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# Hydrothermal Synthesis and Structural Characterization of a Coordination Polymer Containing Heptanuclear Co$_7$($\mu_3$-OH)$_8$ Clusters

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## Introduction

Extended frameworks of coordination polymers based on complexes of transition metals and multifunctional bridging ligands are currently of great interest in research.[1] Frequently, mononuclear metal centers linked by multifuntional bridging ligands into various structures were found, which are the compromised results of the metal coordination and the ligand geometry. The structures of the products are also affected by the reaction conditions governing the hydrolysis of the metal salt used in the synthesis. Inorganic moieties such as clusters,[2] chains,[3] or layers[4] may be formed and linked by multidentate organic bridging ligands to form hybrid organic−inorganic structures. In view of the rich source of high nuclearity, the oxo-bridged products in 3-D metal carboxylates,[5] and the potentials in building stable coordination polymers containing chelating ligands,[6] we have carried out hydrothermal (or solvothermal) syntheses in systems containing both monodentate N-donor and chelating O-donor ligands. For the N-donor ligand, we have used the nonaromatic amine ligand, such as piperazine, for the ease of controlling the reaction pH by simply adjusting the ligand ratios. Herein, we reported a novel coordination polymer that contains new heptanuclear hydroxo-bridged Co(II) clusters in the form of corner-fused double cubanes.

## Experimental Section

**Synthesis of Co$_7$($\mu_3$-OH)$_8$(ox)$_3$(ppz)$_3$. 1** was prepared from the reaction mixture of CoSO$_4$·7H$_2$O (1 mmol), piperazine (ppz) (8 mmol), H$_2$C$_2$O$_4$·2H$_2$O (2 mmol), and distilled water (10 mL) in a Teflon-lined acid digestion bomb with an internal volume of 23 mL under autogenous pressure at 180 °C for 3 days. Pure orange crystals of **1** were collected in yield of 22%. Crystals with suitable size for single-crystal X-ray analysis were produced with the same reaction condition, unless 2 mmol of boric acid was added. The X-ray diffraction (XRD) and the elemental analysis indicated the two samples were the same. The XRD patterns of both samples agreed well with that calculated from single-crystal data. Elemental analysis calcd: C, 20.19; H, 3.58; N, 7.85. Found: C, 20.22; H, 3.49; N, 7.81. The infrared spectrums (KBr disk) were recorded on a Nicolet 460 Protégé spectrometer. Main IR bands: 3582 (s), 3224 (s), 2960 (m), 2949 (m), 2922 (m), 2865 (m), 1629 (w), 1459 (m), 1437 (m), 360 (m), 1308 (m), 1247 (m), 1109 (s), 695 (w). Thermogravimetric analysis was carried out in nitrogen at a heating rate of 10 °C/min (Perkin-Elmer Instruments, TGA 7). Magnetic susceptibility was measured under 5000 Oe from 2 to 300 K (SQUID, Quantum Design).

**Table 1.** Crystallographic Data for **1**[a,b]

| | |
|---|---|
| empirical formula | Co$_7$($\mu_3$-OH)$_8$(C$_4$N$_2$H$_{10}$)$_3$(C$_2$O$_4$)$_3$ |
| cryst syst | trigonal |
| $a$, Å | 14.990(1) |
| $c$, Å | 12.835(2) |
| $V$, Å$^3$ | 2497.6(4) |
| $Z$ | 3 |
| fw | 1071.05 |
| space group | $R\bar{3}$ |
| temp, °C | 22 |
| $\lambda$ | 0.71073 |
| $\rho_{calcd}$, g/cm$^{-3}$ | 2.136 |
| $\mu$, cm$^{-1}$ | 34.9 |
| R1 | 0.0499 |
| wR2 | 0.0801 |

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = [\sum w(|F_o|^2 - |F_c|^2)^2/\sum w(|F_o|^2)^2]^{1/2}$, $w = [\sigma^2(F_o{}^2) + 0.0200P]^2 + 16.6041P]$, where $P = (F_o{}^2 + 2F_c{}^2)/3$.

**Single-Crystal X-ray Structure Analysis.** The structure of **1** was determined by single-crystal X-ray methods, and their crystallographic data are summarized in Table 1. A suitable crystal (0.1 × 0.1 × 0.125 mm) was glued on a glass fiber and mounted on a Smart CCD diffractometer using Mo K$\alpha$ radiation. Intensity data were collected for indexing in 1271 frames with increasing $\omega$ (width of 0.3° per frame). Unit cell dimensions were determined by a least-squares fit of 512 reflections. Of the 5403 reflections collected, 1231 unique reflections were considered observed ($I_{obs} > 2\sigma(I)$) after Lp and absorption corrections. The absorption correction was based on symmetry-equivalent reflections using the SADABS programs.[7] On the basis of systematic absences and statistic intensity distribution, the space group was determined to be $R\bar{3}$. Direct methods were used to locate the Co atoms first, and the remaining oxygen, carbon, and nitrogen atoms were found from successive difference maps. All H atoms were located on difference Fourier maps calculated at the final stage of structure refinement. The final cycles of refinement, including the atom coordinates and anisotropic thermal parameters for all non-hydrogen atoms and fixed atomic coordinates and isotropic thermal parameters for the hydrogen atoms, converged at R1 = 0.0499 and wR2 = 0.0801. In the final difference map, the deepest hole was −0.58 e Å$^{-3}$, and the highest peak was 0.57 e Å$^{-3}$. Anomalous and secondary extinction corrections were applied. All calculations were performed using the SHELXTL programs.[8] The crystallographic data are summarized in Table 1.

## Results and Discussion

The selected bond lengths are in Table 2. The basic structural unit in **1** is the heptanuclear hydroxo-bridged Co(II) clusters

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10.1021/ic010164w CCC: $20.00

**Table 2.** Selected Bond Lengths (Å) for **1**

| | | | |
|---|---|---|---|
| Co(1)−O(2) × 6 | 2.073(2) | Co(2)−O(2) | 2.060(2) |
| Co(2)−O(2)[a] | 2.092(2) | Co(2)−O(3) | 2.102(3) |
| Co(2)−O(4) | 2.137(3) | Co(2)−O(1) | 2.138(2) |
| Co(2)−N(1) | 2.148(3) | O(3)−C(1) | 1.251(4) |
| O(4)−C(1)[b] | 1.254(4) | N(1)−C(2) | 1.457(5) |
| N(1)−C(3) | 1.465(5) | C(2)−C(3)[c] | 1.502(6) |
| C(1)−C(1)[b] | 1.568(7) | | |

[a] Symmetry transformations used to generate equivalent atoms: $-x + y, -x, z$. [b] $-x - 1/3, -y + 1/3, -z + 1/3$. [c] $-x - 2/3, -y - 1/3, -z + 2/3$.

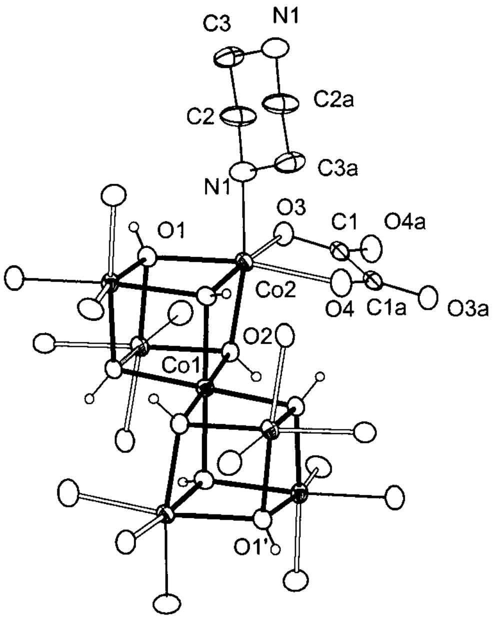

**Figure 1.** Structural unit of **1** showing the hydroxo-bridged heptanuclear clusters (50% thermal ellipsoids).

with the $\bar{3}$-axis on the O(1)−Co(1)−O(1) line (Figure 1). O(1) and O(2) are both coordinated to three cobalt atoms and have bond valence sums[9] of 0.90 and 1.07, respectively. These values suggest that both O(1) and O(2) are hydroxyl groups, and this is consistent with the strong OH stretching found in IR. There are two unique cobalt atoms, both of which are in octahedral centers. Co(1) is coordinated by six oxygens of $\mu_3$-hydroxyl groups and is located on special position 3a. The six symmetry-equivalent Co(2) atoms in the heptanuclear core are arranged in a staggered fashion, three up and three down along the *c*-axis. Co(2) is coordinated by three oxygens from $\mu_3$-hydroxyl groups, two oxygens from $\mu$-oxalate ligands, and one nitrogen from $\mu$-piperazine ligands. The magnetic susceptibility measurements and the bond valence calculations (Co(1), 1.90; Co(2), 2.14) suggested that both cobalt atoms were in the second valence state. The shortest Co···Co separations in the cluster are Co(1)···Co(2) = 3.212 Å and Co(2)···Co(2) = 3.052 Å, which are not short enough for any metal−metal bonding. Each of the six Co(2) atoms in $[Co_7(\mu_3\text{-}OH)_8]^{6+}$ is further bridged by one dianionic bisbidentate $\mu$-oxalate bridging ligand and one bismonodentate $\mu$-piperazine bridging ligand, with two other Co(2) atoms belonging to two different $Co_7(\mu_3\text{-}OH)_8$ clusters to form a neutral 3-D framework (Figure 2). The framework of **1** contains small triangular channels along the *c*-axis, and alternating oxalate and piperazine ligands form the walls of the channels (Figure 2). Consequently, each $Co_7(\mu_3\text{-}OH)_8$ cluster in **1** is linked through six oxalate ligands and six piperazine ligands to 12 other $Co_7(\mu_3\text{-}OH)_8$ clusters. Heptanuclear cobalt complexes containing N-donor and O-donor ligands are rare, and the known examples have a very irregular shape.[10,11] While cobalt−oxygen clusters of single cubane,[12] face-shared triple cubanes,[13] and some other polynuclear cobalt−oxygen compounds have been reported,[14] the cobalt−hydroxyl cluster of corner-shared double cubanes is unprecedented. The hydroxo-bridged heptanuclear metal cluster of the fused double-cubane type is only known for copper.[15] The occurrence of the title compound may result from the suitable pH and size of the combined ligands used in the reaction. The $[Co_7(\mu_3\text{-}OH)_8]^{6+}$ core in **1** can be considered as being built up from connecting two $[Co_3(OH)_4]$ units and one Co cation. The $[Co_3O_4]$ core, the partial cubane, has been found in many molecular compounds with different ligands in which hydrogen bonding contributes significantly to stabilize the trinuclear structure.[16] The $[Co_3(OH)_4]$ core is also a basic building unit in $Co(OH)_2$, which has the $CdI_2$ structure. Interestingly, while several reported polynuclear cobalt−oxygen compounds[17] and one coordination solid[18] can be viewed as containing a fragment of the $Co(OH)_2$ layer, the cobalt arrangement of the heptanuclear cluster found in **1** is similar to the smallest unit of the extended octahedra in the spinel structure.

Thermogravimetric analysis of **1** performed under $N_2$ shows the first weight loss of 53.0% from 300 to 400 °C. This corresponds to the loss of all the ligands in **1**, which forms

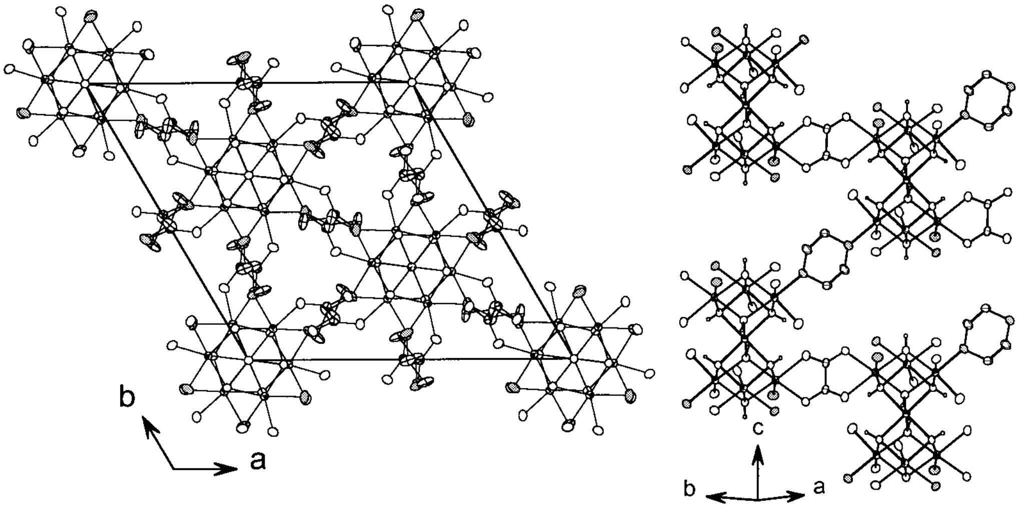

**Figure 2.** (a) Projection view of **1** along the *c*-axis showing the small triangular channel. (b) View of linkages between the heptanuclear clusters; part of the bridging ligands are omitted for clarity.

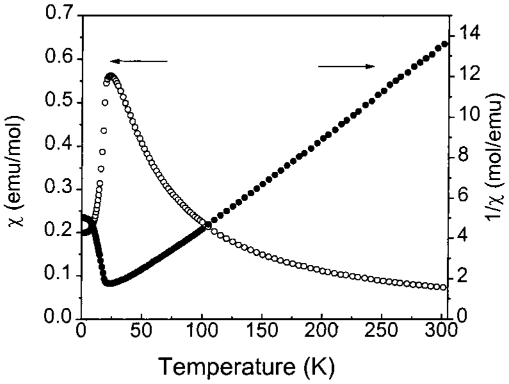

**Figure 3.** Variable-temperature magnetic susceptibility for **1**.

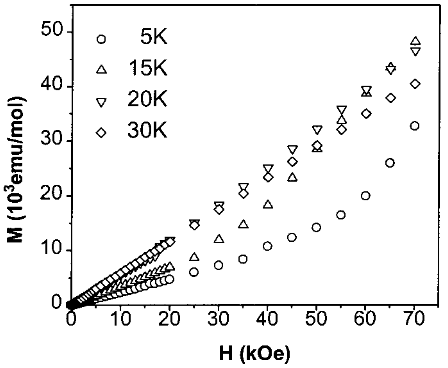

**Figure 4.** Field dependence of magnetization at 5, 15, 20, and 30 K for **1**.

$Co_3O_4$ (theoretical, 52.5%). The variable-temperature magnetic susceptibility was measured from 2 to 300 K (Figure 3). The linear behavior of $1/\chi(T)$ above 50 K obeys well the Curie–Weiss equation ($C = 22.0$ emu K per formula, $\theta = -2.76$ K). The effective magnetic moment per metal atom calculated from the Curie constant, 5.02 $\mu_B$, is in the range of experimentally observed values for high spin Co(II) ions. The $\chi-T$ curve appears to be an antiferromagnet with $T_N$ at about 26 K. The small Weiss constant is not consistent with the medium value of $T_N$ of 26 K. This indicates that some ferromagnetic contribution may exist that drives the Weiss constant to the positive side. Consequently, a small Weiss constant was observed. The field dependence of magnetization was measured at 5, 15, 20, and 30 K (Figure 4). At 30 K, the M(H) behavior is paramagnetic. At 5 K (less prominent at 15 and 20 K), the M(H) slope increased at high field is characteristic of metamagnetism. This is consistent with assuming that the title compound has both the ferrimagnetic interaction within the clustesr and the antiferromagnetic interaction between the clusters (via oxalate anions).

The work has demonstrated that proper selection of mixed monodentate N-donor ligands and chelating O-donor ligands in the hydrothermal reaction may be used to prepare coordination polymers based on new types of polynuclear clusters.

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**Supporting Information Available:** X-ray crystallographic file of $Co_7(\mu_3\text{-}OH)_8(C_4N_2H_{10})_3(C_2O_4)_3$ in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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