled with two molecules of ethanol and six molecules of water that are disordered. The void volume of the cavities of both complexes are 2028 and 917 Å^3 for **1** and **2**, respectively, which equals 28 and 24% of the unit cell volume.[8]

Variable temperature magnetic susceptibility data for a crystalline sample of complexes **1** and **2** were measured on a SQUID susceptometer (2–300 K) with an applied external field of 1 kG. The value of χT for complex **1** at 300 K (1.1 emu K mol^{-1}) (Fig. 3, left) is in excellent agreement with that expected for three non-interacting electrons (1.125 emu K mol^{-1}). Upon cooling, χT gradually decreases consistently with the presence of relatively strong antiferromagnetic interactions between the Cu(II) ion and the two coordinated PTMMC radicals. In accordance with the X-ray molecular and crystal structures, the experimental data were analyzed on the basis of a symmetrical linear three $S = 1/2$ model, modified to take into account the presence of intermolecular interactions (θ) in the molecular field approximation ($J/k_B = -23.1$ K, $\theta = -0.7$ K and $g = 2.028$).[9]

The magnetic behavior found for complex **2** differs from that reported for complex **1**. As can be seen in Fig. 3 (right), the value of χT at 300 K is 0.9 emu K mol^{-1}, which is still far from that expected for four non-interacting electrons (1.5 emu K mol^{-1}). Such a divergence is consistent with the presence of strong antiferromagnetic interactions between the Cu(II) ions and between the Cu(II) ions and the PTMMC coordinated radicals. Upon cooling, χT gradually decreases down to 70 K, where it reaches a plateau at a value of 0.7 emu K mol^{-1}. Below 30 K, the χT value abruptly decreases to 0.4 emu K mol^{-1} at 2 K most likely due to the presence of intermolecular antiferromagnetic interactions. The data was nicely fitted to a magnetic model based on a symmetrical butterfly arrangement of the two metal ions and two organic radicals (inset of Fig. 3(b))[10] modified to take into account intermolecular interactions ($\theta = -1.7$ K) in the molecular field approximation. The value of the *body*/*body* interaction, $J_{13} = -350$ K, is within the range of those previously reported for the same kind of interaction in other paddle-wheel Cu(II) dimers,[11] whereas the value of the *wing-tip*/*body* interaction, $J = -21.3$ K, is similar to that previously reported for the Cu(II)/PTMMC radical interaction in complex **1**. The fact that both exchange coupling parameters, J and J_{13}, are negative indicates that any two neighboring spins tend to align antiferromagnetically. However, the topological arrangement of metal ions and organic radicals in the butterfly structure results in a spin-frustration due to the presence of competing interactions. Consequently, the ground state of complex **2** is degenerated, with the following two different states, in the format (S_T,S_{13},S_{24}), the triplet state (1,0,1) and the singlet state (0,0,0). This is one of the scarce examples of a spin-frustrated system composed of organic radicals and metal ions.[12]

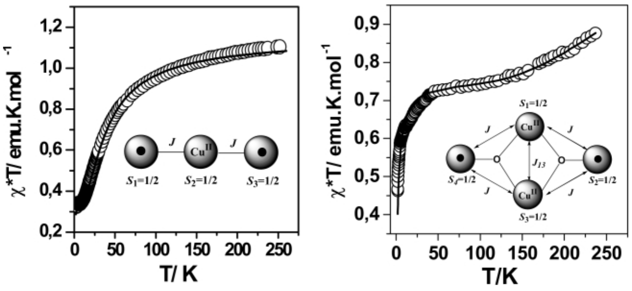

Fig. 3 Temperature dependence of the magnetic susceptibilities for complex **1** (left) and **2** (right). The solid lines were calculated as described in the text. The inset figures show the schematic arrangements of the metal ions and organic radicals.

In summary, we have shown that the carboxylic substituted perchlorotriphenylmethyl radical is a good coordinating ligand to obtain new complexes following the metal-radical approach. Controlling the reaction conditions, we have been able to obtain a mononuclear complex, as well as a paddle-wheel dinuclear complex exhibiting a exotic spin-frustration behaviour. Further studies to expand the range of structural motifs, structural dimensionalities and magnetic behaviours of metal-radical complexes based on polychlorinated triphenylmethyl radicals, either mono- or trifunctionalised with carboxylic groups, are currently underway.

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Notes and references

† *Crystal data* for **1**: monoclinic, $P2_1/c$, $a = 25.644(4)$, $b = 15.118(3)$, $c = 18.580(3)$ Å, $\beta = 92.18(1)°$, $V = 7198(2)$ Å^3, $Z = 4$, λ(Mo-Kα) = 0.71073 Å, 9744 reflections collected, 3134 independent reflections with $I > 2\sigma(I)$, $R1 = 0.071$, $wR2 = 0.168$, GOF = 1.15. There is a 5:1 disorder of the Cu(H$_2$O)$_3$ unit with the coordinated Cu atom, which occurs in major part between O(1) and O(3), and in the minor part between O(2) andO(4). *Crystal data* for **2**: monoclinic, $P2_1/c$, $a = 26.296(2)$, $b = 16.9040(9)$, $c = 8.5648(6)$ Å, $\beta = 93.760(3)°$, $V = 3798.9(4)$ Å^3, $Z = 2$, λ(Mo-Kα) = 0.71073 Å, 12387 reflections collected, 2724 independent reflections with $I > 2\sigma(I)$, $R1 = 0.060$, $wR2 = 0.115$, and GOF = 1.22. Data were measured on a Nonius KappaCCD. For **1**, the structure solution was done with SHELXS86 and the refinement with SHELXL93. For **2**, SHELX97 was used. CCDC 186141 (**1**) and 186142 (**2**). See http://www.rsc.org/suppdata/cc/b2/b209884a/ for crystallographic data in CIF or other electronic format.

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