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A $\{Co_{32}\}$ Nanosphere Supported by *p-tert*-Butylthiacalix[4]arene

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The high-nuclearity coordination clusters of transition metal cations have been receiving growing attention due to their interesting electronic and magnetic properties which contribute to their potential as nanoelectronic components, metalloenzyme models, nanoscale catalysts, and molecular magnets.[1−5] Although there is much progress made in the practical and theoretic approaches, the design and synthesis of such materials remain an elusive goal. Among the strategies for this goal, applying a well designed multidentate organic ligands in constructing high-nuclearity clusters has been gaining more and more favor.[6] A variety of clusters involving cobalt cations such as Co_7,[7] Co_8,[8] Co_{10},[9] Co_{12},[10] Co_{13},[7a,10] Co_{19},[9] and Co_{20}[11] have been reported. However, to the best of our knowledge, Co^{II}_{24}[12,13] is the largest cobalt aggregate reported to date. *p-tert*-Butylthiacalix[4]arene (H_4TC4A), possessing four phenoxyl groups and four bridge sulfur atoms, has been proved to be a good multidentate ligand in constructing polynuclear complexes.[14−19] There are also some samples with lower nuclearity cobalt aggregates.[15a,19] Herein we present a novel compound containing a giant spherical $[Co^{II}_{24}Co^{III}_{8}(\mu_3\text{-}O)_{24}(H_2O)_{24}(TC4A)_6]$ unit as an exception, which contains a $\{Co_{32}\}$ cluster capped by six *p-tert*-butylthiacalix[4]arene molecules (Figure 1). The syntheses, three isomeric structures,[20] and magnetic properties of this cobalt compound will be discussed.

Isomer **1a** was obtained by the solvothermal reaction of $Co(AcO)_2\cdot 4H_2O$ and H_4TC4A in a 1:1(v/v) $MeOH/CHCl_3$ mixed solvent (total 10 mL) with several drops of water at 130 °C. With the increasing amount of H_4TC4A, isomers **1a** and **1b** can be obtained within the same batch. Isomer **1c** formed by recrystallizing **1a** or **1b** in toluene. All the extended structures of these three isomers are stacked by some neutral spherical units involving a $\{Co_{32}(\mu_3\text{-}O)_{24}(H_2O)_{24}\}$ cluster core and six capping TC4A molecules (Figure 1), and some disordered solvent molecules located in the interstices whose contribution was subtracted in the structure refinement.

The diameter of the spherical units ($C_{butyl}\cdots C_{butyl}$*) is ~23.4 Å and that of the inner cluster core (Co1 $\cdots$Co1*) is ~10.6 Å. The spherical units can be thought to be assembled by six $\{Co_4(TC4A)\}$ subunits around a $\{Co_8\}$ cube, in which all the cobalt atoms are bridged by 24 μ_3-oxygen atoms. Although there are several compounds reported containing $\{M_4(TC4A)\}$ subunits, few examples with two or more such subunits bonded to each other are observed.[14−18] Notably, six calixarenes are arranged in an "up−up" fashion and are capping on the faces of a cube (Figure 1). As far as we know, this is the only example for the calixarenes in an octahedral arrangement. Although there has been a report with six calixarenes bonded to one $\{Ho_{12}\}$ cluster, those six *p*-tert-butylsulfonylcalix[4]arenes are located on a ring.[21]

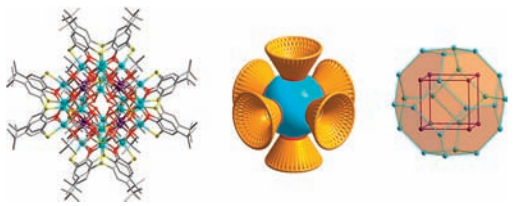

Figure 1. A spherical $\{Co_{32}(\mu_3\text{-}O)_{24}(H_2O)_{24}(TC4A)_6\}$ unit (left), its scheme (middle), and the Co^{II}_{24} sodalite core with an encapsulated Co^{III}_{8} cube (right).

Analysis of the Co−O bond distances (taking **1a** as an example, hereafter the same) showed that the Co4 site might be occupied by the Co^{III} atom while the others (Co1−Co3) are occupied by the Co^{II} atoms. So the formula for the spherical units should be $[Co^{II}_{24}Co^{III}_{8}(\mu_3\text{-}O)_{24}(H_2O)_{24}(TC4A)_6]$, which is also supported by the fact that no absorption peaks for the CH_3COO^- or OH^- anions were found in IR spectra. Each Co^{II} site is coordinated by two phenoxyl oxygen, one sulfur, and two μ_3-O atoms and two coordinated water molecules, while the Co^{III} site is in a distorted octahedral coordination environment with three μ_3-O atoms and three coordinated water molecules. The water molecules are weakly bonded as evidenced by the relatively longer Co−O distances (2.13−2.35 Å). MALDI-TOF mass spectra were applied to detect the isolated spherical units dispersed in toluene. A mass record corresponding to a cluster with the formula being $[Co^{II}_{24}Co^{III}_{8}(\mu_3\text{-}O)_{24}(TC4A)_6]$ ($m/z = 6572$) was observed, suggesting the loss of coordinated water molecules in the mass spectrum analysis.

Another fascinating characteristic of the spherical units is given by a Co^{II} sodalite cage encapsulating a Co^{III} cube (Figure 1). The quadrilateral face of the sodalite cage features a templating TC4A molecule. Although the sodalite topology is common in the zeolite-related compounds, it is rarely observed in the organic−inorganic hybrid complexes.[22] The Co−Co distances in the edge (linked by $O_{phenoxyl}$) and the cross (free of linkers) of the Co^{II}_4 square are ca. 3.49 and 4.94 Å, respectively, while that in the sharing edge of the hexagons connected by μ_3-O is ca. 3.16 Å. In the inner Co^{III}_{8} cube, the edge length is ca. 4.62 Å. The $Co^{II}-O_{phenoxyl}-Co^{II}$ angles range from 118.6° to 119.1°, which are much larger than the $Co^{II}-\mu_3\text{-}O-Co^{II}$ angles (ranging from 98.9° to 99.7°) and $Co^{II}-O_{water}-Co^{II}$ angles (ranging from 95.9° to 96.1°) but are comparable to those in the phenoxyl mediated cobalt clusters.[7b,13] This work on the Co_{32} cluster might shed some light onto the design and growth of

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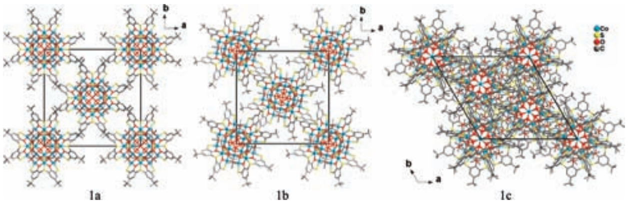

Figure 2. Assemblies of the spherical $\{Co_{32}\}$ units in three isomers.

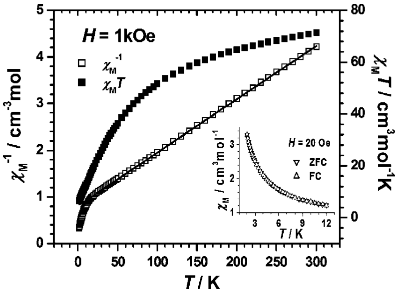

Figure 3. Plots of $\chi_M T$ vs T and $1/\chi_M$ vs T for **1a** in a 1000 Oe field. Inset: Temperature dependencies of ZFC and FC of **1a**.

high symmetry and high nuclearity clusters with some intriguing physical properties distinguished from the lower nuclearity clusters.[23]

Isomers **1a** and **1b** both crystallize in the tetragonal system but with the space groups *I*4/*mmm* and *I*4/*m*, respectively. Isomer **1c** crystallizes in a trigonal system with space group $R\bar{3}$ (Figure 2). Viewed along the *c* axis, the extended structures of isomers **1a** and **1b** exhibit a similar arrangement of the spherical units. Upon close observation, one can find that, compared with those in **1a**, all the spheres in **1b** rotate clockwise along a direction parallel to the *c* axis by ~34°. However, different from **1a** and **1b** stacked by the body-centered tetragonal lattices, the extended structure of **1c** can be assigned to a face-centered cubic (FCC, cubic closest packing) structure with a typical ABCABC··· stacking pattern of the spherical units. That means the spherical units have been assembled again in the recrystallization process from toluene, which might give a new thread in rearranging the clusters in the supramolecular chemistry.

The temperature-dependent magnetic susceptibility of complex **1a** was investigated in 2−300 K with a 1000 Oe applied field (Figure 3). The $\chi_M T$ value of complex **1a** at 300 K is 71.40 cm^3 mol^{-1} K, which is much larger than the spin-only value of 24 isolated high-spin d^7 ions (45.0 cm^3 mol^{-1} K), owing to the significant orbital contributions of the distorted octahedral Co^{II} ions.[7−13] For per Co^{II} center, the experimental $\chi_M T$ value at room temperature is 2.98 cm^3 mol^{-1} K, which is consistent with the typical value of the Co^{II} ion (for Co^{II}, the $\chi_M T$ value normally ranges from 2.7 to 3.4 cm^3 mol^{-1} K). However, the assumption of 32 Co^{II} centers in the cluster would result in a lower $\chi_M T$ value of 2.23 cm^3 mol^{-1} K, being out of the usual range. It is in accord with the structure that there are 24 high spin Co^{II} cations and 8 low spin Co^{III} centers. As the temperature is lowered, the $\chi_M T$ value decreases gradually to a minimum of 6.27 cm^3 mol^{-1} K at 2 K. The reciprocal magnetic susceptibilities in 50−300 K follow the Curie−Weiss Law of $1/\chi_M = (T - \theta)/C$ with Curie constant $C = 87.96$ cm^3 mol^{-1} K and Weiss constant $\theta = -70.98$ K, which indicates an antiferromagnetic interaction between the metal centers in the Co$_{32}$ cores.[10] This compound shows no single molecule magnet behavior above 2 K.

In conclusion, a novel complex with a $\{Co_{32}\}$ cluster core capped by six *p*-*tert*-butylthiocalix[4]arene molecules has been obtained by a solvothermal method and its three isomers were observed. The $\{Co_{32}\}$ cluster can be thought of as a sodalite Co$^{II}_{24}$ cage encapsulating a Co$^{III}_{8}$ cube. The calixarenes capping six faces of a hexahedron exhibit a unique arrangement for the calixarenes. In two isomers, the calixarene-capped $\{Co_{32}\}$ spherical units are arranged into a body-centered cubic lattice, while they are assembled in a cubic closest packing pattern in the third isomer. This work promotes the route for the design and growth of high nuclearity clusters with the multidentate calixarene ligands and indicates a feasible way to rearrange the cluster units in the crystal.

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Supporting Information Available: Synthetic details, TGA, IR, mass spectra, magnetic data and X-ray structural data (CIF, additional structural plots). This material is available free of charge via the Internet at http://pubs.acs.org.

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(20) $C_{240}H_{312}Co_{32}O_{72}S_{24}$ (**1**). **1**·$(CHCl_3)_{12}(H_2O)_{110}$ (**1a**): tetragonal, *I*4/*mmm*, $a = b = 27.0173(4)$ Å, $c = 29.0170(5)$ Å, $V = 21180.5(6)$ Å^3, $Z = 2$, $R1 = 0.0962$ for $[I > 2\sigma]$; **1**·$(CHCl_3)_{12}(H_2O)_{69}$ (**1b**): tetragonal, *I*4/*m*, $a = b = 25.1839(18)$ Å, $c = 35.168(3)$ Å, $V = 22305(3)$ Å^3, $Z = 2$, $R1 = 0.0847$ for $[I > 2\sigma]$; **1**·$(C_7H_8)_{16}(H_2O)_{73}$ (**1c**): trigonal, $R\bar{3}$, $a = b = 24.567(2)$ Å, $c = 61.843(6)$ Å, $V = 32325(5)$ Å^3, $R1 = 0.0814$ for $[I > 2\sigma]$.
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