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A Mn^{II}_5 tetragonal pyramid stabilized by *p-tert*-butylcalix[8]arene: Synthesis, structure and magnetic property

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ABSTRACT

A compound, $[Mn_5(H_4C8A)(OH)_2(C_3H_6NO_2)(DMF)_5(CH_3O)_{1.5}(HCO_2)(C_2H_3O_2)_{0.5}]\cdot 2DMF\cdot CH_3OH$ (**1**) (H_8C8A = *p-tert*-butylcalix[8]arene, DMF = *N,N′*-dimethylformamide), was synthesized by the solvothermal method in the mixed CH_3OH/DMF (1:1) solvent. Compound **1** is featured with a tetragonal pyramid-like Mn^{II}_5 cluster encircled within a calix[8]arene molecule with a 'pleated loop' conformation. Magnetic study indicates that the Mn^{II} centers exhibit antiferromagnetic interactions.

Calixarenes have also been documented to be a versatile ligand to construct polynuclear compounds [1]. In recent years, the coordination chemistry of calixarenes have drawn increasing attention, especially for calix[4]arenes [2]. However, the coordination chemistry of *p-tert*-butylcalix[8]arene (H_8C8A) (Scheme 1) has been studied relatively less [3]. It might be due to the facts such as limited solubility, poor control over stereoselective substitution reactions at the rims, and high flexibility of the molecules itself which leads to a variety of conformations and hence hinders long-range order in the solid state [4]. Based on this in mind, we employ the solvothermal method which has been widely used in the synthesis of the coordination compounds [5] to explore the coordination chemistry of calix[8]arene. We successfully obtained a series of compounds based on calix[8]arene, $[Ln^{III}_6Co^{II}_8(C8A)_2]$ (Ln = Sm, Gd, Dy) [6]. Herein, we present another example for the coordination chemistry of *p-tert*-butylcalix[8]arene, $[Mn_5(H_4C8A)(OH)_2(C_3H_6NO_2)(DMF)_5(CH_3O)_{1.5}(HCO_2)(C_2H_3O_2)_{0.5}]\cdot 2DMF\cdot CH_3OH$ (**1**). As we know, only one Mn-calix[8]arene compound has been reported, in which a Na_4Mn_2 cluster housed within two *p-tert*-butylcalix[8]arenes [3d]. In the present work, compound **1** is featured with a straw hat-shaped Mn_5-H_4C8A entity, in which the Mn_5 cluster exhibits a tetragonal pyramidal arrangement and is encircled by a calix[8]arene molecule adopting a 'pleated-loop' conformation.

The colorless crystals of compound **1** were synthesized by the reaction of H_8C8A, $Mn(CH_3COO)_2\cdot 4H_2O$, KCl and triethylamine in a 1:1 (v/v) MeOH/DMF mixed solvent at 130 °C for 3 days [7]. The addition of KCl to the reaction is necessary and it may act as a mineralizing agent in the synthesis of compound **1** [8]. If no KCl were added, a clear solution could be obtained. The color of the solution changed quickly from reddish brown to black in the ambient environment and some precipitation appeared after evaporation for several days at room temperature.

The molecular structure of compound **1** is shown in Fig. 1. It crystallizes in the monoclinic system with space group $P2_1/n$ [9]. In the asymmetric unit, there are five crystallographically independent Mn sites and a *p-tert*-butylcalix[8]arene molecule. Four manganese ions (Mn1–Mn4) are coplanar, and each of them is octahedrally coordinated by two phenol oxygens, one carboxylate oxygen, one methoxy, one DMF and one hydroxyl. Four MnO_6 octahedra are interconnected by the edge-shared and corner-shared mode to form a square. The angles of Mn(1)–Mn(2)–Mn(3), Mn(2)–Mn(3)–Mn(4), Mn(3)–Mn(4)–Mn(1), and Mn(4)–Mn(1)–Mn(2), are of 90.26°, 89.68°, 90.23° and 89.82°, respectively. The fifth Mn ion is coordinated by one DMF, one in situ generated formate anion [10], two methoxy and two hydroxy, and located upwardly on the square to form a tetragonal pyramid. The distances between Mn(5) and Mn(1), Mn(2), Mn(3) or Mn(4) are of ca. 3.31, 3.33, 3.41 and 3.37 Å, respectively. The Mn–O distances are in the range of 2.13–2.28 Å, which are consistent with the reported data [11]. Bond valence sum calculations (BVS) suggested that all the manganese ions are divalent [12]. The angles of Mn–O–Mn are listed in Table S1. One in situ generated *N,N*-dimethylcarbamate anion [10] bonds the Mn_4 square from the other side. *p-tert*-Butylcalix[8]arene captured the Mn_5 core through the phenol oxygen atoms. So a straw hat-shaped pentanuclear entity was formed. This pentanuclear core based on calixarenes was rarely reported. To date, only two examples have been obtained. One is a similar tetragonal pyramidal

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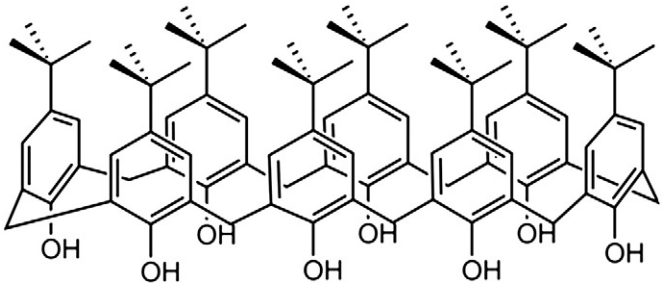

Scheme 1. *p-tert*-Butylcalix[8]arene (H_8L).

arranged cluster core based on calix[6]arene reported by Kajiwara et al. [13]. In those calix[6]arene based compounds, one hydroxide anion bridges four metal atoms at the bottom of the pyramidal. The other was reported during the preparation of our manuscript, in which five metal atoms are arrayed in two vertex-sharing partial cubane [14].

Different from those with a 'double-cone' conformation in $[Ln^{III}{}_6Co^{II}{}_8(C8A)_2]$ (Ln = Sm, Gd, Dy) compounds [6], in compound **1**, *p-tert*-butylcalix[8]arene adopts a 'pleated loop' conformation with eight phenol oxygen atoms in coplanar (the maximum deviation is 0.16 Å). The angles between the aryl rings and this oxygen plane are in the range of 34.5–40.5°. According to the Ugozzoli–Andreetti convention [15], the actual φ and χ torsion angle values, which define the solid-state conformation of C8A, are +79.8, −77.7; −96.4, +96.6; +83.1, −78.7; −88.9, +90.8; +78.7, −82.5; −95.3, +94.3; +82.8, −78.9; −91.2, +87.3. The cavity formed by the hydroxyl groups with the distances between the transannular oxygen centers are 6.91 Å for O(1) to O(5), 7.63 Å for O(2) to O(6), 7.63 Å for O(3) to O(7) and 6.91 Å for O(4) to O(8). In compound **1**, the in situ generated carboxylate group interconnects four Mn atoms with diagonal distances are 5.09 Å for Mn(1)–Mn(3) and 5.07 Å for Mn(2)–Mn(4). The cavity of the calix[8]arene molecule matches the square base of the tetragonal pyramid well, which leads to no great distortion from the free molecule (adopted the 'pleated-loop' conformation forming a 'hydrogen bonded cyclic array' within eight phenol oxygens [16]). The plane through the Mn_4 square base is nearly parallel to that through eight phenol oxygen atoms and the dihedral is 0.2°. It is uncommon that all the phenol oxygen atoms of the calix[8]arene participate in the coordination with the metal atoms unchanging its conformation. To our knowledge, this phenomenon was only observed in some uranium complexes in which two uranium ions bonded with all the eight phenol oxygen atoms [3c].

Based on the charge balance, four phenolic hydroxyl groups keep undeprotonated and form four intramolecular hydrogen bonds. The O···O distances for the hydrogen bonding are in the range of 2.41–2.46 Å, which are consistent with the reported examples [3c,d,5]. Two adjacent phenol units generate a partial cavity similar to a half-calix[4]arene fragment. Four DMF molecules bonding the Mn_5 core reside in these four partial cavities (Fig. 1) and interconnect the calixarene molecule through C–H···π interactions with a C··· aromatic centroid distance being of 3.26 to 3.88 Å (typical for H_4C[4]A solvates [17]). As shown in Fig. 2 and Fig. S1, the neutral straw hat-shaped molecules are interconnected to each other by O–H···O hydrogen-bonding, C–H···π interactions and van der Waals interactions. Some co-crystallized solvent molecules such as DMF and methanol filled in the space among calix[8]arenes to form a 3D supramolecular extended structure.

Thermal analysis for compound **1** was carried out under an air atmosphere with a heating rate of 10 °C·min^{-1}. Compound **1** can easily lose

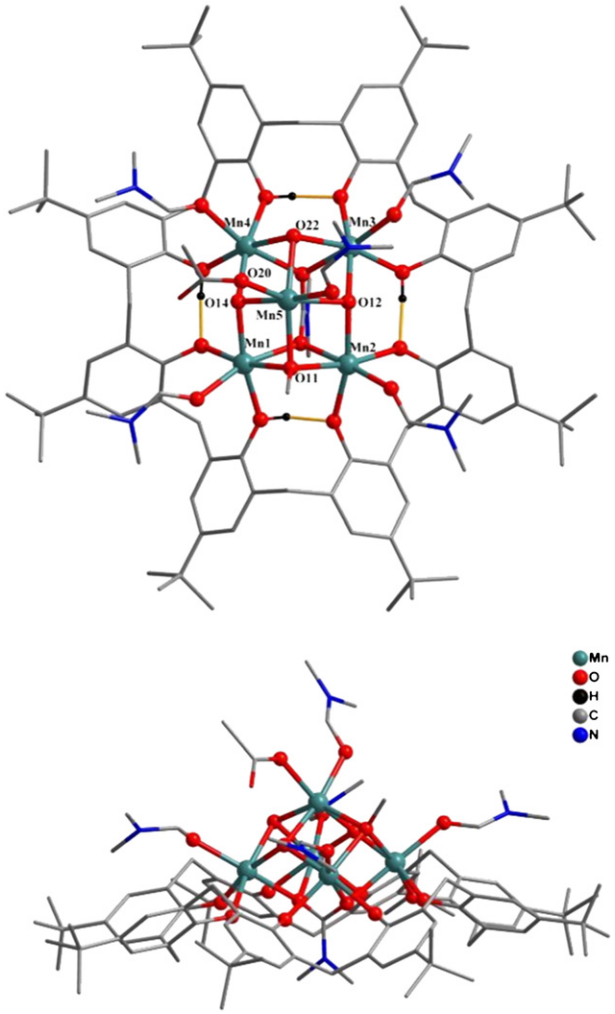

Fig. 1. Top view (upper) and side view (bottom) of a straw hat-shaped entity in **1**. The Mn_5 core is captured by calix[8]arene exhibits a tetragonal pyramidal arrangement. The yellow sticks represent hydrogen bondings. Other hydrogen atoms are omitted for clarity.

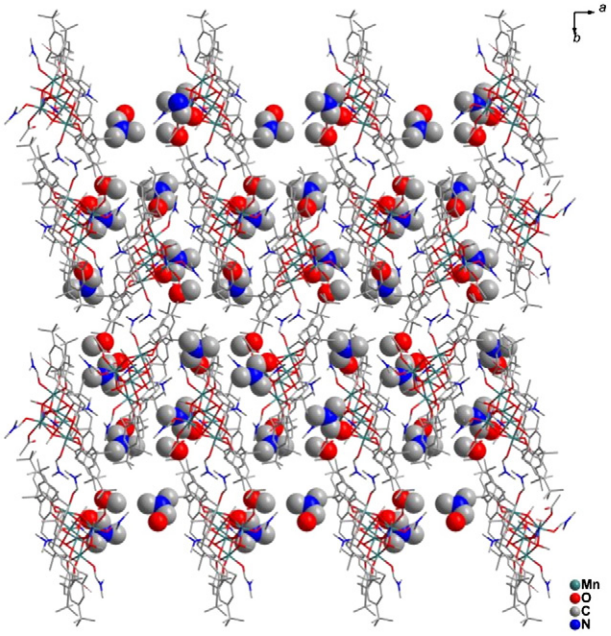

Fig. 2. Packing of the extended structure view along the c axis.