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Trading Templates: Supramolecular Transformations between {Co^II_13} and {Co^II_12} Nanoclusters

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The design of polynuclear transition metal clusters remains motivated by the generation of new materials which display interesting magnetic[1−3] or catalytic[4,5] properties or can function as nanoelectronic components[6−8] or metalloenzyme models.[9] One crucial aspect of any approach to functional molecule-based materials is the ability to induce systematic transformations to a given molecular framework or supramolecular architecture, that is, to fine-tune electronic or magnetic properties. While this has been successfully demonstrated in, for example, a wide variety of polyoxometalate-based materials,[10,11] step-by-step variations of high-nuclearity coordination compounds have been limited to few examples.[11] In recent work, we were able to show that a family of isostructural pure and mixed-metal dodecanuclear nickel(II) and cobalt(II) complexes was accessible, providing a route to the systematic variation of magnetic properties, and that these could be accessed by combined stoichiometric and pH control.[12]

Here we report on "nuclearity switching" to a (previously reported)[12] {Co_12}[7+] cation, [Co^II_12(OH)_12(OAc)_9(CO_3)(*trans*-tachH)_6]^[7+] (**1a**; *trans*-tach = *cis,trans*-1,3,5-triaminocyclohexane), from a {Co_13}[4+] cation, [Co^II_13O_3(OH)_12(OAc)_10(*trans*-tachH)_6]^[4+] (**2a**). We also demonstrate that the {Co_13} cluster core, **2a**, is a parental species to **1a** and forms in the absence of "external" ligand templates. Structurally, **2a** represents a replacement of the carbonate dianion in **1a** by a five-coordinate cobalt(II) center, [CoO_3(OAc)]^[5−], which, due to crystallographic disorder, has pseudo-tetrahedral coordination geometry (Figure 1).

The nanoscale {Co_13} cluster, isolated as [Co^II_13O_3(OH)_12(OAc)_10-(*trans*-tachH)_6](OAc)_4·10MeOH·9H_2O (**2** = **2a**·(OAc)_4·10MeOH·9H_2O), is prepared by addition of cobalt(II) acetate tetrahydrate (0.096 g, 0.388 mmol) to a methanolic solution of *trans*-tach (0.050 g, 0.388 mmol) under a nitrogen atmosphere with sufficient addition of dilute aqueous acetic acid to achieve a pH of 7.5. From the resulting deep red solution, diffraction quality crystals are obtained by diffusion of diethyl ether into the mother liquor.

The cluster core of **2a** (Figure 1) comprises three identical {Co^II_4-(OH)_4} cubane units which are symmetrically linked around a Co^II cation via three μ_3-oxo bridges. Although there are many known structures containing cobalt-oxo cubanes, there are few examples in which more than two such units are linked.[13−17] The three cubane subunits in **2a** are arranged such that the cobalt cations on their *inner-face* positions and the three μ_3-oxo ligands to which they are coordinated lie on a plane. With the exception of the central unit, **2a** has mirror symmetry about this plane while the central cobalt cation is disordered above and below it. The coordination sphere of this central unit is completed by an acetate ligand which is symmetrically disordered over three positions. The three cubanes are further linked by three pairs of acetate anions bridging the *inner-face* cobalt cations of adjacent cubane units. An additional acetate
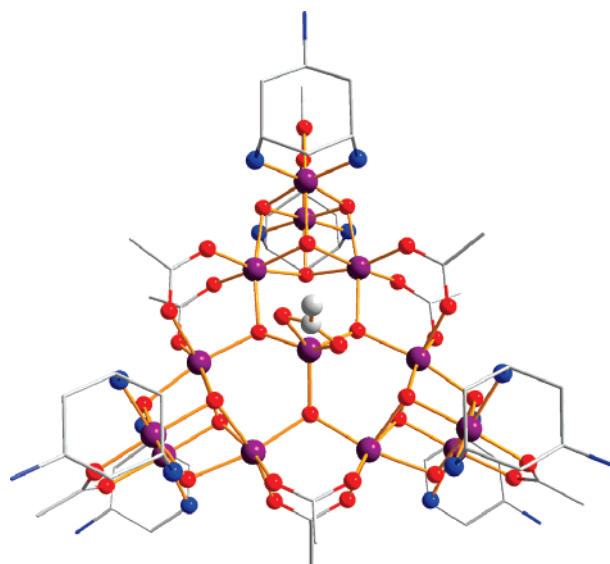
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Figure 1. Ball-and-stick representation of cluster cation **2a**. Cobalt cations: purple, oxygen: red, carbon: gray, nitrogen: blue. Hydrogen atoms are omitted for clarity. Common color scheme used throughout.

anion bridges the two *outer-face* cobalt cations of each cubane, aligned perpendicular to the equatorial plane of **2a**. The octahedral coordination spheres of the six *outer-face* Co^II cations are completed by *trans*-tach ligands binding through the two *cis* amino groups in a bisaxial−monoequatorial conformation with the protonated pendant *trans*-amine groups being oriented away from the center of the cluster. This is the expected conformation for *trans*-tach[12,18−20] and allows the ligand to act as a bischelating moiety while leaving the pendant *trans*-amine available for hydrogen bonding to noncoordinated solvent molecules and counterions.

The acetate bridges in compound **2** are thought to originate from cobalt(II) acetate as the use of dilute perchloric acid in place of acetic acid still leads to crystals of **2** being observed, while the use of different cobalt(II) salts in the presence of acetic acid does not. Furthermore, the pH at which the reaction is carried out is critical in controlling the formation of **2** because at pH > 8.0 there is sufficient carbonate available for the formation of **1** and at pH < 6.8 *trans*-tach becomes doubly protonated and is precipitated as a white solid. The availability of carbonate is known to be the limiting factor in the formation of **1a**, and even at pH 7.5, the addition of a small amount of K_2CO_3 completely prevents crystallization of **2**. Furthermore, crystals of **1** (**1a**·(OAc)_7·12MeOH) can be obtained from a methanolic solution of **2** if a carbonate source is provided. Given these observations, we conducted electrospray mass spectrometric experiments on a solution of **2**, which demonstrate that **2a** (without terminating ligands) is present in solution (Figure 2). Electrospray measurements show that **2a** can be converted into **1a** (Figure 2 A,B) via the addition of K_2CO_3 (Scheme 1). Therefore,
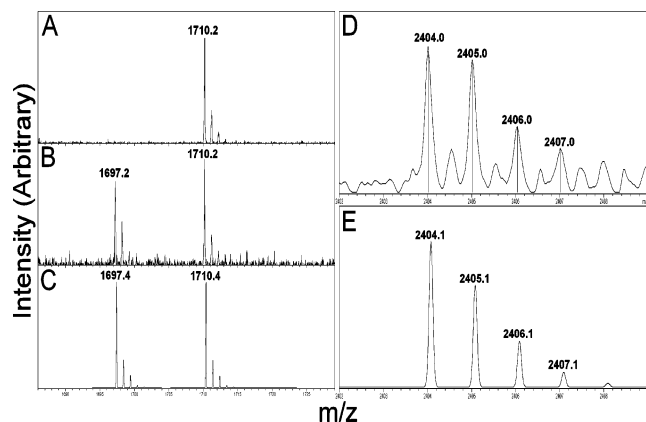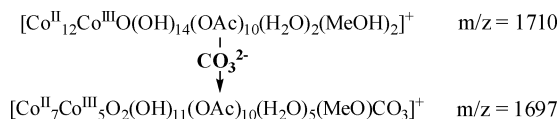
Figure 2. (A) ESI-MS measurement of **2** mother liquor under N_2. (B) Sample after addition of K_2CO_3. (C) Simulated isotopic envelopes for m/z = 1697, $[Co^{II}_7Co^{III}_5O_2(OH)_{11}(CH_3CO_2)_{10}(H_2O)_5(CH_3O)CO_3]^+$, and m/z = 1710, $[Co^{II}_{12}Co^{III}O(OH)_{14}(CH_3CO_2)_{10}(H_2O)_2(CH_3OH)_2]^+$. (D) CSI-MS measurement of **2** mother liquor under N_2. (E) Simulated isotopic envelope for $[Co^{II}_{13}O_5(OH)_{11}(OAc)_{10}(C_6H_{16}N_3)_6]^+$.

Scheme 1. Conversion of {Co_{13}} Species to {Co_{12}} on Addition of K_2CO_3

$$[Co^{II}_{12}Co^{III}O(OH)_{14}(OAc)_{10}(H_2O)_2(MeOH)_2]^+ \qquad m/z = 1710$$

$$CO_3^{2-}$$

$$[Co^{II}_7Co^{III}_5O_2(OH)_{11}(OAc)_{10}(H_2O)_5(MeO)CO_3]^+ \qquad m/z = 1697$$

these studies demonstrate that the {Co_{13}} represents a common unit in the construction of the {Co_{12}} species, and that both species are present without the need for sophisticated terminating ligands. Using the cryospray MS attachment at 233 K allows **2a** to be seen in its entirety, including capping ligands (Figure 2D) and indeed as ligand-capped cubane building block fragments with the formula $[(Co^{II}Co^{III}_3O_4)(OAc)_2(trans\text{-}tach)_2]^+$.

This illustrates how CSI-MS may be used to monitor and devise the correct experimental conditions to exchange the ligands terminating each of the cluster types, which will have a dramatic effect on the observed magnetic properties. While both {Co_{12}} (as previously reported)[12] and {Co_{13}} compounds are characterized by both intramolecular antiferromagnetic and ferromagnetic coupling (see Supporting Information), changing the ligand from *trans*-tach to (1*H*-benzimidazol-2-yl)methanol causes all-ferromagnetic exchange coupling and SMM properties at very low temperatures.[17]

Comparison of **1a** and **2a** reveals that they differ mainly around the central unit where the three μ_3-oxo ligands are further apart in **2a** due to the Co—O (2.04 Å) bond length exceeding the C—O (1.30 Å) bonds of the carbonate anion in **1a**. Since the position of the three cubane units is locked by the acetate bridges, the bonds between the cubanes and the three μ_3-oxo bridges of the central unit are shortened in **2a**. Thus, the two cluster units have nearly the same outer dimensions, despite the large difference in the central unit (Figure 3). Compounds **1** and **2** both crystallize in the same hexagonal symmetry group, with the unit cell containing two cluster units offset in alternating layers. These are arranged such that any three adjacent clusters in one layer describe the vertices of an equilateral triangle. The cluster units do not have any direct interaction with one another but are interconnected in the crystal lattice through hydrogen bonded acetate anions associated with each *trans*-tach moiety arranged around the cluster unit above and below (crystallographic *c*-axis) the pendant *trans*-amino nitrogen atoms of the ligands. The protonated *trans*-amino group takes part in two further hydrogen bonding interactions to the acetate anions of the two adjacent cluster units in the next packing layer. Further
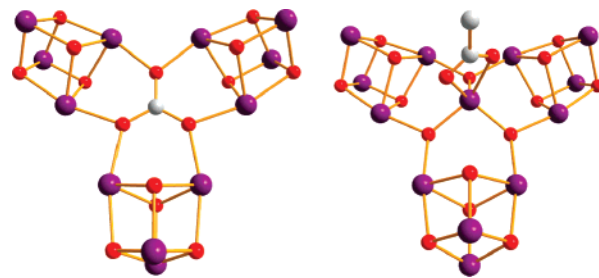

Figure 3. Comparison of cores of **1a** (left) and **2a** (right), capping *trans*-tach ligands omitted for clarity.

interactions with disordered solvent methanol molecules are also observed in the crystal structure.

In conclusion, a tridecanuclear Co^{II} cluster comprising a $[CoO_3(OAc)]^{5-}$ core template surrounded by three symmetrically linked cubane subunits, capped and stabilized by *trans*-tach ligands, has been isolated and identified via mass spectrometry as a parental architecture of a dodecanuclear Co^{II} cluster family. This supramolecular transformation is induced by addition of CO_3^{2-} anions as alternative templates. Future work will build on ligand/template exchange to construct related architectures with radically different physical properties.

Supporting Information Available: Synthesis, magnetic data, and crystallographic file (CIF) for **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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