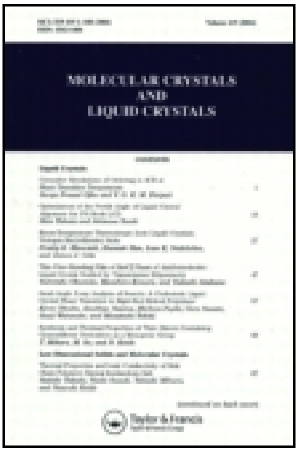

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Hydrothermal Synthesis and Structural and Magnetic Characterization of the Coordination Bonding Network Co II (H 2 O) 2 carboxy-cinnamate

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Hydrothermal Synthesis and Structural and Magnetic Characterization of the Coordination Bonding Network $Co^{II}(H_2O)_2$carboxy-cinnamate

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The hydrothermal synthesis, single crystal X-ray structure and magnetic properties of a new cobalt(II)-carboxy-cinnamate complex is described. Reaction of Co(II), carboxy-cinnamic acid ($C_{10}H_8O_4$) and NaOH at 120°C yield the coordination network, $Co(H_2O)_2$carboxy-cinnamate (**1**). **1** crystallizes in the monoclinic system, a= 11.3236(4), b= 6.6084(4), c= 7.2011(6) Å, β= 101.948(5)°, V= 527.2(1) Å^3, space group $P2_1/c$, Z = 2. **1** possesses a three-dimensional coordination-bonding network consisting of layers of CoO_6 bridged by the tetra-dendate carboxy-cinnamate. Its magnetic moment decreases on lowering temperature due to spin-orbit coupling and no interaction between cobalt ions is observed.

Keywords: carboxylate; cobalt; coordination polymer; magnetic properties

INTRODUCTION

Enhancing the range of design strategies for the synthesis of extended molecular solids is of considerable interest in recent years due to their technological applications[1-10]. Developing multi-dentate ligands containing N- or O-donors as structure directives for metal complexes is the most common approach. For example, polypyridine ligands are widely used and a number of one-, two- and three-dimensional frameworks have been designed and characterized[5,11-15]. Extended polycarboxylate ligands are potentially good candidates for generating coordination networks and considerable efforts are devoted to prepare porous metal-polycarboxylate assemblies. Several examples are known with terephthalate (BDC) or benzenetricarboxylate (BTC). These complexes have been subjected to gas sorption and magnetic studies[6,10,12,16-21]. We have recently found some interesting magnetic compounds containing mono-carboxylates as spacers or dicarboxylates and tricarboxylates as connectors. Their magnetic properties range from ferrimagnetic with Curie temperatures of up to 60 K and coercivity of 20 kOe to metamagnetic exhibiting remanance and coercivity in excess of 50 kOe at 2K. For the later compound, we have systematically modified the interlayer distances by changing the number of carbon atoms between the carboxylate groups[22]. Together with the metamagnet, $Co_2(OH)_2$carboxy-cinnamate, we obtained a paramagnetic phase, $Co(H_2O)_2$carboxy-cinnamate[23]. Here, we report the x-ray crystal structure and the magnetic properties of this new cobalt(II) carboxy-cinnamate complex. The three-dimensional network is built up from cobalt ions and carboxy-cinnamate ligand.

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EXPERIMENTAL

The magnetic measurements of the complexes were studied by a Quantum Design MPMS-XL SQUID magnetometer in the temperature range 2 - 300 K and fields up to 5 Tesla and Princeton Applied Research Vibrating Sample magnetometer. X-ray powder diffraction data were collected on a Siemens D-500 diffractometer with Co Kα radiation at room temperature.

Preparation of $Co(H_2O)_2$(carboxy-cinnamate) (1)

The complex was synthesized according to a similar procedure used for $Co(H_2O)_2$terephthalate[23]. Pink powder, $Co_2(OH)_2$carboxy-cinnamate, and red crystals, $Co(H_2O)_2$carboxy-cinnamate, are obtained. The crystals were first separated from the pink powder by decantation and then manually under microscope. The crystals were washed with water and acetone and allowed to dry in air.

Anal. Calcd for $CoO_6C_{10}H_{10}$: C, 42.13; H, 3.54; Found: C, 42.17; H, 3.50

X-ray Crystallography and Structure Solution

Similar procedure of Co(H_2O)$_2$(terephthalate) was applied for the structure determination of **1**[23]. Toward the end of the refinement of the structure, C(3) and C(4) atoms appeared to be disordered and were finally refined as 50% occupancy at the two sites.

Crystal data for Co(H_2O)$_2$(carboxy-cinnamate)

$C_{10}H_{10}CoO_6$; M_w = 285.12; crystal size 0.15 × 0.10 × 0.10 mm^3; monoclinic, a = 11.3236(4) Å, b = 6.6084(4) Å, c = 7.2011(6) Å, β = 101.948(5)°, V = 527.2(1) Å^3, space group $P2_1/c$, Z = 2, D_c = 1.81 gcm^{-3}, μ(Mo Kα) = 1.642 cm^{-1}, No. reflections measured = 1317, No. observations = 1061 ($I > 3.00\sigma(I)$). R (R_w) = 0.057 (0.077). Maximum and minimum residual electron densities 0.709 e$^-$/Å^3 and -0.647 e$^-$/Å^3.

RESULTS AND DISCUSSION

Similar complexes found in the hydrothermal reaction of Co(II) and terephthalate[22,23], are found with carboxy-cinnamate. This provides a better structure property relation to be derived since in terephthalate the carboxylate groups are separated by six carbon atoms and in carboxy-cinnamate there are eight. Figure 1 shows a fragment of the structure of the red crystals with the atom-numbering scheme. The cobalt ions exhibit octahedral geometry comprising four oxygen atoms of carboxy-cinnamate ligands and two oxygen atoms of water molecules. Two water molecules coordinate in *trans*-positions with the shortest bond distances of 2.083(3) Å are indicative of an axially compressed octahedron. The bond angles lie in the range 87.3(1)-92.7(1)°. The cell parameters (b and c) are similar to those found in Co(H_2O)$_2$(BDC), where BDC is benzendicarboxylate (a= 18.274(3) Å, b= 6.5438(9) Å, c= 7.296(1) Å, β= 98.6(3)°, V= 862.5 Å^3)[23]. These results indicate a similar layered structure to Co(H_2O)$_2$(BDC) but an increase of the interlayer separation as expected for a longer acid. The structure consists of layers of octahedral cobalt ions parallel to the bc plane separated by the carboxy-cinnamate, giving an interlayer distance of 11.3 Å. (Figure 2) Each layer contains *trans*-Co(H_2O)$_2$ connected by four O-C-O bridges of the carboxylate groups of the carboxy-cinnamate ion. Within the layer the cobalt ions are arranged nearly in a square with the shortest Co•••Co distance of 4.9 Å and second nearest is 6.6 Å. One of the characteristic structural features of this compound is the 3-D framework as shown in Figure 2. The small residual electron density in the difference Fourier maps indicates that there are no other small molecules in the small channels present.

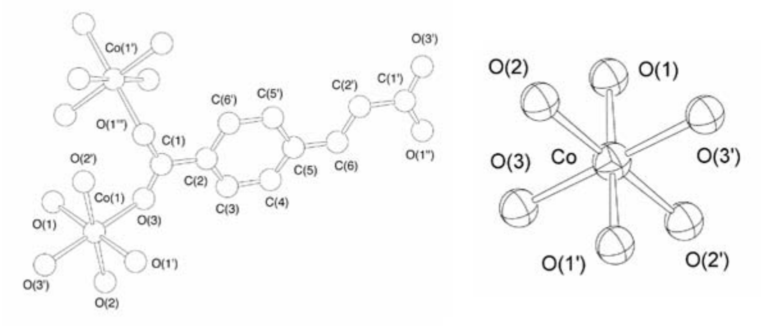

FIGURE 1. Structure of **1** showing the numbering scheme (left) and the coordination of the cobalt atoms. (right) Hydrogen atoms are omitted for clarity.

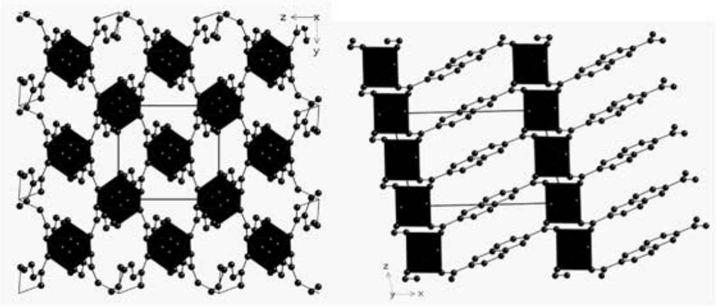

FIGURE 2. Projection of the crystal structure along the *a*-axis(left) and *b*-axis (right) showing the different shapes of the channels.

The magnetic properties of the compound were studied as a function of temperature in a fixed magnetic field and the isothermal magnetization in field up to 5 Tesla at 2 K. It behaves as a Curie-Weiss paramagnet above 150 K with Curie constant of 2.95 cm^{3}K/mol and a Weiss constant of -18.6 K. The effective magnetic moment at 300 K is μ_{eff} = 4.7 μ_{B}. These behaviors are typical for cobalt(II) ion in an octahedral environment with an enhance moment due orbital contribution and a lowering at low temperatures due to the effect of spin-orbit coupling[28].

CONCLUSION

Two structural phases are obtained in the reaction of Co(II) and terephthalate or carboxy-cinnamate; one is paramagnetic with similar magnetic properties and the other is a metamagnet where the critical field is reduced on replacing terephthalate by carboxy-cinnamate.

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