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Open Pentameric Calixarene Nanocage

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Supporting Information

ABSTRACT: A novel open helmetlike coordination cage has been synthesized based on Co_4-calixarene shuttlecock-like secondary building units and in situ generated phosphate anions, where the opening of the cage comprises a large 16-membered ring. The above unprecedented Co_{20} nanocage presents the first pentameric calixarene coordination compound. Sorption behavior and magnetic properties are also investigated.

The exploration for high-nuclearity transition-metal cage complexes has attracted growing attention because of not only their wonderful architectures[1] but also their widespread applications in encapsulating guest molecules,[2] gas separation and storage,[3] nanoscale catalysts,[4] and so on.[5] A variety of coordination cages with distinct geometries and various sizes have been reported in recent years.[6] However, there are very few reports on the construction of coordination cages using molecular building blocks as large vertices.

p-tert-Butylthiacalix[4]arene (H_4BTC4A; Figure 1a), as an emerging and particular ligand in calixarene chemistry,[7] possesses four hydroxyl groups at the lower rim and four sulfur bridge atoms, which have been documented as good candidates to construct polymetallic complexes.[8] H_4BTC4A ligands always bond the metals directly by their phenolic oxygen atoms and sulfur bridges. It is also found that one thiacalix[4]arene molecule can bind to four metal ions, simultaneously forming a tetranuclear metal entity acting as an excellent secondary building unit (SBU), which can be bridged by different linkers into high-nuclearity coordination complexes. For example, they can be linked into isolated sandwich-like Co_8, saddlelike M_{12} (M = Co, Ni), wheel-like Co_{16} clusters, tetragonal-prismatic Co_{32} nanocages, and one-dimensional chains by in situ generated nitrogen-donor ligands,[9] a large metallamacrocycle Co_{24} by 1,2,4-triazole molecules,[10] a wavelike belt or Co_{16} squares with aromatic dicarboxylates,[11] and a series of calixarene-supported octahedral coordination Co_{24} nanocages by 6 Co_4-TBC4A SBUs with 8 tripodal ternary aromatic carboxylates[12] or 12 1,4-benzenedicarboxylates as linkers.[13]

In spite of the fact that calixarenes are facile to construct polymetallic complexes, there are no reports on polymetallic complexes supported by five calixarene molecules. To our best knowledge, all of the reported calixarene-based polymetallic complexes are assembled by mono-, bi-, tri-, tetra-, hexa-, or octameric calixarene units.[14] Our group is particularly interested in the design and synthesis of new solid inorganic−organic hybrid materials based on calixarene.[9a,13,15] In this paper, we present the first pentameric calixarene coordination cage, $[Co_{20}(BTC4A)_5(\mu_2\text{-}H_2O)(\mu_3\text{-}OH)_4(HPO_4)_8]_2\cdot 2DMF\cdot 8CH_3OH$ (**1**) (DMF = *N,N*-dimethylformamide). Herein, the crystal structure, sorption behavior, and magnetic properties of the title compound are presented and discussed.

Red block crystals of **1** were obtained under solvothermal reaction by mixing $Co(ClO_4)_2\cdot 6H_2O$, H_4BTC4A, and H_2PO_3 in a 3:1:2 molar ratio in DMF−CH_3OH mixed solvents (1:1, v/v) at 160 °C. Powder X-ray diffraction (PXRD) analysis confirms the phase purity of the bulk product (Figure S5 in the Supporting Information, SI). Single-crystal X-ray diffraction analysis shows that Co_4-TBC4A SBUs are linked by eight HPO_4^{2-} anions to form an unprecedented open helmet-shaped Co_{20} structural motif (Figure 1b).

Compound **1** crystallizes in the triclinic system with space group $P\bar{1}$, featuring a nanosized open coordination cage. The asymmetric unit is large and contains two open Co_{20} nanocages and some disordered solvent molecules, whose contribution has been subtracted from the diffraction data by the *SQUEEZE* command in *PLATON*[16] (see the SI). Each Co_{20} nanocage is constructed from five Co_4-TBC4A SBUs acting as the metal vertexes and eight HPO_4^{2-} linkers through a [5 + 8] condensation. Here we only provide one structure of a half-open Co_{20} nanocage as a generic description (Figure 1c) because these two thiacalix[4]arene-supported Co_{20} cages are structurally analogous and show similarity in their coordination environments. Co1, Co3, and the opening four cobalt (Co8, Co12, Co16, and Co20) ions are five-coordinated in a distorted square-pyramidal coordination geometry with two phenoxyl oxygen atoms, one sulfur atom, and two oxygen atoms from two different HPO_4^{2-} anions, while the other 14 cobalt sites are six-coordinated in a distorted octahedral geometry with two phenoxyl oxygen atoms, one sulfur atom, and two oxygen atoms from two different HPO_4^{2-} anions, as well as one other component (μ_2-H_2O for Co2 and Co4 and μ_3-OH for other cobalt cations). It should be noted that phosphates are excellent ligands for making polymetallic complexes because their different anionic forms can adopt various coordination modes. In compound **1**, all HPO_4^{2-} anions are generated by an in situ reaction of H_2PO_3 and adopt two coordination modes. Four HPO_4^{2-} anions in the lower part of the helmet bind to four cobalt

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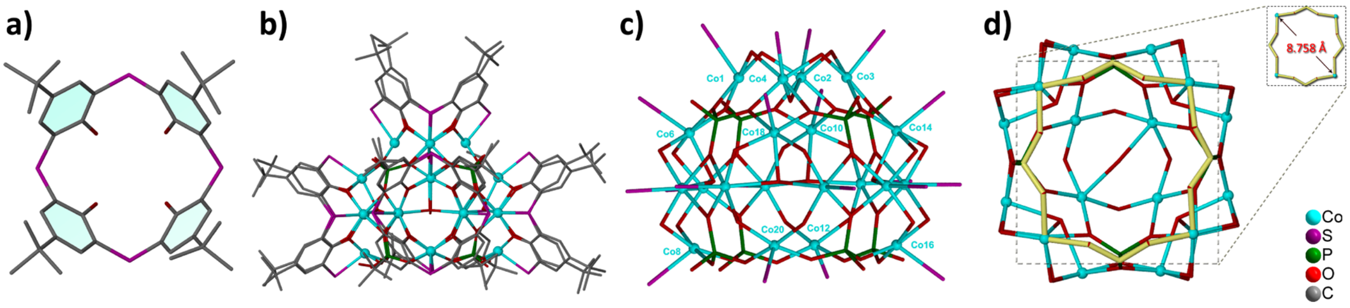

Figure 1. (a) H_4BTC4A. (b) Helmetlike $[Co_{20}(BTC4A)_5(\mu_2\text{-}H_2O)(\mu_3\text{-}OH)_4(HPO_4)_8]$ nanocage of compound **1**. Hydrogen atoms are omitted for clarity. (c) Icosanuclear Co_{20} core within the title coordination cage. (d) Solid yellow line representing the opening of **1**.

cations with a [4.2110] coordination mode, while the other four HPO_4^{2-} anions bind to six cobalt cations with a [6.2220] binding mode in this structure.[17] It should be pointed out that the Co_4-TBC4A SBU in the upper part of the helmet adopts different conformations compared to the other four Co_4-TBC4A SBUs. Those four cobalt ions (Co1, Co2, Co3, and Co4) from the upper Co_4-TBC4A SBU form an approximate rhombus shape and house a μ_2-H_2O molecule, while the other Co_4 clusters adopt an approximate kitelike shape and encapsulate a μ_3-OH ion (Figure S1 and Table S1 in the SI). The metal oxidation states and the protonation levels of all oxygen atoms in the title coordination cage are established by cobalt and oxygen bond-valence-sum calculations,[18] charge balance, and detection of metric parameters. Moreover, all cobalt ions in the title complex are divalent, which is also confirmed by magnetic measurement.

Compared with the octahedral coordination cages, which are assembled by Co_4-TBC4A SBUs with tripodal ternary aromatic carboxylates,[12] the open Co_{20} nanocage can be thought of as five Co_4-TBC4A SBUs occupying the vertices of a defect octahedron missing one vertex, in which the opening of the cage exhibits a 16-membered ring consisting of four cobalt, four phosphorus, and eight oxygen atoms (Figure 2). With close examination, one can find that the repeating unit for the 16-membered ring is −[Co−O−P−O]−. The longest distance between the diametrically opposed atoms in the ring is about 8.758 Å (Figure 1d). Moreover, this open nanocage has a small inner cavity volume of around ca. 380 $Å^3$ (Figure S2 in the SI), which is smaller than those of the octahedral Co_{24} nanocages linked by aromatic carboxylates.[12,13] Upon crystal packing, the extended structure of **1** exhibits a skewed bilayer structure stacked by the nanocages through van der Waals interactions, $\pi\cdots\pi$, $C-H\cdots\pi$, and hydrogen-bonding interactions. These Co_{20} nanocages construct two antiparallel layers in an opening-to-opening fashion via weak interactions (Figure S3 in the SI). Its free space and interstices of the lattice are occupied by DMF and CH_3OH molecules. Thermogravimetric analysis (TGA) suggests that the thermal stability of the title coordination cage can be maintained at more than 360 °C (Figure S4 in the SI).

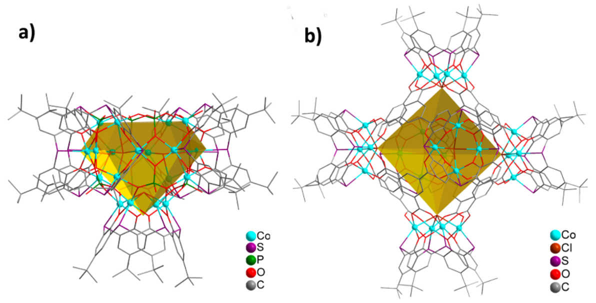

Figure 2. (a) $[Co_{20}(BTC4A)_5(\mu_2\text{-}H_2O)(\mu_3\text{-}OH)_4(HPO_4)_8]$ coordination cage compared with (b) the $[Co_{24}(BTC4A)_6(\mu_4\text{-}Cl)_6(TC)_8]^{6-}$ coordination cage (ref 12).

The calculated free volume of compound **1** with removal of guest solvent molecules is ∼38.9% by *PLATON*. To determine the architectural rigidity and permanent porosity of **1**, the gas adsorption isotherms of activated samples are determined. As shown in Figure 3, the N_2 sorption of **1** exhibits a pseudotype I isotherm with saturated N_2 uptake of 148 $cm^3\ g^{-1}$ at 77 K and 1.0 bar, a characteristic of materials with permanent microporosity, corresponding to Langmuir and Brunauer−Emmett−Teller surface areas of 579 and 388 $m^2\ g^{-1}$, respectively. A pore volume of 0.23 $cm^3\ g^{-1}$ is calculated by the Horvath−Kawazoe method. N_2 sorption isotherms show adsorption/desorption hysteresis, which might be due to adsorption of the interstices between the layers and the aforementioned partially blocked apertures by the adjacent layers.

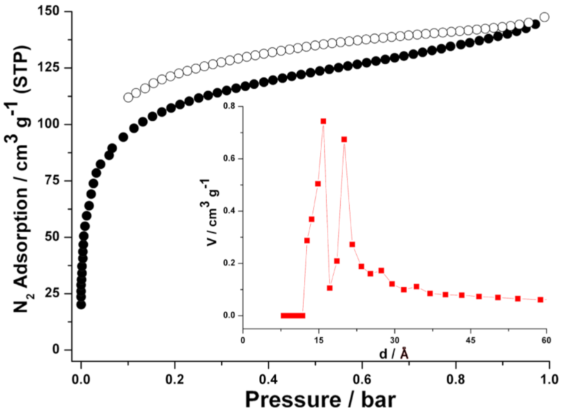

Figure 3. Experimental N_2 sorption isotherm at 77 K for **1**: (●) adsorption; (○) desorption. The inset shows the pore-size distribution incremental pore volume (V) versus the pore width (d).

The temperature dependence of magnetic susceptibility is performed on the polycrystalline sample of compound **1** in the 2−300 K range under an applied field of 1000 Oe, as shown in Figure 4. The room temperature $\chi_m T$ is 96.14 $cm^3\ K\ mol^{-1}$ for the title compound, which is significantly higher than the calculated spin-only values of 75 $cm^3\ K\ mol^{-1}$ ($g = 2$) for 40 isolated Co^{II} spin carriers. This can be explained on the basis of the orbital contribution of Co^{II}, which is known to be significant in an octahedral field.[19] For this compound, the $\chi_m T$ product gradually decreases and then falls rapidly to 3.77 $cm^3\ K\ mol^{-1}$ at 2 K. The Curie−Weiss law fit of the data above 50 K gives the

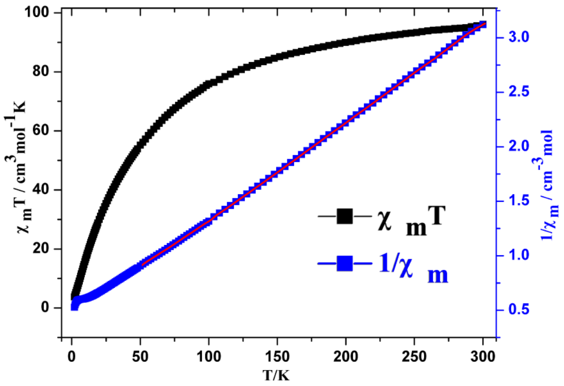

Figure 4. Temperature dependence of magnetic susceptibility of **1** in a 1000 Oe field. The solid red line is a fit of the experimental data of **1** using the Curie–Weiss law.

Curie constant $C = 105.33$ cm^3 mol^{-1} K and the Weiss constant $\theta = -45.65$ K for **1**. The negative Weiss constant indicates the presence of antiferromagnetic interaction between the metal centers and/or the spin–orbit coupling effect of Co^{II}.

In conclusion, we have demonstrated formation of the first pentameric calixarene coordination cage through a [5 + 8] condensation with in situ generated phosphate ligands. It is possible to get more complicated and interesting nanocages with other auxiliary phosphate ligands and other metal centers. Our efforts to explore these possibilities are ongoing.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Synthesis, crystallographic data in CIF format (CCDC 958793 for **1**), supplementary figures, TGA and PXRD pattern of compound **1**, and other materials. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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