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Polynuclear Cobalt(II/III) Sulfites: Synthesis, Structure, and Magnetic Properties of the Octanuclear Cluster $(NH_4)_{11}(Li\subset[Co_4^{II}Co_4^{III}(SO_3)_{16}(NH_3)_8])\cdot 10H_2O$ Encapsulating a Lithium Cation

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Partial oxidation of an aqueous solution of $Co^{II}Cl_2\cdot 6H_2O$ with $(NH_4)_6[Mo_7^{VI}O_{24}]\cdot 4H_2O$ in the presence of $(NH_4)_2SO_3\cdot H_2O$ and LiCl, at pH $\approx$ 5.3, leads to isolation of the octanuclear cluster $(NH_4)_{11}(Li\subset[Co_4^{II}Co_4^{III}(SO_3)_{16}(NH_3)_8]\cdot 10H_2O)$, **1**. The structure of the anion of **1** consists of a central $[Co_4^{II}]$, almost ideal square planar unit, and a pair of symmetry-related Co^{III} dimers above and below the Co_4^{II} plane grafting onto the tetramer by 16 bridging sulfite groups. The $[Co_8(SO_3)_{16}(NH_3)_8]^{12-}$ cluster encapsulates a lithium cation which lies at the center of the Co_4^{II} square.

The interest in transition metal−sulfite chemistry has been steadily increasing over the past few years, as it has become apparent that this area represents a rich source of high-nuclearity clusters with interesting structural and physicochemical properties.[1,2] In addition, very recently, a few open-framework metal−sulfites appeared in the literature.[3] Thus far, to the best of our knowledge, only mononuclear cobalt(III) mono-[4] or *cis*-di[5]-sulfite species have been prepared and structurally characterized. In these cobalt(III) compounds, the sulfite group is always S-bonded to the cobalt(III) center, in marked contrast to the predictions of Pearson's HSAB principles.[6] The only polynuclear cobalt−sulfite species structurally characterized is the trinuclear mixed-valence compound $[Co^{II}Co_2^{III}(\mu_2\text{-}SO_3)_2L_2(ROH)_2]$.[7] In this case, the ligation of the sulfite group to the cobalt centers in a μ_2-η^1:η^1-O,S coordination mode is supported by a tetradentate Schiff-base ligand L^{2-}. Here, we report the synthesis and structural and physicochemical characterization of the octanuclear mixed-valence $4Co^{II},4Co^{III}-SO_3^{2-}$ cluster, $(NH_4)_{11}(Li\subset[Co_4^{II}Co_4^{III}(SO_3)_{16}(NH_3)_8]\cdot 10H_2O)$, **1**.

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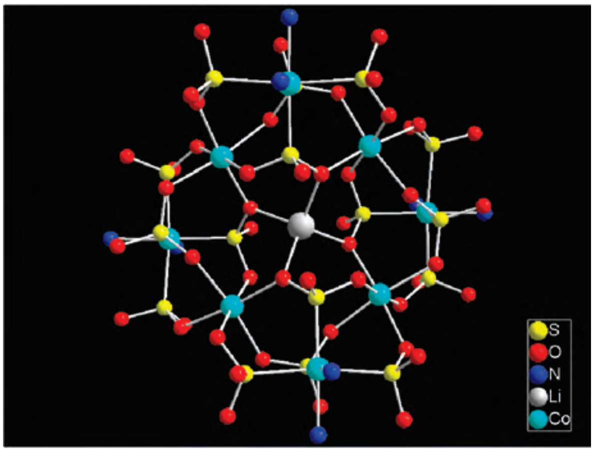

Figure 1. Ball-and-stick representation of the anion of **1**.

Compound **1**was prepared by treating $Co^{II}Cl_2 \cdot 6H_2O$ (2.1 mmol) and $(NH_4)_6[Mo_7{}^{VI}O_{24}] \cdot 4H_2O$ (0.28 mmol) in concentrated (37%) HCl/H_2O (25 mL, 1:4 v/v, pH approximately 0) with solid $(NH_4)_2SO_3 \cdot H_2O$. Upon the addition of $(NH_4)_2SO_3 \cdot H_2O$ (98 mmol), the pH of the solution changed to 5.3, and its color turned from pink to dark, brick-red. Then, solid LiCl (24 mmol) was added to the solution, and red crystals of **1**[8] were obtained by the slow vapor diffusion of methanol (yield 40%, based on cobalt). When NaCl is substituted for LiCl, red crystals of compound **2** are formed. Unfortunately, the quality of the crystals of compound **2** was too poor to allow the X-ray crystal structure to be solved. On the basis of elemental analysis and IR and UV−vis spectroscopies, we believe that compound **2** has a similar composition to that of compound **1**. The presence of the templating lithium or sodium cation is of vital importance to get compounds **1** and **2**. If KCl, RbCl, or CsCl was substituted for LiCl or NaCl, a red amorphous precipitate was formed. At this point, it is worth mentioning that the sulfite anion does not reduce molybdenum(VI) to molybdenum(V)[1f] in the system $Mo^{VI}-SO_3{}^{2-}$. When the reaction for the synthesis of **1** was conducted under an argon atmosphere, compound **1** was also isolated, which means that Mo^{VI} oxidizes Co^{II} to Co^{III}.

As shown in Figure 1, the anion of **1** is an octanuclear mixed-valence $Co_4{}^{II}Co_4{}^{III}$ cluster supported by bridging sulfite groups. In the $[Co_8(SO_3)_{16}(NH_3)_8]^{12-}$ cluster, four cobalt(II) nuclei form an almost ideal square-planar arrangement and a pair of symmetry-related Co^{III} dimers lie above and below the $Co_4{}^{II}$ plane grafting onto the tetramer by the 16 bridging sulfite groups. The $[Co_8(SO_3)_{16}(NH_3)_8]^{12-}$ cluster encapsulates a lithium cation which lies at the center of the $Co^{II}{}_4$ square. The configuration of this octanuclear cluster[9] is significantly different from those in the other reported octanuclear cobalt clusters which display a cage, a ring, a planar triangular tetramer with two pairs of symmetry-related cobalt atoms, or irregular arrangements or consist of Co_4O_4 cubane fragments.[10] In addition, the $[Co_8(SO_3)_{16}(NH_3)_8]^{12-}$ aggregate is supported by only inorganic ligands, and this is in marked contrast to the octanuclear clusters reported thus far, which are supported by organic ligands. The four Co(II) ions and four sulfite ligands construct a metallamacrocyle.[11] The cobalt(III) atoms possess a severely distorted (CoN_2S_4) octahedral coordination and are ligated to four sulfite (two μ_2-(S,O), one μ_3-(S,O,O), and a μ_4- η^1:η^1:η^2-(S,O,O)) sulfur atoms, as well as two *cis*-ammonia nitrogen atoms. In the equatorial plane, there are two *cis*-sulfur atoms and two *cis*-nitrogen atoms, while in the axial positions, there are two sulfur atoms. The two equatorial Co−S distances were found to be similar [2.1841(9) and 2.2026(10) Å], and they appeared to exercise a considerable trans influence on the opposing Co−N distances [1.996(3) and 1.993(3) Å], which were found to be significantly longer than the average Co−N distances [$\approx$ 1.96 Å] in $Co^{III}-NH_3$ or amine compounds.[5,12] The two axial Co−S distances were also found to be similar [2.2954(10) and 2.3050(10) Å] but substantially longer than the other two *cis*-Co−S distances, presumably due to a mutual trans influence. The Co(III)···Co(III) distances were found to be 8.7774(7) Å. The four cobalt(II) centers are six-coordinate (six oxygen atoms from sulfite ligands) in a configuration that closely approximates octahedral. The Co−O distances are very similar with a mean value of 2.074(3) Å, and the average *cis*-[O−Co−O] and *trans*-[O−Co−O] angles have the values 90.06(11)° and 173.97(11)°, respectively. The lithium atom possesses a tetrahedral geometry and is surrounded by four sulfite oxygen atoms with mean d(Li−O) and [O−Li−O] values 2.058(3) Å and 109.54(9)°, respectively. Neighboring ($Li\subset[Co_8(SO_3)_{16}(NH_3)_8]$)$^{11-}$ clusters are linked together with strong hydrogen bonds between the hydrogen atoms of the ammonium cations and of the sulfite oxygen atoms of each cluster to form a

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(8) Anal. calcd. (%) for $Co_8H_{88}LiN_{19}O_{58}S_{16}$: N, 11.70; H, 3.90; S, 22.56; Co, 20.74. Found: N, 11.52; H, 3.58; S, 21.55; Co, 19.94. IR (KBr, cm^{-1}): 3424s, 3167s, 3029s, 2831sh, 1640m, 1402s, 1295w, 1275w, 1145sh, 1120s, 1075w, 1038w, 1007s, 947s, 647s, 555w, 512w. The thermal decomposition of compound **1** occurs in five consecutive steps in the temperature range 25−820 °C. The total weight loss (obsd = 72.68%, calcd = 71.57%) corresponds to the removal of 11 water (10 crystalline and one water molecule from dehydroxylation), 19 ammonia, and 16 sulfur dioxide molecules.

(9) Crystal data for **1**: $Co_8H_{88}LiN_{19}O_{58}S_{16}$, $M_r = 2274.24$, tetragonal, $I4_1/a$, $a = b = 22.4965(9)$ Å, $c = 17.3793(7)$ Å, $V = 8801.1(6)$ Å^3, $Z = 8$, $\rho = 1.785$ g cm^{-3}, $\mu = 1.964$ mm^{-1}, $F(000) = 4647$, GOF = 1.102. A total of 79 019 reflections were collected and 8989 are unique ($R_{int} = 0.0274$). R1/wR2 = 0.0490/0.1464 for 8989 reflections [$I > 2\sigma(I)$] and 263 parameters.

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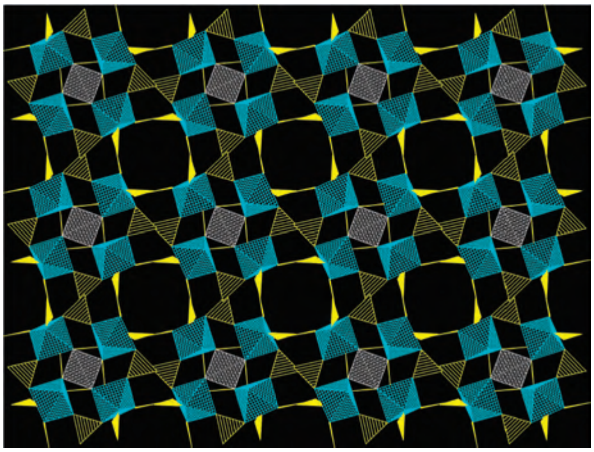

Figure 2. The polyhedral representation of the crystal structure of **1** as seen along the *c* direction.

three-dimensional structure[13] with one-dimensional channels along the *c* axis (Figure 2).

The four Co(II) centers in their octahedral CoO_6 environments represent d^7 high-spin ($^4T_{1g}$, $S = 3/2$) centers that exhibit significant spin–orbit coupling. On the basis of the structure of **1**, the only unpaired electrons will be on the Co^{II} centers, since the Co^{III} ions are low-spin ($t_{2g}{}^6$, $S = 0$). Thus, from the magnetic viewpoint, compound **1** is effectively tetranuclear. Solid-state dc magnetic susceptibility measurements were performed for **1** in the range 2–290 K under a field of 0.1 T. χT decreases from 11.4 emu K mol^{-1} at 290 K to 4.9 emu K mol^{-1} at 2.0 K. Field-dependent magnetization measurements at 2.0 K show the system approaching saturation at 5.0 T, reaching $m/(g\mu_B) = 7.9$. The χT versus T behavior shown in Figure 3 may be interpreted as reflecting zero-field splitting of the quartet ground state[14] and intramolecular antiferromagnetic exchange interactions between the four Co^{II} centers mediated by the sulfite ligands.

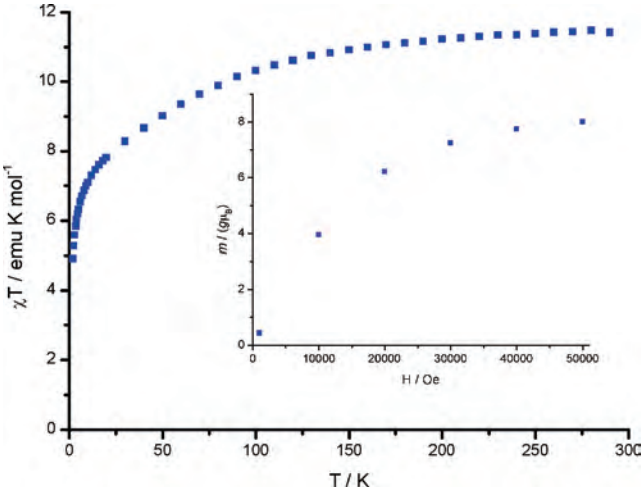

Figure 3. Temperature dependence of χT for **1** at 0.1 T (blue squares). Inset: Field dependence of the magnetization at 2.0 K.

In summary, the first inorganic octanuclear cobalt cluster with a Co_8 configuration has been synthesized and structurally and physicochemically characterized. The isolation of **1** demonstrates that supramolecular assembly of the Co_8 core (and possibly of other polynuclear architectures) may occur even in the absence of organic ligands. The use of the sulfite anion, which is a flexible inorganic ligand with a large number of coordination modes, some of which are unique among oxy anions, might lead to isolation of the clusters or open-framework architectures with new structural features and novel properties that are absent in the more rigid frameworks constructed by metal ions and organic ligands.

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Supporting Information Available: A CIF file giving data for the title compound. This material is available free of charge via the Internet at http://pubs.acs.org.

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