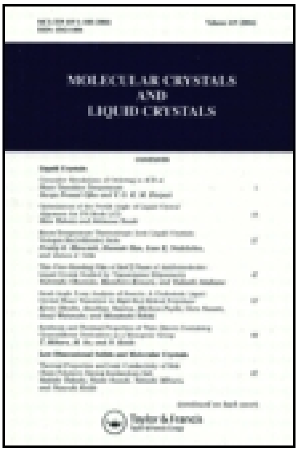

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Hydrothermal Synthesis and Characterization of a Two-Dimensional Cobalt (II) Complex Containing Cinnamate Anion

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Hydrothermal Synthesis and Characterization of a Two-Dimensional Cobalt (II) Complex Containing Cinnamate Anion

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Synthesis, structure and magnetic properties of the hydrothermal reaction product of cobalt (II) ion and the mono-carboxylic acid, *trans*-cinnamic acid, (cina) are described. The 2-D coordination polymer, $[Co(cina)_2(H_2O)_2]n$, consists of square-grid layers with O-C-O bridging the cobalt atoms sandwich by $–CHCHC_6H_5$ in the galleries· The temperature dependence of the magnetic moment revealed a lowering at low temperatures due to the presence of spin orbit coupling.

Keywords: cobalt; cinnamic acid; hydrothermal; layered

INTRODUCTION

Organic-inorganic layered materials are of great current interest due to their intriguing structural diversity and potential functions as catalytic, selective polymerization support, optical and magnetic materials. In these materials, the organic molecules can exhibit selective and reversible reactions, while the inorganic layers including transition metals provide the electronic and magnetic properties[1,2]. Construction of such coordination frameworks makes use of supramolecular chemistry and crystal engineering. The carboxylate ligands have been well documented and are well known as versatile anions which can coordinate metal ions in mono- or tri-atomic (including *syn-syn*, *syn-anti* and *anti-anti* bi-dentate) modes. Although a series of polymeric complexes containing the carboxylate ligands has been reported, uncharacterized polymers were often obtained in conventional solution reaction[3]. Considering the advantage of hydrothermal synthesis[4], we recently began work on the construction of extended framework. Here, we describe the hydrothermal synthesis and characterization of a new 2-D coordination polymer, $[Co(cina)_2(H_2O)_2]_n$, with the mono-carboxylate ligand, *trans*-cinnamate (cina).

EXPERIMENTAL

Magnetic Susceptibility and Infrared Measurements

Magnetic susceptibilities were measured between 2 to 300 K on a Quantum Design MPMS5S SQUID magnetometer. A crystalline sample of the complex was placed in a Japanese pharmacopoeia #5 gel capsule. Infrared spectra were recorded by transmission through a KBr pellet.

Preparation of $[Co(cina)_2(H_2O)_2]_n$

All chemicals were obtained from Tokyo Kasei Co. and used without further purification.

$Co(NO_3)_2$•$6H_2O$ (0.5 g, 0.0017 mol) was dissolved in distilled water (*ca.* 20 ml) and solution of *trans*-cinnamic acid (0.51 g, 0.0034 mol) and NaOH (0.13 g, 0.0034 mol) in distilled water (*ca.* 20 ml) was added. The mixture was placed in the Teflon liner of an autoclave that was then sealed and heated to 120 °C for 1 day. It was allowed to cool to room temperature in a water bath. Pale pink crystals are obtained. The crystals were washed with water and acetone. The crystals are allowed to air dry.

Anal. Calcd: $CoC_{18}O_6H_{18}$; C, 55.54; H, 4.66. Found: C, 54.67; H, 4.62

Infrared: 680m, 720 m, 780m, 880m, 980m, 1070w, 1250w, 1420s, 1450m, 1540s, 1580m, 1640s, 3020w, 3060w, 3080w, 3240mbr, 3340mbr, 3460mbr

X-ray Crystallography and Structure Solution

A single crystal was glued on the top of a glass fiber and diffraction data were collected on a Brucker SMART APEX CCD area detector employing graphite monochromated Mo-Kα (0.71073 Å) with ω scan mode. The data were collected at room temperature. The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods and expanded using Fourier techniques. The hydrogen atoms of $[Co(cina)_2(H_2O)_2]_n$ were located from Difference Fourier maps and the hydrogen atoms of water were placed at ideal positions. The non-hydrogen atoms were refined anisotropically. The final cycle of full-matrix least-squares refinement was based on 1957 of observed reflections and 115 variable parameters and converged (large parameter shift was σ times its e.s.d.) with weighted and agreement factors of $R = \sum||F_o|-|F_c||/\sum|F_o|$, $R_w = [\sum w(|F_o|-|F_c|)^2/\sum w|F_o|^2]^{1/2}$. The convergence gave final R of 0.092 and R_w of 0.127.

RESULTS AND DISCUSSION

The structure and atomic numbering scheme of $[Co(cina)_2(H_2O)_2]_n$ is shown in Figure 1. The crystal belongs to the monoclinic system $C2/c$, a=36.564(5) Å, b=6.4037(9) Å, c=7.327(1) Å, β=92.101(4) °, V=1714.5(4) Å^3 and Z=4. X-ray structure analysis of this compound revealed the conformation of a 2-D layer structure (Figure 2). The carboxylate ligands bridge metal ions in tri-atomic *syn-syn* conformation to generate a 2-D layered compound. Within the layer the cobalt atoms are arranged in a pseudo square fashion with nearest Co-Co distances of 4.865 Å and second and third nearest Co at 6.404 and 7.327 Å, respectively. The pseudo square arrangement of cobalt atoms in $[Co(cina)_2(H_2O)_2]_n$ is very similar to that found in $[Co(H_2O)_2BDC]$ (BDC = benzene 1,4-dicarboxylate or terephthalate). $[Co(H_2O)_2BDC]$ crystallized in the monoclinic system $C2/c$, a=18.274(3) Å, b=6.548(9) Å, c=7.296(1) Å, β=98.6(3) °, V=862.5 Å^3 and Z=4[4]. Comparing $[Co(cina)_2(H_2O)_2]_n$ and $[Co(H_2O)_2BDC]$, the cell parameters of b- and c-axes are similar to each other. However, the cell parameters of a-axis in $[Co(cina)_2(H_2O)_2]_n$ and that in $[Co(H_2O)_2BDC]$ correspond to the interlayer distance of 18.5 Å and 9.14 Å, respectively. The difference of interlayer separation between the two compounds is due to the coordination ability of the ligands. The layers are held together by dicarboxylate BDC to yield a tightly held 3-D solid, on the other hand mono-carboxylate cina has no ability to connect the layers. Co(II) has octahedral coordination geometry comprising four oxygen atoms of cina ligands and two water molecules. The octahedron consists of the water molecules (O(3) and O(3')) coordinated to the *trans*-position and the oxygen atoms (O(1), O(2), O(1') and O(2')) of bidentate cina ligands. Co-O distances of 2.091(2) Å (Co-O(3)) and 2.066(2) and 2.096(2) Å (Co-O(2) and Co-O(1) carboxylate). The angles lie in the range 85.20(9)-94.80(9) °. The shortest Co-O(2) of 2.066(2) Å are indicative of the axially compressed octahedral geometry around the metal center. The bond distances of Co-OH_2 are similar to those found in [$Co(H_2O)_2BDC$], on the other hand the longest bond distances of 2.119 Å (Co-O carboxylate) give axially elongated octahedral geometry.

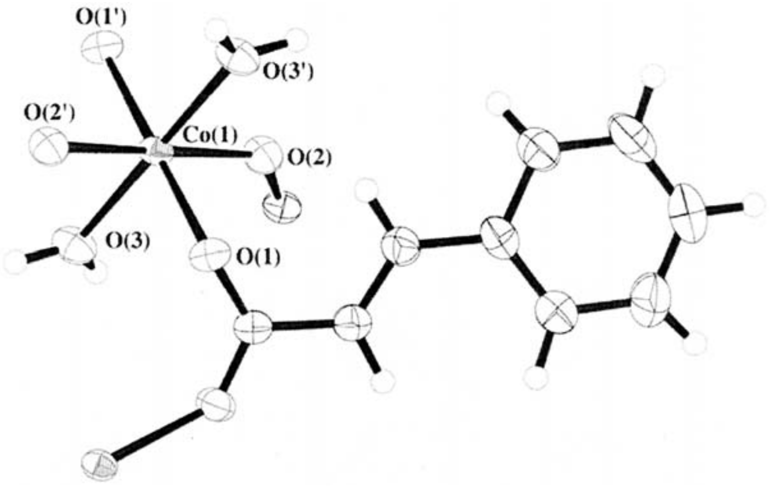

FIGURE 1 The X-ray crystal structure of the complex of [$Co(cina)_2(H_2O)_2$]$_n$.

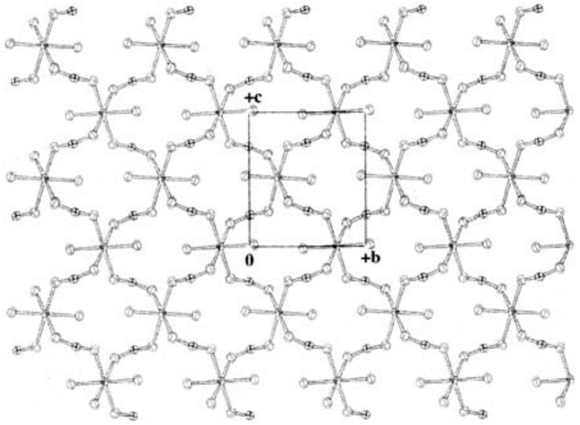

FIGURE 2 Projection of the crystal structure of $[Co(cina)_2(H_2O)_2]_n$ along the a-axis.

The IR spectrum displays a set of sharp bands and a set of broad bands. The broad bands are derived from the carboxylate and CoO_6 vibrations. The sharp bands are derived from the modes of *trans*-cinnamic acid skeleton. The presence of a broad feature in the stretching region (3240, 3340 and 3460 cm^{-1}) corresponds to water. The antisymmetric stretching carboxylate mode is assigned to the 1540 cm^{-1} band but the symmetric stretching mode is overlapped by cina skeleton.

The magnetic properties of $[Co(cina)_2(H_2O)_2]_n$ were measured over the temperature range of 2-300 K. The temperature dependence of the inverse susceptibility and the product of susceptibility and temperature are shown in Figure 3. The complex behaves as a Curie-Weiss paramagnet above 100 K with a Weiss constant of –24.05 K and a Curie constant of 2.78 cm^3 K mol^{-1}. The effective magnetic moment (μ_{eff}) per cobalt ion is 4.54 μ_B at room temperature which is consistent with that expected for an octahedral cobaltous ion. The negative Weiss constant may indicate antiferromagnetic interaction between nearest neighbor cobalt ions. The χT values decrease from 2.57 cm^3 K mol^{-1} at 300 K to 0.79 cm^3 K mol^{-1} at 2K. The high temperature value of χT is higher than 1.88 cm^3 K mol^{-1}, the value that would be expected for one $S = 3/2$ spin. Nevertheless, it is consistent with the anisotropic nature of the metal ion where the orbital contribution is important. The temperature dependence is as expected for isolated Co(II) in octahedral geometry and the lowering of the moment at low temperature is due to the effect of spin-orbit.

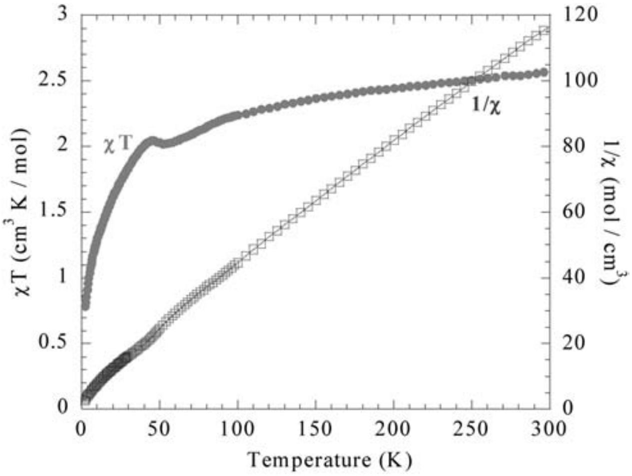

FIGURE 3 Temperature dependence of the inverse susceptibility and the product of susceptibility and temperature for $[Co(cina)_2(H_2O)_2]_n$.

In conclusion, we have synthesized and characterized a novel 2-D layer compound in which cobalt ions are arranged in a pseudo square fashion. The temperature dependence of magnetic susceptibilities revealed the presence of spin orbit coupling for the cobalt ion.

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