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A Unique Mn_2Gd_2 Tetranuclear Compound of *p-tert*-Butylthiacalix[4]arene

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A calixarene complex with tetragonal $Mn^{II}_2Gd^{III}_2$ tetranuclear units was synthesized in solvothermal conditions, where the addition of a small amount of water was crucial for the formation of the target compound. In the structure, two tail-to-tail *p-tert*-butylthiacalixarenes are located in a C-shaped mode with a dihedral angle of 14.29° but not in the conventional antiparallel arrangement and form a sandwich-like subunit with an in-between Mn_2Gd_2 unit. Both calixarenes assume similar cone shapes of C_{2v} symmetry but are pinched to different extents. The extended structure is constructed by supramolecular stacking of the sandwich-like units with the interstices filled by the solvent. The magnetic property of the title compound has been examined.

Considerable attention has been drawn to 3d−4f heterometallic complexes because of their magnetic properties, especially because some of them behave as single-molecule magnets,[1−3] since Gatteschi et al. reported ferromagnetic coupling between Gd^{III} and Cu^{II} in two Cu_2Gd trinuclear compounds.[4] Generally, the well-organized multidentate ligands are more effectual for the construction of heterometallic compounds, and a series of copper−lanthanide compounds have been reported.[5] However, there are few examples for the manganese(II)−lanthanide(III) heterometallic compounds.[6,7] *p-tert*-Butylthiacalix[4]arene (TC4A), possessing four phenoxyl groups together with four sulfur bridge atoms, has been proven to be a good multidentate ligand in constructing the polynuclear complexes with alkali metal,[8,9] transition metal,[10−13] or lanthanide species.[14] To the best of our knowledge, nearly all of the polynuclear units concerning TC4A are reported to be monometallic. Here we present a Mn_2Gd_2 tetranuclear unit as an exception. The synthesis, structure, and magnetic property of the first 3d−4f heterometallic compound with TC4A will be described below.

The compound, $\{Mn_2[Gd(CH_3OH)_2]_2(OH)(TC4A)_2\}(OH)\cdot 10.04CH_3OH\cdot 1.4H_2O$ (**1**), was first obtained by solvothermal treatment of a mixture of $Mn(Ac)_2\cdot 4H_2O$, $Gd(Ac)_3\cdot 4H_2O$, and TC4A in the mixed solution of CH_3OH and $CHCl_3$ with the accidental addition of a little water. Further work showed

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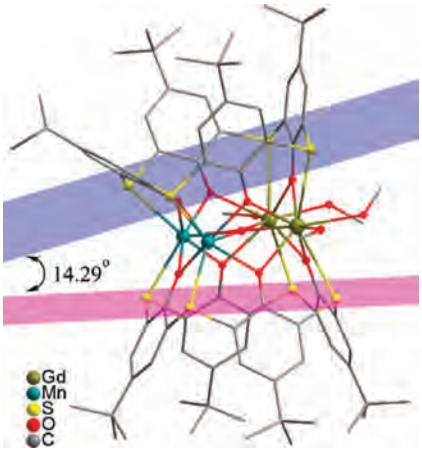

Figure 1. Molecular structure of compound **1** showing the dihedral angle between two calixarenes. The hydrogen atoms and solvent molecules are omitted for clarity.

that the deliberate addition of a small amount of water does result in a good yield of the target compound, which might be due to the fact that water molecules not only are involved in the crystal structure but also are the resource of the hydroxide ion (see Figure S1 in the Supporting Information for IR spectra). Single-crystal X-ray diffraction determination[15] reveals that the extended structure is constructed by supramolecular stacking of some isolated sandwich-like units and the solvent molecules filled in the interstices. The essential feature of compound **1** is given by the sandwich-like units that result from two tail-to-tail calixarene molecules and an in-between tetragonal μ_4-OH−Mn−Mn−Gd−Gd cluster (Figure 1).

In the structure of compound **1**, there are four crystallographic positions for the metal atoms (Mn1, Mn2, Gd1, and Gd2) adopting a tetragonal Mn−Mn−Gd−Gd mode as shown in Figure 2. Both Mn1 and Mn2 are seven-coordinated by four phenoxyl oxygen atoms, two sulfur atoms, and a μ_4-OH in a distorted decahedron mode. The bond lengths and angles (Table S1 in the Supporting Information) are similar to those reported in the monometallic Mn^{II}TC4A complexes.[12,13] On the basis of the tabulated bond-valence parameter for the Mn^{II}−O (r_0 = 1.790 Å) and Mn−S (r_0 = 2.20 Å) bonds,[16] the empirical valences of atoms Mn1 and Mn2 both sum to 2.17. The gadolinium centers exhibit a nine-coordinated geometry by bonding to four phenoxyl oxygen atoms, two sulfur atoms, two CH_3OH oxygen atoms, and a μ_4-OH. All phenoxyl oxygen atoms are bonded to two metal atoms simultaneously to stabilize the tetragonal Mn−Mn−Gd−Gd arrangement. The Mn···Mn, Mn···Gd, and Gd···Gd separations in the present complex are 3.137(2), 3.345(9)/3.363(1), and 3.629 (1) Å, respectively, which are comparable to the reported M···M or Ln···Ln separations in heterometallic complexes of other calixarene derivatives and might indicate significant electronic interactions between the metal ions.[11−14,17]

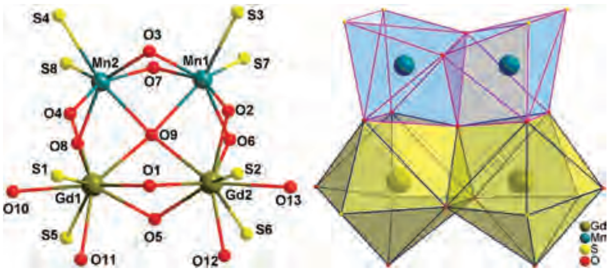

Figure 2. Ball-and-stick (left) and polyhedral (right) representation of the Mn_2Gd_2 core.

A metal coordination polyhedron shares two triangle planes with two adjacent ions to form a $(MnO_4S_2)_2$-μ_4-OH-$(GdO_6S_2)_2$ core (Figure 2). Furthermore, this core is bonded by two tail-to-tail TC4A ligands to form a sandwich-like unit. However, it is uncommon that these two tail-to-tail calixarene molecules are not located in the conventional antiparallel arrangement observed in the monometallic TC4A sandwiches[8] but form a C-shaped unit with the metal atoms (Figure 1). The dihedral angle between two planes formed by the sulfur atoms of the upper and bottom calixarenes is 14.29°. The formation of the bent sandwich-like unit might be due to, on the one hand, the flexibility of the macrocycle, which allows the TC4A ligand to bond to different metal atoms simultaneously, and, on the other hand, the smaller radius of the manganese atom than the gadolinium atom in the tetragonal Mn−Mn−Gd−Gd unit, which forces calixarene molecules to incline to one side. So, it is expected that the change of the radius ratio of the transition-metal atoms (M^{II}, 3d) and lanthanide atoms (Ln^{III}, 4f) may facilitate different dihedral angles between two TC4A ligands and the alterable distances between metal ions, which might be helpful in the design of polynuclear units with interesting magnetic properties. It should be pointed out that two TC4A ligands in one sandwich-like unit adopt different conformations. Namely, one of the TC4A entities adopts an approximately symmetrical cone conformation (with two oppositely oriented $C_{Butyl}\cdots C_{Butyl}$ distances being about 9.57 and 9.05 Å and the dihedral angles between the opposite aromatic rings being 45.700° and 49.197°), while the other processes a pinched cone conformation ($C_{Butyl}\cdots C_{Butyl}$ distances, 8.72 and 10.35 Å; dihedral angles, 65.070° and 40.778°; Figure S2 in the Supporting Information).

The extended structure is constructed by the stacking of the sandwich-like units via hydrogen-bonding interactions

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(15) Crystal data for **1**: $C_{94.04}H_{148.94}Gd_2Mn_2O_{25.43}S_8$, M = 2367.41 g mol^{-1}, monoclinic, *C2/c*, a = 35.358(5) Å, b = 14.627(5) Å, c = 45.311(5) Å, α = 90.00°, β = 96.543(5)°, γ = 90.00°, V = 23281(9) Å^3, Z = 8, D_{calcd} = 1.351 g cm^{-3}, μ = 1.543 mm^{-1}, T = 150(2) K, θ_{max} = 25.0°, $F(000)$ = 9781, crystal dimensions 0.22 × 0.16 × 0.15 mm^3, reflections collected/unique, 77 489/20 527 (R_{int} = 0.0470), final R1 = 0.0549, wR2 = 0.1466 [$I > 2\sigma(I)$], GOF = 1.06. The X-ray intensity data for compound **1** were collected on a Bruker SMART APEX CCD diffractometer with graphite-monochromatized Mo Kα radiation (λ = 0.710 73 Å) operated at 2.0 kW (50 kV, 40 mA). The crystal structure was solved by means of direct methods and refined employing full-matrix least squares on F^2 (*SHELXTL-97*).[19] All of the non-hydrogen atoms were refined anisotropically except some isolated molecular atoms, which were refined without hydrogen atoms. See the Supporting Information for further details. CCDC reference number 698364. The atomic coordinates for this structure have been deposited with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, upon request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.

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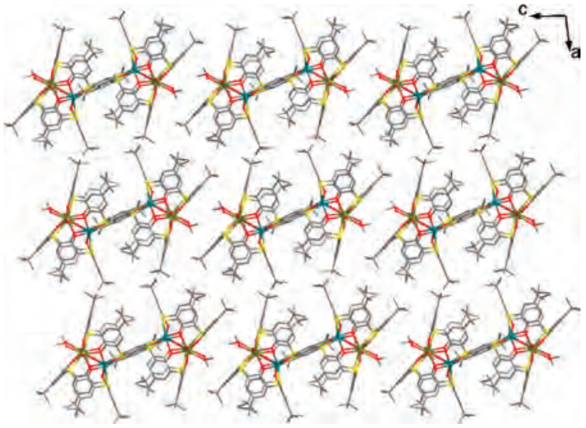

Figure 3. View of the extended structure of compound **1** with the hydrogen atoms and solvent molecules omitted for clarity.

(Figure 3 and Table S2 in the Supporting Information), and the interstices are filled by the isolated solvent methanol and water. The solvent-accessible void volume calculated with *PLATON*[18] reaches 36.0% of the unit cell volume (i.e., 8384.6 vs 23281.0 Å^3). The attempt to demonstrate the stability of the structure (i.e., compare the tetragonal Mn−Mn−Gd−Gd unit with the Mn−Gd−Mn−Gd arrangement or the stability of calixarenes pinched to different extent) by theoretical calculations was not successful because of too many atoms in a sandwich-like subunit and the complicated electronic configuration of the gadolinium atom.

The magnetic property of the title compound was examined (Figure 4), which reveals that the $\chi_M T$ value increases slightly from 24.09 cm^3 mol^{-1} K at 300 K to a maximum of 24.57 cm^3 mol^{-1} K at 42 K and then decreases dramatically to 4.93 cm^3 mol^{-1} K at 2 K. The reciprocal magnetic susceptibilities in 50−300 K follow the Curie−Weiss equation of $1/\chi_M = (T - \theta)/C$ with Curie constant $C = 23.99$ cm^3 mol^{-1} K and Weiss constant $\theta = 2.38$ K, which indicates a weak ferromagnetic interaction between the metal centers in the $Mn^{II}_2Gd^{III}_2$ cores. The constant $\chi_M T$ value of 24.09 cm^3 mol^{-1} K and Curie constant C are consistent with the value of 24.50 cm^3 mol^{-1} K expected for four independent ions ($2Mn^{II} + 2Gd^{III}$) with $g = 2.0$.[1,6,7] The dramatic decrease of $\chi_M T$ at low temperature might arise from the field saturation effect. The interactions among the $Mn^{II}_2Gd^{III}_2$ cores would be ruled out because they are well separated from each other by the bulky TC4A ligands.

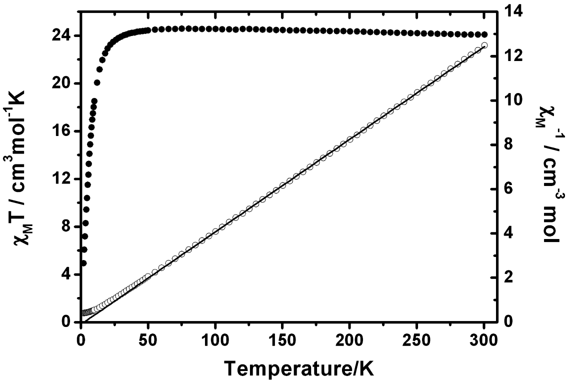

Figure 4. Plots of $\chi_M T$ and $1/\chi_M$ vs T for **1** in a 1000 Oe field.

In summary, compound **1** represents the first example of a 3d−4f heterometallic compound constructed with *p-tert*-butylthiacalix[4]arene. The unique structure featuring tetragonal Mn−Mn−Gd−Gd units and the bent sandwich-like subunits opens new perspectives in the design of multifunctional materials. For instance, the substitution of bridging ligands for CH_3OH as well as the use of other 3d or 4f metals might lead to networks with different dimensionality or compact tetranuclear units, which should be good candidates for porous materials or molecule-based magnets. These efforts are currently ongoing.

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Supporting Information Available: Crystallographic data in CIF format, synthesis detail, IR spectra, and other materials. This material is available free of charge via the Internet at http://pubs.acs.org.

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