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An Unusually Stable Trinuclear Manganese(II) Complex Bearing Bulk Carboxylic Radical Ligands

Daniel Maspoch,[†,‡] Jordi Gómez-Segura,[†] Neus Domingo,[§] Daniel Ruiz-Molina,*,[†] Klaus Wurst,[‖] Concepció Rovira,[†] Javier Tejada,[§] and Jaume Veciana*,[†]

Institut de Ciència de Materials de Barcelona (CSIC), Campus Universitari, 08193 Bellaterra, Catalonia, Spain, Facultad de Física, Universitat de Barcelona, Diagonal 647, 08028 Barcelona, Spain, and Institut für Allgemeine Anorganische und Theoretische Chemie, Universität Innsbruck, A-6020, Innrain 52a, Austria

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A trinuclear Mn^{II} cluster based on the versatile polychlorinated triphenylmethyl carboxylic radical ligand has been characterized by X-ray crystallography and magnetic measurements, representing a rare example of a Mn^{II} trinuclear linear structure with six open-shell ligands.

The design of new molecular clusters containing numerous open-shell centers is a topic of great current interest because of their nanosized structures and resultant magnetic properties.[1] In their development, carboxylate-based ligands have become basic thanks to their capacity to act as bridgelike linkers. So far, a large diversity of molecular polynuclear systems involving carboxylate ligands, such as manganese or ferric clusters with "single-molecular magnet" behavior,[2] metallic [Cr^{III}, Co^{II}, etc.] wheels,[3] or large first-transition-metal-based cluster aggregates,[4] have been described. Moreover, the formation of such polynuclear clusters has been shown to be favored by the use of highly sterically demanding carboxylates.[5] For instance, bulky carboxylate-based ligands such as triphenyl acetate, pivalate, or halogen-substituted carboxylates have induced a series of unusual polynuclear cages.[6]

To complement such studies, our group has recently initiated a scientific project focused on the use of new bulky carboxylic ligands with an additional open-shell character, the so-called polychlorinated triphenylmethyl (PTM) radicals.[7] The open-shell character of these ligands is expected to enhance the magnetic dimensionality in comparison with systems made up of paramagnetic metal ions and diamagnetic coordinating ligands, according to the well-known "metal-radical" approach.[8] In a previous work, we showed for the first time how the monocarboxylic PTM radical (**1**, PTMMC; Figure 1), in addition to being highly sterically demanding, is capable of interacting magnetically with a coordinated Cu^{II} metal ion.[9] This was a seminal work on the quest for new 0-D clusters combining open-shell ligands.[10]

Following this approach, herein we report the synthesis and structural and magnetic characterization of a new trinuclear Mn^{II} complex, $[Mn_3(PTMMC)_6(EtOH)_6]\cdot 6EtOH$ (**2**), bearing six carboxylic ligands **1** and representing a rare

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* To whom correspondence should be addressed. E-mail: vecianaj@icmab.es (J.V.) and dani@icmab.es (D.R.-M.).

[†] Institut de Ciència de Materials de Barcelona (CSIC).

[‡] Present address: Institute for Nanotechnology, Northwestern University, 2145 Sheridan Road, Evanston, IL 60208.

[§] Universitat de Barcelona.

[‖] Universität Innsbruck.

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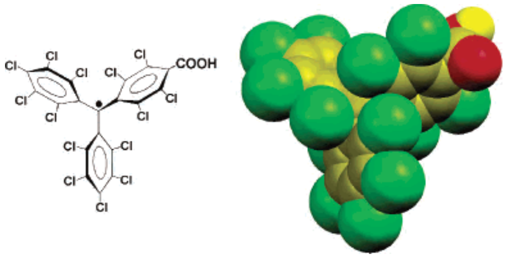

Figure 1. Space-filling diagram representing the molecular structure of **1**.

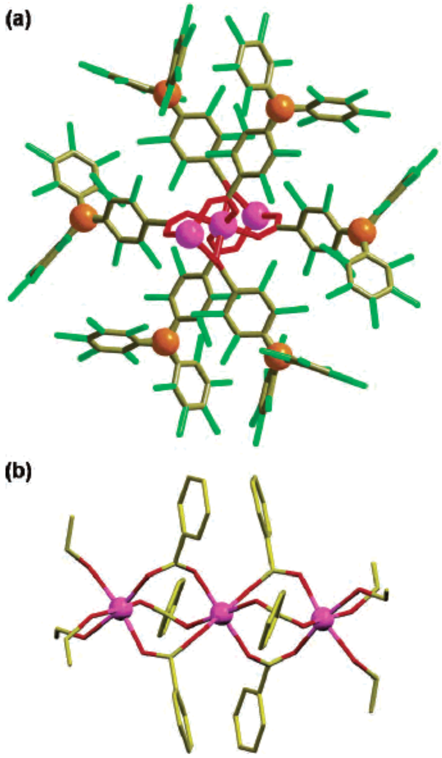

Figure 2. (a) Structure and (b) core–shell of **2** (Mn, violet balls; C, brown; O, red; Cl, green). In part a, radical methyl C atoms are represented as orange balls. Ethanol and solvent molecules are omitted for clarity.

example of a manganese cluster with several carboxylic radical ligands.

Reaction of $Mn(MeCO_2)_2 \cdot 4H_2O$ and radical **1** (1:2) in ethanol at room temperature for 3 h, followed by slow evaporation, produced red blocks of **2** after 2 months. Single-crystal X-ray analysis revealed a nanosized trinuclear manganese complex connected by six bridgelike bidentate PTMMC radicals (Figure 2).[11] Complex **2** has a crystallographic S_6 symmetry, involving 3-fold axes crossing the two outermost Mn^{II} ions and the central Mn^{II} ion, which is located on an inversion center. This leads to a linear manganese complex, with a central Mn^{II} site connected to both lateral Mn^{II} ions through six carboxylate-substituted radicals **1**. All carboxylates are coordinated in a syn–syn geometry with bond distances of 2.154(2) and 2.146(2) Å, which separates Mn ions with a distance of 4.27 Å. The remaining coordinative positions of each external Mn ion are occupied by three ethanol molecules. In this configuration, complex **2** adopts a quasi-planar disklike geometry formed by all six voluminous radicals **1** surrounding the trimeric Mn^{II} core and the ethanol molecules that are pointing out of the disk plane (Figure 3).

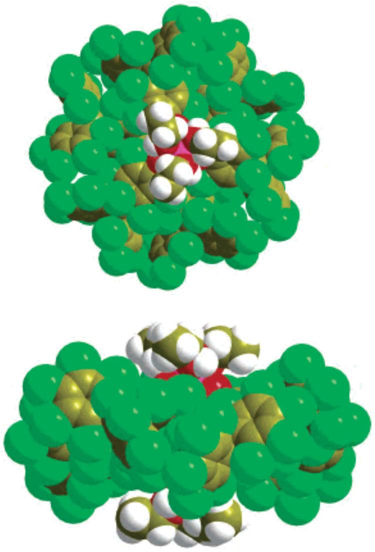

Figure 3. Disklike geometry (front and lateral views) of complex **2**. Note that ethanol ligands point out the plane formed by the trinuclear Mn^{II} connected by the six radicals **1**.

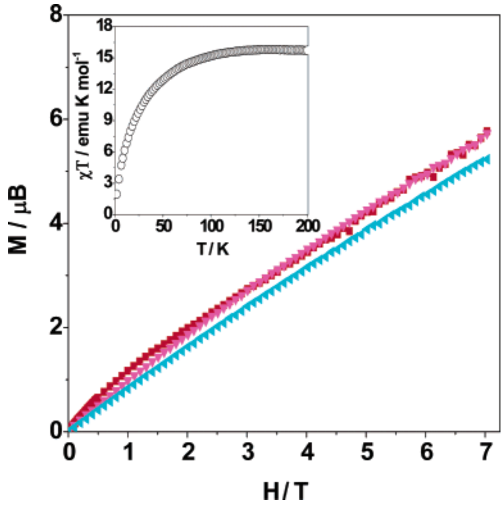

Figure 4. Magnetic field dependence of the magnetization for **2** at 1.8 K (■, red), 5 K (▼, magenta), and 10 K (triangle solid left, cyan). The inset shows the temperature dependence of χT product from 1.8 to 200 K.

This causes an intramolecular distance of 2.4–2.5 nm between the external chlorine atoms of opposite PTMMC radicals. External positions of the chlorine atoms also induce a stacking of **2** through Cl····Cl contacts. Sheets of **2** connected through 24 Cl····Cl contacts per molecule are laterally shifted and also held together through 24 Cl····Cl contacts per molecule, yielding an ABCABC arrangement.

Magnetic susceptibility measurements were done on single crystals of **2** embedded on eicosane (Figure 4) to fix at low temperature their relative positions with respect the external magnetic field. The χT vs T plot (inset of Figure 4) shows a χT value of 16.1 $emu \cdot K \cdot mol^{-1}$ at 300 K, which is in good agreement with the value of 15.4 $emu \cdot K \cdot mol^{-1}$ expected for

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(11) For a complex with a similar manganese core–shell, see: Menage, S.; Vitols, S. E.; Bergerat, P.; Codjovi, E.; Kahn, O.; Girerd, J.-J.; Guillot, M.; Solans, X.; Calvet, T. *Inorg. Chem.* **1991**, *30*, 2666.

three Mn^{II} ions ($s = {}^5/_2$) and six radical ligands ($s = {}^1/_2$). This value remains constant on upon a decrease in the temperature down to 150 K, whereupon a continuous decrease is observed until a value of 1.46 emu·K·mol^{-1} at 1.8 K is reached. Such a decrease of the χT value is consistent with the presence of dominant intramolecular antiferromagnetic interactions through the Mn···O−C−O···Mn pathway and between the Mn···PTMMC radicals and, to a lesser degree, from intermolecular antiferromagnetic interactions through Cl···Cl contacts. In support of this is the fact that intermolecular magnetic interactions between metal complexes derived from the PTMMC radical are generally very weak.[7,8] Variable-field magnetization was also measured at different temperatures (1.8, 2.0, 2.5, 3.0, 3.5, 5.0, 7.5, and 10.0 K) over an applied field range of 0−7 T. At a given temperature, the magnetization value increases following the Brillouin law up to 2 T, whereupon a linear increase with the applied field is observed (Figure 4). Variations in the temperature slightly modify the M vs H plots. In the entire temperature range studied, the magnetization value never saturates even at the highest field because of field-induced level crossings and the high density of the spin states being populated. Accordingly, the magnetization value at 7 T in the entire temperature range studied oscillates between 5.1 and 5.8 μ_B, which are far from the 10.5 μ_B expected for the saturation value.

The results previously described for **2** differ from those recently described for a related linear trinuclear $[Mn^{III}Mn^{II}_2]$ complex, which exhibits ferromagnetic exchange between the three Mn ions and a single-molecule magnet behavior.[12] Therefore, on the quest for new polynuclear complexes with topologies that endorse high-spin ground states and the presence of Jahn−Teller distorted Mn^{III} ions, new reactions with the carboxylic ligand **1** were assayed. Among them, ligand substitution reactions with radical **1** on $[Mn_{12}O_{12}(piv)_{16}(H_2O)_4]$ (**3**) and on $Mn(MeCO_2)_3 \cdot 2H_2O$ were performed. Ligand replacement of the pivaloic carboxylates (piv = ${}^tBuCO_2^-$) of complex **3** by radical **1** in an ethanol/CH_2Cl_2 mixture did not yield the expected Mn_{12} derivative but a mixture of products from where complex $[Mn_3(PTMMC)_6(EtOH)_6] \cdot 6EtOH$ (**2**) was characterized by X-ray crystallography and magnetic susceptibility measurements. Surprisingly, radical **1** reacts with the Mn_{12} core to yield the linear trinuclear Mn^{II} complex **2**, most likely because of its strong acid character and large dimensions.[13] Similar results were obtained on a further attempt to obtain the corresponding Mn_{12} derivative by a direct comproportionation reaction between a Mn^{II} source and Mn^{VII} (MnO_4^-) in the presence of the carboxylic acid **1**. Final efforts to obtain a Mn^{II}/Mn^{III} mixed-valence complex were attempted by direct reaction of radical **1** with a source of Mn^{3+}, like $Mn(MeCO_2)_3 \cdot 2H_2O$. Intriguingly, this reaction yielded once more complex **2**, a fact that has been attributed to a competitive oxidative decarboxylation of Mn^{III} catalyzed in the presence of **1**.[14]

In summary, we have described a new example of a linear trinuclear Mn^{II} complex bearing six PTM carboxylic radicals that exhibit intramolecular antiferromagnetic interactions. Surprisingly, the different synthetic strategies used with radical **1** yielded unambiguously complex **2** as the main reaction product. Further work is currently underway to better understand the different synthetic mechanisms and to explore new Jahn−Teller distorted metal ions such as Co^{II}.

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Supporting Information Available: Experimental details, crystallographic data (CIF format), and detailed magnetic field dependence of the magnetization plot for **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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