194 *Inorg. Chem.* **1999,** *38,* 194−196

An Extended Solid from the Solvothermal Decomposition of Co(Acac)$_3$: Structure and Characterization of $Co_5(OH)_2(O_2CCH_3)_8{\cdot}2H_2O$

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Received March 12, 1998

Introduction

In the course of investigating solvothermal routes for conversion of molecular precursors to oxide materials, we have observed many interesting extended structures of intermediates. For example, solvothermal treatment of Fe(acac)$_3$ forms crystals of $Fe(O_2CCH_3)_2$, $Fe_5(O_2CCH_3)_{10}{\cdot}2H_2O$, and $Fe_3O(O_2CCH_3)_4$.[1] In all cases, these intermediate phases contain only Fe(II) centers, even though the starting molecule is an Fe(III) complex. A key factor in this chemistry is the ability of the solvothermal fluid to attain an intermediate temperature whereby the products can form and crystallize before they completely decompose to simple binary metal oxides. This method is quite versatile in that the nature and temperature of the solvothermal fluid can be varied over a wide range. This partial decomposition of metal complexes is a very promising route to new extended solids. Keeping in mind that Co^{3+} is less easily reduced than Fe^{3+}, we extended our studies to the solvothermal decomposition of Co(acac)$_3$. The product of this methodology is reported.

Experimental Section

Cobalt(III) acetylacetonate was used as received from Strem. Thermogravimetric data were obtained on a DuPont instruments model 951 analyzer using a Pt foil container, nitrogen purge, and a temperature ramp of 10 °C/min. Powder X-ray diffraction was performed on a Scintag XDS 2000 $\theta-\theta$ diffractometer with Cu Kα radiation ($\lambda = 1.5406$ Å). The infrared spectrum of a single crystal of **1** was recorded on a Nicolet Magna-IR 550 Spectrometer using a SpectraTech Microscope attachment. Magnetic susceptibility measurements were taken with a Quantum Design SQUID MPMS-5S magnetometer at 1 T from 4.99 to 300 K. Measured susceptibility data were corrected for the contribution of the sample holder. Elemental analysis was performed by Atlantic Microlabs.

Synthesis of $Co_5(OH)_2(O_2CCH_3)_8{\cdot}2H_2O$ (1). Pyrex tubes were each loaded with Co(acac)$_3$ (0.20 g, 0.56 mmol), H_2O (80 μL, 4.4 mmol), and tetrahydrofuran (THF, 2.0 mL). After subjection to two freeze−pump−thaw cycles on a vacuum line, the tubes were sealed at a length of 12 cm and internal volume of 5.8 mL. The tubes were then placed inside an autoclave and 2300 psi of Ar was introduced as counterpressure to prevent bursting during the reaction. After being heated at 255 °C for 5 days, the light tan crystalline product was filtered and washed with petroleum ether under a stream of argon (yield: 0.095 mmol, 85% based on Co). The identity of the bulk sample was confirmed by matching the powder diffraction pattern to that calculated from the single-crystal structure (vide infra). Since the compound decomposes in air over several days to an XRD amorphous pink powder, it was stored in an argon atmosphere drybox. The infrared spectrum consists of a series of very broad bands from 3700 to 2700 and 1600−600 cm^{-1}. Anal. Calcd: C, 22.96; H, 3.61. Found: C, 23.01; H, 3.36.

Table 1. X-ray Crystallographic Data[a,b]

empirical formula	$C_{16}H_{30}Co_5O_{20}$
fw	837.07
space group (No.), *Z*	$I4_1/a$ (No.88), 8
a, Å	23.693(2)
c, Å	11.565(5)
V, Å^3	6492(3)
calcd density, g/cm^3	1.713
μ, mm^{-1}	2.576
R,[c] wR[d]	0.0596, 0.0684

[a] All data were collected at 293 K, Mo Kα radiation, $\lambda = 0.710\,73$ Å. [b] Three standards were measured. One decayed by 9%, one by 4%, and the other <1%. [c] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [d] $wR = [\sum w\{|F_o| - |F_c|\}^2/\sum|F_o|^2]^{1/2}$; $w = 1/[\sigma^2 F + 0.0005F^2]$.

Crystallography. Single-crystal X-ray data were collected on a Nicolet R3m/V four-circle diffractometer equipped with graphite monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å). A crystal of dimensions 0.60 × 0.22 × 0.10 mm^3 was isolated under Nujol, and mounted with epoxy inside a glass capillary. The reported unit cell parameters and body-centered lattice were determined from 48 centered reflections ($28 < 2\theta < 48°$). Data were collected using an $\omega/2\theta$ scan mode with a variable scan speed of 1−15°/min, and subsequently corrected for Lorentz and polarization effects. An absorption correction was applied based on psi scan data of six averaged reflections. The space group, $I4_1/a$ (No. 88), was uniquely determined by systematic absences in the complete intensity data set. The structure was solved in origin choice 2 by direct methods, and refined on $|F|$ by full-matrix least-squares techniques using SHELXTL-Plus software.[2] Cobalt atoms were located in initial *E* maps. The remainder of the non-hydrogen atoms were obtained from subsequent difference Fourier maps and thermally refined anisotropically (except for C1). The thermal parameters for C1 were nonpositive when attempts were made to refine them anisotropically and thus were held isotropic. The hydroxyl hydrogen (H1) was placed 0.85 Å from O1, assuming idealized geometry around O1. Methyl hydrogen atoms were introduced in idealized positions and refined isotropically with a group thermal parameter. They were held 0.96 Å from their respective carbon atoms using a riding model. Although the thermal parameters for the O10 solvent molecule are rather large, this may be expected for a moiety in such a loosely bound environment. Additionally, the two hydrogen atoms on the water were not located, which artificially contributes to the thermal motion of O10. If the occupancy of O10 is refined, the site occupancy factor obtained is 0.84 (1.68 H_2O/formula unit) and the average thermal of O10 is 46% smaller, but the *R* factor only drops to 0.0594. Because of the inherent uncertainty in simultaneously refining occupancy and thermal parameters, the refinement reported assumes full occupancy of the water of crystallization. A summary of the crystallographic details is given in Table 1.

Results and Discussion

Solvothermal treatment of Co(acac)$_3$ in a THF solution containing 4 vol % H_2O gives $Co_5(OH)_2(O_2CCH_3)_8{\cdot}2H_2O$ (**1**) in high yield. This methodology leads to reduction of the metal center with oxidative hydrolytic cleavage of the acac ligand. Crystals of **1** grow from a common point, giving the appearance of a flower. Each “petal” is a single crystal having one dimension (presumably along *c*) much longer than the other two. The structure of **1** can be understood as a three-dimensional grid of hexacoordinated Co atoms. To emphasize the Co−O framework, the two views in Figure 1 have been drawn as CoO_6 polyhedra, with all C and H atoms omitted. When this tetragonal structure is viewed along the unique axis (Figure 1a), one sees

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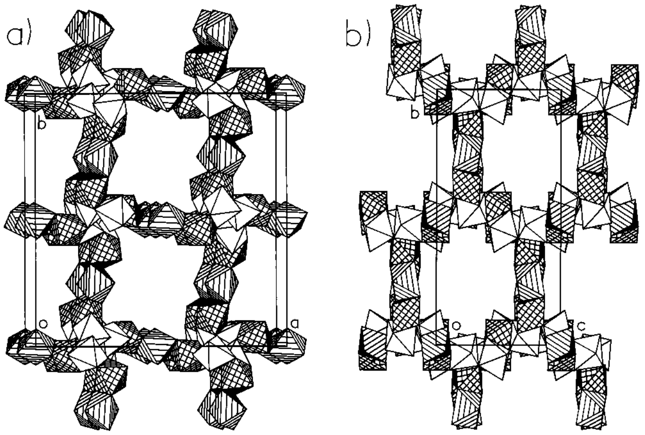

Figure 1. The Co−O framework of **1**, viewed (a) along the *c* axis and (b) along the *a* axis. Cobalt atoms are at the centers of the polyhedra, and O atoms at the vertexes. Co1 polyhedra are open, Co2 polyhedra are lined, and Co3 polyhedra are crosshatched while carbon and hydrogen atoms are omitted.

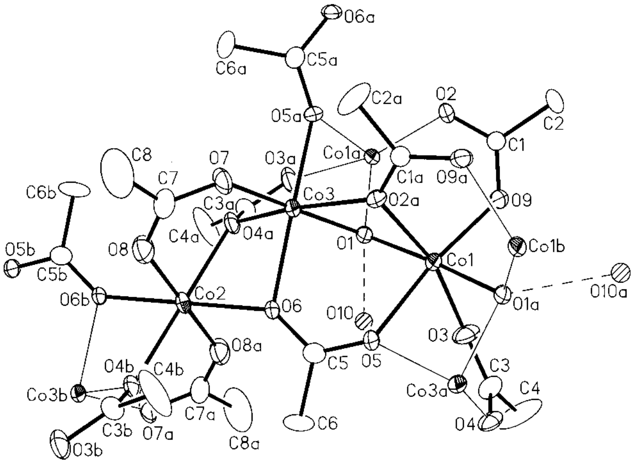

Figure 2. Chain of Co centered octahedra with full complement of acetate ligands found in **1**. Thin lines are drawn to symmetry equivalent cobalt atoms for which the complete coordination environment is not given. Dashed lines indicate hydroxide−water hydrogen bonds. Cobalt atoms are full thermal ellipsoids, oxygen atoms are principal ellipsoids, carbon atoms are boundary ellipsoids (all at the 50% probability level), and oxygen atoms of water are lined spheres. Hydrogen atoms omitted for clarity.

rows and columns of octahedra, forming a square grid. However, when viewed along the *a* axis (Figure 1b), a nearly hexagonal motif is apparent. The Co1 centers (no shading of polyhedra) are at the corners of the squares (Figure 1a), and lie near centers of roto-inversion. The Co2 atoms (parallel lined polyhedra) lie on inversion centers while the Co3 atoms (crosshatched polyhedra) link between the other two Co centers through shared edges of the CoO_6 building blocks. A series of 4_1 screw axes run along the centers of the large channels between polyhedra. It should be emphasized that although there appear to be large channels in the structure as drawn, these gaps are actually filled by methyl groups from the acetate ligands.

Figure 2 shows a portion of **1**, illustrating the details of the bonding. All Co atoms are six coordinate, with Co−O_{Ac} bond lengths ranging from 2.033(8) to 2.211(6) Å (average = 2.13 ± 0.06 Å), and Co−OH bond lengths of 2.008(7), 2.018(7), and 2.042(6) Å (average = 2.02 ± 0.02 Å). The Co−μ_3-OH bond distances observed in **1** are about 0.1 Å shorter than those reported by Coucouvanis et al. in $[(py)_5Co_3(\mu_3\text{-}OH)(OAc)_3(cat)]$,[3] however, both have comparable Co−O_{Ac} bond distances. In contrast, many other Co−O_{Ac} distances reported are up to 0.25 Å shorter.[4] Three acetate ligands are η^1,η^2 coordinated, while the fourth (O5,O6,C5,C6) is η^2,η^2, which is a rare coordination mode.[5] Trans bond angles around Co centers range from 165.8(3) to 180.0(1)°, and cis angles vary from 77.8(3) to 101.8(2)°. The shortest Co···Co separations in the structure are in the three edge-shared bioctahedra (Co1a···Co3a (3.079 Å), Co1···Co3 (3.150 Å), and Co2···Co3 (3.170 Å)). Co1 and Co1a share only one vertex (O1) and are separated by 3.496 Å. None of these distances is sufficiently short to imply any metal−metal bonding. All bond distances within the acetate ligands are typical. Selected distances and angles are given in Table 2.

Table 2. Selected Bond Distances (Å) and Angles (deg)

Co1−O1	2.008 (6)	Co1−O1a	2.018 (7)
Co1−O2a	2.162 (6)	Co1−O3	2.143 (6)
Co1−O5	2.211 (6)	Co1−O9	2.066 (7)
Co2−O4a	2.163 (7) × 2	Co2−O6	2.161 (6) × 2
Co2−O8	2.033 (8) × 2	Co3−O1	2.041 (6)
Co3−O2a	2.156 (7)	Co3−O4a	2.123 (7)
Co3−O5a	2.164 (6)	Co3−O6	2.164 (6)
Co3−O7	2.016 (7)		

O1−Co1−O1a	174.4(3)	O1−Co1−O2a	78.4(3)
O1−Co1−O3	95.4(3)	O1−Co1−O5	91.0(2)
O1−Co1−O9	95.2(3)	O1a−Co1−O3	87.2(3)
O1a−Co1−O5	84.3(2)	O1a−Co1−O9	89.6(3)
O1a−Co1−O2a	98.0(3)	O2a−Co1−O3	165.8(3)
O2a−Co1−O5	83.2(2)	O2a−Co1−O9	101.8(2)
O3−Co1−O5	84.2(3)	O3−Co1−O9	91.3(3)
O5−Co1−O9	172.7(2)	O4−Co2−O4a	180.0(1)
O4−Co2−O6	79.2(2) × 2	O4−Co2−O6a	100.8(2) × 2
O4−Co2−O8	88.6(3) × 2	O4a−Co2−O8	91.4(3) × 2
O6−Co2−O6a	180.0(1)	O6−Co2−O8	90.2(3) × 2
O6a−Co2−O8	89.8(3) × 2	O8−Co2−O8a	180.0(1)
O1−Co3−O2	77.8(3)	O1−Co3−O4	89.3(3)
O1−Co3−O5	85.0(2)	O1−Co3−O6	87.5(2)
O1−Co3−O7	174.1(3)	O2−Co3−O4	167.1(3)
O2−Co3−O5	87.4(2)	O2−Co3−O6	99.3(2)
O2−Co3−O7	96.5(3)	O4−Co3−O5	91.4(3)
O4−Co3−O6	80.0(3)	O4−Co3−O7	96.4(3)
O5−Co3−O6	168.6(3)	O5−Co3−O7	96.3(3)
O6−Co3−O7	92.1(3)	Co1−O1−Co1a	120.5(3)
Co1−O1−Co3	102.1(3)	Co1a−O1−Co3	98.6(2)
Co1−O2a−Co3	93.7(3)	Co2−O4a−Co3	95.4(3)
Co1−O5−Co3a	89.4(2)	Co2−O6−Co3	94.3(3)

The hydroxyl ligand (O1, H1) bridges Co1, Co1a, and Co3. We assign this ligand as μ_3-OH rather than μ_3-oxo since H1 is within hydrogen bonding distance to O10 of a nearby water molecule (2.89 Å), and results in a charge-balanced compound, and has a bond valence sum of 1.24(2) (excluding the hydrogen) while the calculated valence sums for O2 to O9 range from 1.74(5) to 2.01(6).[6] The hydroxide formulation is also consistent with TGA behavior (see below) and the appearance of broad O−H stretches in the IR which suggest more than just stretches due to water molecules. We assign O10 to be a water molecule hydrogen bonded to H1. The hydrogen atoms of the water molecule were not located. Two oxygen atoms of acetate ligands are also close enough for hydrogen bonding (O10···O9 at 2.998

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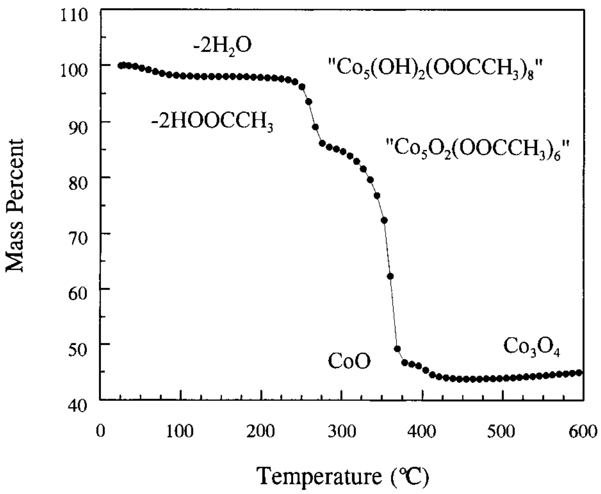

Figure 3. Thermogravimetric analysis of **1**.

Å and O10···O3 at 3.076 Å),[7] but placing water molecule hydrogen atoms along these vectors leads to unreasonable geometries.

Thermal Analysis. Three distinct mass loss regions are seen in TGA of the title compound (Figure 3). The first mass loss (at 85 °C) corresponds to loss of H_2O. It is somewhat surprising that this occurs below the boiling point of water. We attribute this facile loss to the low degree of hydrogen bonding holding the water in the crystal lattice. The observed mass loss of 1.7(2)% corresponds to 0.8(2) equiv of H_2O per formula unit. Full occupancy of the sites would give 2 equiv of H_2O per formula unit. Most likely, water is irreversibly diffusing out of the structure, and thus the water content could be highly variable. The next mass loss (260 °C) corresponds to loss of 2 equiv of acetic acid. The two mobile protons of the hydroxide ligands presumably transfer to acetates, liberating two $HOOCCH_3$ molecules (loss calculated = 14, observed = 11(3)). At this stage, an intermediate of nominal composition "$Co_5O_2(OOCCH_3)_6$" should be present. The final steps (350 and 410 °C) are decomposition of the remaining acetate ligands, giving Co_3O_4 and CoO as the final products observed by XRD. The minimum observed weight percent of 44% (at ca. 440 °C) approximates that expected for CoO (46 wt %). We attribute the slight mass increase at the highest temperatures to conversion of CoO to Co_3O_4 via adventitious O_2.

Magnetic Measurements. The compound shows simple Curie–Weiss paramagnetic behavior from 30 to 300 K (Figure 4). The best linear fit yields $C = 16.3$, and $\theta = -20.4$. This Curie value yields a spin-only μ_{eff} of 5.11 μ_B per mole of cobalt,

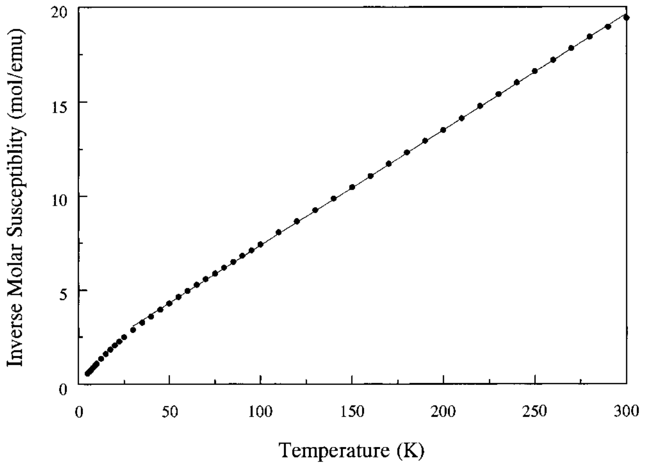

Figure 4. Inverse molar susceptibility as a function of temperature. Line is best fit of data (solid dots).

which is typical of high-spin Co(II) centers (4.7–5.2 μ_B).[8] This is also in agreement with bond valence calculations which give Co1 = 2.05(3), Co2 = 1.94(3), and Co3 = 1.98(4).[6] At 30 K the compound appears to undergo a weak ferromagnetic transition.

Conclusions

In the course of examining conversions of molecular precursors to oxide materials by solvothermal methods, we have found interesting structures of intermediate compounds. Thermal hydrolysis of $Co(acac)_3$ leads to reduction of the metal centers to form the title phase in high yield. The reduction of the metal center is accompanied by the oxidative hydrolytic cleavage of the acac ligand. This is similar to the behavior observed for $Fe(acac)_3$ in solvothermal fluids.[1] The water molecules of the title compound are loosely held in the structure by minimal hydrogen bonding, and are easily lost below 100 °C. The facile loss of acetic acid suggests that the ligand combination of hydroxide and acetate is especially effective in oxide precursor materials.

Acknowledgment. Financial support for this research was provided by the National Science Foundation (Grant CHE-9102548). We wish to thank Thomas P. Thrash of the Department of Chemistry at Rice University for collecting the magnetic susceptibility data.

Supporting Information Available: Listings of complete crystallographic details, all atomic positions with isotropic and anisotropic thermal parameters, complete geometrical parameters, bond valence sums and a full thermal ellipsoid plot (7 pages). Ordering information is given on any current masthead page.

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