

## Isolated Co<sub>15</sub> Clusters and Their Assembly into a 3D Network: Conformation-Directed Synthesis

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Isolated clusters of 15 Co atoms interconnected by six organic linkers, each with two carboxylic and one phosphonic groups, N(CH<sub>2</sub>COO<sup>-</sup>)<sub>2</sub>(CH<sub>2</sub>PO<sub>3</sub><sup>2-</sup>), are synthesized with deprotonated *trans*-cyclohexanehexacarboxylic acid, C<sub>6</sub>H<sub>6</sub>(COO<sup>-</sup>)<sub>6</sub>, as counteranions. The *cis* conformation of the latter, on the other hand, coordinates to the same clusters by replacing the terminal water ligands and links them into a 3D network.

The metal–organic frameworks (MOFs) are consistently recognized for their enormous variety of topologies, many of them spectacular, and for their wide spectrum of potential applications.<sup>1</sup> Many MOFs are constructed from preformed secondary building units, which are typically a few metal atoms grouped into a cluster that is chelated by carboxylic groups.<sup>2</sup> At the same time, despite the importance of nanoclusters in numerous applications such as recognition, storage, catalysis, and single-molecule magnets,<sup>3</sup> very little progress has been made in using such large clusters as building blocks for the hierarchical assembly of MOFs.<sup>4</sup> Such assemblies are of particular interest because the extended structures can be easily controlled, their stoichiometry can be precisely

defined, and the porous, electronic, magnetic, and optical properties of the compounds would be more predictable.<sup>5,6</sup>

We have been exploring for nanoscale clusters of transition metals by using multifunctional nondivergent ligands with multiple ligating sites. In order to build frameworks of such clusters, we then introduce divergent multifunctional ligands that may act as linkers. Here we report the synthesis of an isolated cationic nanocluster made of 15 Co atoms held together by *N*-(phosphonomethyl)iminodiacetic acid [N(CH<sub>2</sub>-COOH)<sub>2</sub>(CH<sub>2</sub>PO<sub>3</sub>H<sub>2</sub>), H<sub>4</sub>L] and charge-balanced with deprotonated *trans*-1,2,3,4,5,6-cyclohexanehexacarboxylic acid [C<sub>6</sub>H<sub>6</sub>(COOH)<sub>6</sub>, H<sub>6</sub>E] in [Co<sub>15</sub>L<sub>6</sub>(H<sub>2</sub>O)<sub>24</sub>][*trans*-E]·xH<sub>2</sub>O (**1**). We also report the hierarchical assembly of the same clusters into a 3D network, where they are linked by the *cis* conformation of the hexacarboxylate, i.e., [Co<sub>15</sub>L<sub>6</sub>(*cis*-H<sub>3</sub>E)<sub>2</sub>(H<sub>2</sub>O)<sub>18</sub>]·12H<sub>2</sub>O (**2**). The deprotonated H<sub>4</sub>L acid is a tripodal ligand with two clawlike carboxylate and one clawlike phosphonate groups that offer the possibility for incorporating more metal atoms into high-nuclearity clusters. The hexacarboxylate, on the other hand, provides multiple binding sites and conformations for further linkage of the clusters into coordination polymers.

The hydrothermal reaction of Co(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O with H<sub>4</sub>L and H<sub>6</sub>E resulted in crystals with two distinctly different morphologies, blocklike for **1** and hexagonal prisms for **2** (details are given in the Supporting Information). Their structures were determined by single-crystal X-ray diffraction,<sup>7</sup>

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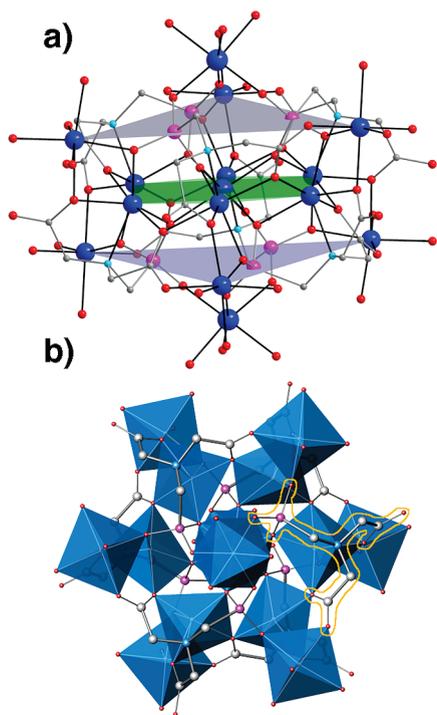
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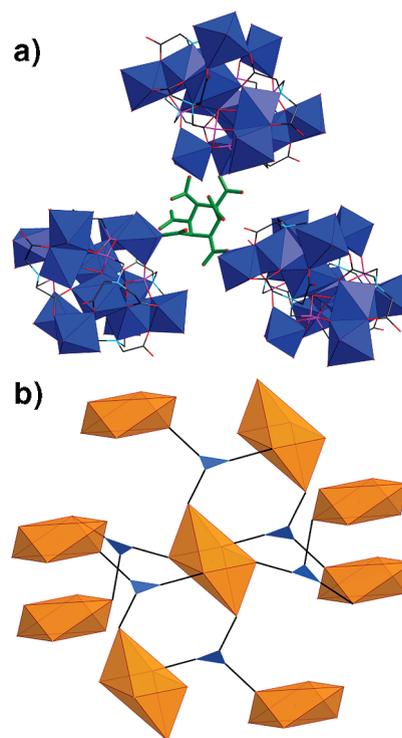
(7) Crystal data: **1**, triclinic,  $P\bar{1}$ ,  $a = 14.4481(8)$  Å,  $b = 15.5519(8)$  Å,  $c = 16.1103(8)$  Å,  $\alpha = 96.037(2)^\circ$ ,  $\beta = 107.798(2)^\circ$ ,  $\gamma = 101.151(2)^\circ$ ,  $V = 3328.9(3)$  Å<sup>3</sup>,  $Z = 2$ ,  $R1/wR2 = 0.0596/0.1820$  for the observed data and  $0.0741/0.1969$  for all data. The ligands coordinating to Co atoms were resolved, but the highly disordered solvent molecules could not be modeled properly. Instead, the diffuse electron density peaks were treated with the SQUEEZE routine within the PLATON software package. Crystal data: **2**, monoclinic,  $C2/c$ ,  $a = 19.9721(8)$  Å,  $b = 22.1174(1)$  Å,  $c = 24.3182(1)$  Å,  $\beta = 95.552(2)^\circ$ ,  $V = 10691.7(8)$  Å<sup>3</sup>,  $Z = 4$ ,  $R1/wR2 = 0.0300/0.1005$  for the observed data and  $0.0332/0.1026$  for all data.



**Figure 1.** Nanocluster  $[\text{Co}_{15}\text{L}_6(\text{H}_2\text{O})_{24}]^{6+}$  in **1** (Co, blue; P, pink; O, red; N, sky blue; C, gray): (a) Ball-and-stick representation showing the “layers” perpendicular to the pseudo-3-fold axis (vertical). The eight external Co atoms are ligated by three terminal water molecules each. (b) Polyhedral view along the pseudo- $C_3$ . Outlined in yellow is one of the six L ligands with one phosphonate and two carboxylate groups each.

and the compounds were also analyzed by Fourier transform IR (FT-IR), thermogravimetric analysis (TGA), and powder X-ray diffraction (PXRD). Compound **1** exhibits isolated cationic nanoclusters  $[\text{Co}_{15}\text{L}_6(\text{H}_2\text{O})_{24}]^{6+}$  (Figure 1) with a diameter of ca. 1.6 nm. Their charge is balanced by the hexaanionic *trans*-hexacarboxylate  $\text{C}_6\text{H}_6(\text{COO}^-)_6$ . The 15 Co<sup>II</sup> ions in the cluster are arranged in alternating Co/Co<sub>3</sub>/Co<sub>7</sub>/Co<sub>3</sub>/Co layers along a pseudo-3-fold axis (Figure 1a). The Co<sub>3</sub> triangles are staggered with respect to each other, while the middle Co<sub>7</sub> layer is a close-packed centered hexagon. Each of the 15 Co ions is in a distorted octahedral coordination. The central Co atom is coordinated by six phosphonate O atoms from the six L ligands participating in the cluster, with each O atom shared by one Co atom from the hexagonal ring. Each ring atom is coordinated by such phosphonate O atoms from two L ligands. One of these L ligands also coordinates to these Co atoms by two carboxylate O atoms and its N atom. The sixth coordination is a carboxylate O atom from a third L group. Each Co atom in the Co<sub>3</sub> layers is coordinated by three terminal water molecules and two carboxylate and one phosphonate O atoms from three different L ligands, all shared with Co atoms from the central hexagon. Lastly, the Co atoms capping the top and bottom triangles are coordinated by three phosphonate O atoms and three terminal water molecules. Thus, each L ligand in **1** coordinates to eight Co atoms, with the phosphonate group adopting a  $\mu_5\text{-}\eta^2\text{:}\eta^2\text{:}\eta^1$  bridging mode and the two carboxylate groups exhibiting  $\mu_2\text{-}\eta^2\text{:}\eta^0$  and  $\mu_3\text{-}\eta^2\text{:}\eta^1$  modes.

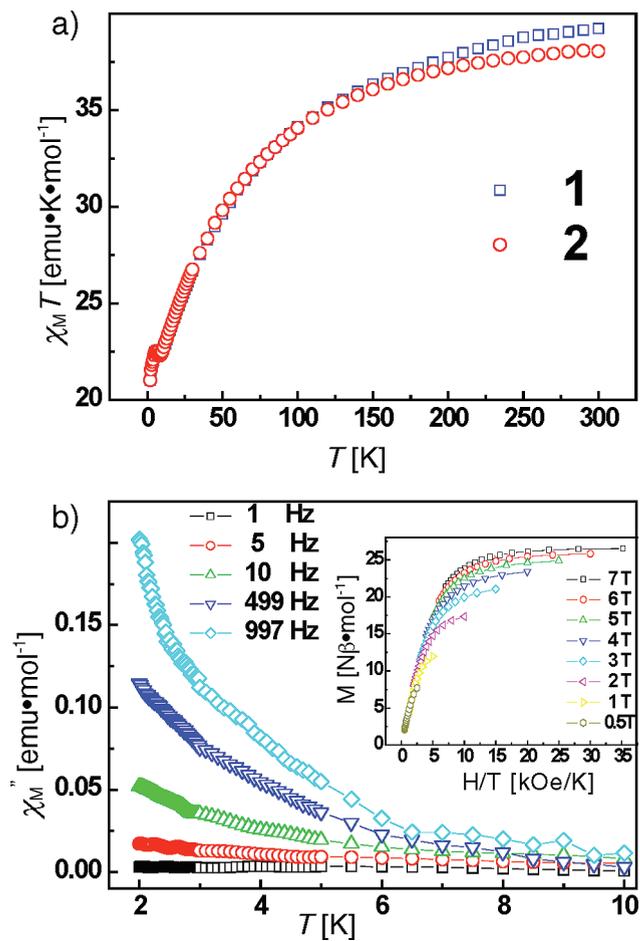
The key structural feature in **1** is the presence of 24 peripheral water molecules coordinated radially outward with respect to the core of the pseudospherical cluster. Such labile ligands are potential targets for ligand exchange with polydentate linkers in order to build extended structures.



**Figure 2.** Structure of **2** showing (a) how the partially deprotonated *cis*-H<sub>3</sub>E ligand coordinates to three Co<sub>15</sub> clusters and (b) how each cluster (orange pseudo-octahedra) bonds to six *cis*-H<sub>3</sub>E (blue triangles) to build a 3D network.

This role here is played by the second ligand in the system, namely, 1,2,3,4,5,6-cyclohexanehexacarboxylic acid but in its *cis* conformation. It is interesting that the *trans* enantiomer, completely deprotonated, acts simply as a counteranion for the Co<sub>15</sub> clusters in **1**, but it directs their assembly into a 3D network as a partially deprotonated *cis* enantiomer H<sub>3</sub>E by coordinating to the clusters in **2**. Apparently, three carboxylic groups in the latter *cis* conformation are appropriately positioned geometrically in order to coordinate to three Co<sub>15</sub> clusters by replacing coordinated water molecules (Figure 2). Thus, each *cis*-E ligand uses the three deprotonated carboxylic groups at positions 1, 2, and 4 to coordinate via one of the O atoms to peripheral Co atoms from three different clusters. Each Co<sub>15</sub> building block is, in turn, coordinated by six *cis*-H<sub>3</sub>E ligands that replace six water molecules and link the building blocks in a network (Figure 2b). It should be pointed out that the Co<sub>15</sub> cluster building block in the network of **2** is exactly the same Co<sub>15</sub> cluster characterized as isolated species in **1** minus six water molecules; i.e., the formula of the cluster is  $[\text{Co}_{15}\text{L}_6(\text{H}_2\text{O})_{24}]^{6+}$  in **1** and  $[\text{Co}_{15}\text{L}_6(\text{H}_2\text{O})_{18}]^{6+}$  in **2**.

The topology of the framework in **2** is quite unusual, a 3,6-connected net with Schläfli's symbol  $(4^2\cdot 6)_2(4^4\cdot 6^2\cdot 8^7\cdot 10^2)$  where the cluster is a six-connected pseudo-octahedral node and the *cis*-H<sub>3</sub>E ligand is a 3-connected node (Figure 2b). The framework exhibits small helical channels along the *b* axis (ca.  $6.9 \times 4.6$  Å, in the Supporting Information). The channels are enclosed within interweaving dual left/right-handed helices with a pitch of 48.6 Å. There are also channels of two different sizes along the *c* axis, ca.  $6.4 \times 4.5$  and  $10.6 \times 3.8$  Å (in the Supporting Information). The channels of the two directions connect to each other and produce an intersecting 3D pore structure occupied by the lattice water molecules.



**Figure 3.** (a) Plots of  $\chi_M T$  vs  $T$  for **1** and **2** at a field of 2 kOe. (b) Temperature dependence of the out-of-phase  $\chi_M''$  ac magnetic susceptibility at different frequencies for **1** obtained at zero external magnetic field,  $H_{ac} = 3$  Oe. The inset shows plots of magnetization vs  $H/T$  for **1** between 2 and 10 K.

Compounds **1** and **2** exhibit very similar magnetic behavior (Figure 3), and this is expected because of the presence of the same magnetically active  $\text{Co}_{15}$  units in both of them. The  $\chi_M T$  values decrease gradually with the temperature starting from 39.23 and 38.06  $\text{emu K mol}^{-1}$  for **1** and **2**, respectively, to a distinct plateau at around 10–5 K. Then they fall again to a minimum value at 2 K for both compounds. It is reasonable to assume that the nonzero plateaus reflect nondiamagnetic ground states for these two compounds. The data above

100 K obey the Curie–Weiss law for **1** and **2** (in the Supporting Information). This clearly suggests an overall antiferromagnetic coupling between the  $\text{Co}^{2+}$  ions within the clusters. However, any further rationalization or simulation of the magnetic properties of the two compounds is impossible because of the combination of an orbitally degenerate ground state for the metal centers<sup>8</sup> and a very complicated structure with many possible exchange interactions between these centers.

The low-temperature variations of the magnetizations of **1** and **2** were recorded at different magnetic fields and different frequencies (inset of Figure 3b and the Supporting Information). Clearly, the magnetization lines at different fields are not superimposed, and this indicates a substantial zero-field-splitting parameter. However, our efforts to extract such a parameter (using ANISOFIT<sup>9</sup>) were hampered by the large orbital contribution of the distorted  $\text{Co}^{2+}$  ions. The alternating-current (ac) magnetic measurements of the two compounds (Figure 3b and the Supporting Information) show small, but nonzero, frequency dependence of the out-of-phase susceptibility ( $\chi_M''$ ). This indicates that slow relaxation of the magnetization may occur at a lower temperature than 2 K.<sup>10</sup>

In summary, a judicious choice of ligands led to the synthesis of isolated nanoscale  $\text{Co}_{15}$  clusters and their subsequent organization into an extended 3D framework. The hierarchical assembly of nanoscale molecules into MOFs may induce the emergence of novel properties at each level of complexity. Despite the large number of magnetic centers within the cluster and their favorable coupling via single O atoms and/or carboxylic groups, however, the cluster does not behave as a single-molecule magnet. The assembly of eventual single-molecule magnets into networks is currently being investigated in our laboratory.

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**Supporting Information Available:** Details for the synthesis, structure determination, and physical property measurements of the two compounds; additional figures of the structures; IR spectra, PXRD patterns, TGA, and magnetization measurements; and a combined CIF file for the structures of the compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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