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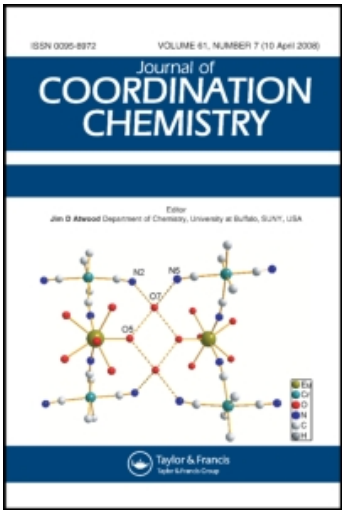

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Coordination polymer incorporating cobalt(II) and glycine acid: structure and magnetism

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Coordination polymer incorporating cobalt(II) and glycine acid: structure and magnetism

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We report the structure and magnetism of a cobalt(II) compound with glycine acid, $Co(C_2H_4NO_2)_2 \cdot H_2O$ (**1**). It crystallizes in the orthorhombic system, space group P2(1)2(1)2(1) with $a = 5.2301(10)$ Å, $b = 10.837(2)$ Å, $c = 13.542(3)$ Å, $R_1 = 0.0448$, w$R_2 = 0.1151$. In **1**, Co(II) has a slightly distorted square-pyramidal geometry defined by two O atoms and two N atoms from two glycine ligands, and by one O atom from an aqua ligand in the apical position. The molecules form a three-dimensional supramolecular network through O–H $\cdots$ O and N–H $\cdots$ O hydrogen bonds. Magnetic characterization shows **1** exhibits a negative Curie–Weiss constant and dominant spin-orbit coupling for Co(II).

Keywords: Coordination polymer; Glycine acid; Magnetic properties

1. Introduction

Metal coordination polymers have been studied widely as an important interface between synthetic chemistry and materials science, with structures, properties, and reactivities not found in mononuclear compounds [1–3].

Structures of cobalt complexes with the amino acids glutamic and aspartic acid [4, 5], histidine [6], glycine [7, 8], phenylalanine [9], alanine [10], methionine [5], *S*-methylcysteine [5], and asparagines [11] have been reported [12, 13]. Less information exists about the magnetic properties of cobalt glycine acid compounds, although glycine acid compounds of copper have received attention. Co(II) has a more complex $3d^7$ configuration, with complications introduced by the orbital and spin degeneracy of the ground state. For Co(II) in an octahedral environment, the ^4F ground term splits into two orbital triplets ($^4T_{1g}$ and $^4T_{2g}$) and one orbital singlet ($^4A_{2g}$), $^4T_{1g}$ being the ground-state multiplet, which is further split by the spin-orbit interaction and by lower symmetry distortions of the ligand field, producing a variety of magnetic behaviors which strongly depend on the molecular structure and resulting energy level scheme [14, 15]. Kahn [15] discusses models to analyze the magnetic properties of Co(II) compounds in octahedral coordination with axial distortion. High-spin [$(S) = 3/2$] or low-spin [$(S) = 1/2$] Co(II)

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compounds depend on the magnitudes of the energy gap between the metal orbitals and the spin pairing energy [15]. Magnetic characterization of these compounds provide information about the electronic structure of single cobalt ions and also about the interactions between them.

We report herein the structure and the magnetic properties of a Co(II) compound with glycine acid, $Co(C_2H_4NO_2)_2 \cdot H_2O$ (**1**). Its structure was solved by X-ray techniques and its TG-DTA properties and magnetic interactions are reported.

2. Experimental

2.1. *Physical measurements*

All reagents are of A.R. grade and used as purchased. Elemental analyses (C, H, N) were performed on a Perkin-Elmer 240 analyzer. Infrared spectra on KBr pellets were recorded on a Shimadzu IR-408 spectrophotometer in the range 4000–400 cm^{-1} and TG runs were taken on a Rigaku TG-DTA standard type thermal analysis system. The compound was heated to 1100°C under nitrogen, at a heating rate of 10°C per min. The variable temperature susceptibility measurements were carried out with a MagLab System 2000 magnetometer in the temperature range 2–300 K at a magnetic field of 10,000 G.

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2.2. *Synthesis*

The title compound was prepared by adding 5 ml of aqueous $Co(NO_3)_2 \cdot 6H_2O$ (0.291 g, 1 mmol) to 10 ml of ethanol solution of glycine (0.075 g, 1 mmol) and refluxing for 2 h. The resulting solution was filtered, and the filtrate kept at room temperature; red blocks of **1** appeared in yields up to 39.65% after two weeks. Elemental analysis calculated for **1**: C, 21.33; H, 4.44; N, 12.44%. Found: C, 21.29; H, 4.36; N, 12.54%.

2.3. *X-ray crystal structure determination*

X-ray crystallography. Suitable single crystals of **1** were carefully selected under an optical microscope and glued to thin glass fibers. The diffraction data were collected on a Siemens SMART CCD diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at 291 K. An empirical absorption correction was applied using the SADABS program [16]. The structures were solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELX-97 program package [17]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms of glycine were generated geometrically; no attempts were made to locate the hydrogen atoms of water. The crystallography details for the structure determination of **1** are presented in table 1. Selected bond distances and angles are listed in table 2.

Table 1. Crystal data and structure refinement parameters for **1**.

Formula	$C_4H_{10}CoN_2O_5$
Molecular mass	225.07
Crystal system	Orthorhombic
Space group	*P*2(1)2(1)2(1)
Unit cell dimensions (Å, °)	
a	5.2301(10)
b	10.837(2)
c	13.542(3)
α	90.00
β	90.00
γ	90.00
V (Å^3)	767.6(3)
Z	4
T (K)	291(2)
D_{Calcd} (g cm^{-3})	1.948
F(000)	460
Goodness-of-fit on F^2	1.095
Final *R* indices [$I > 2\sigma(I)$][a]	$R_1 = 0.0448$, $wR_2 = 0.1557$
R indices (all data)	$R_1 = 0.0502$, $wR_2 = 0.1607$

[a] $R_1 = \sum(|F_o| - |F_c|)/\sum|F_o|$; $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{0.5}$.

Table 2. Selected bond lengths (Å) and angles (°) for **1**.

Co(1)–O(1)	1.961(4)	O(1)–Co(1)–O(3)	93.44(15)
Co(1)–O(3)	1.962(4)	O(1)–Co(1)–N(1)	84.82(16)
Co(1)–N(1)	2.005(4)	O(3)–Co(1)–N(1)	174.8(2)
Co(1)–N(2)	2.017(5)	O(1)–Co(1)–N(2)	178.0(2)
Co(1)–O(5)	2.393(5)	O(3)–Co(1)–N(2)	84.62(18)
O(4)–C(3)	1.234(7)	N(1)–Co(1)–N(2)	97.06(19)

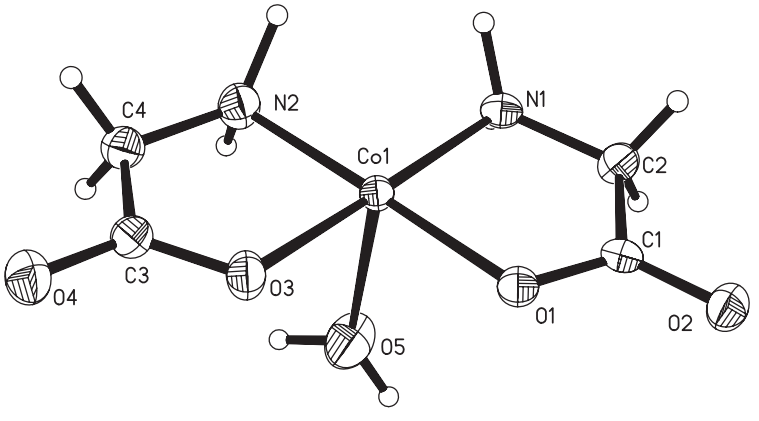

Figure 1. A view of **1** with 30% probability ellipsoids.

3. Results and discussion

3.1. *Crystal structure*

The extended asymmetric unit of Co(II) is shown in figure 1. Co1 is five-coordinate with a N2O3 donor set, two oxygens from carboxylate groups of two different glycine

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Table 3. Hydrogen-bonding geometry and close contacts (Å, °) for **1**.

D–H···A	d(D–H)	d(H···A)	d(D···A)	∠(DHA)
O(5)–H(5F)···O(2)#1	0.96(9)	1.86(9)	2.783(6)	161(7)
O(5)–H(5E)···O(4)#2	0.93(9)	1.91(10)	2.816(7)	163(8)
O(5)–H(5E)···O(3)#2	0.93(9)	2.54(9)	3.238(7)	132(7)
N(1)–H(1G)···O(1)#3	1.03(6)	2.01(7)	3.011(5)	163(6)
N(2)–H(2F)···O(2)#1	1.00(9)	2.57(9)	3.500(8)	155(7)
N(2)–H(2E)···O(3)#3	1.13(12)	2.11(13)	3.111(7)	146(9)
N(1)–H(1H)···O(4)#4	1.00(7)	1.98(7)	2.976(7)	173(6)

Symmetry transformations used to generate equivalent atoms: #1 $-x+1/2$, $-y+1$, $z+1/2$; #2 $-x+1$, $y-1/2$, $-z+3/2$; #3 $x-1$, y, z; #4 $-x$, $y-1/2$, $-z+3/2$.

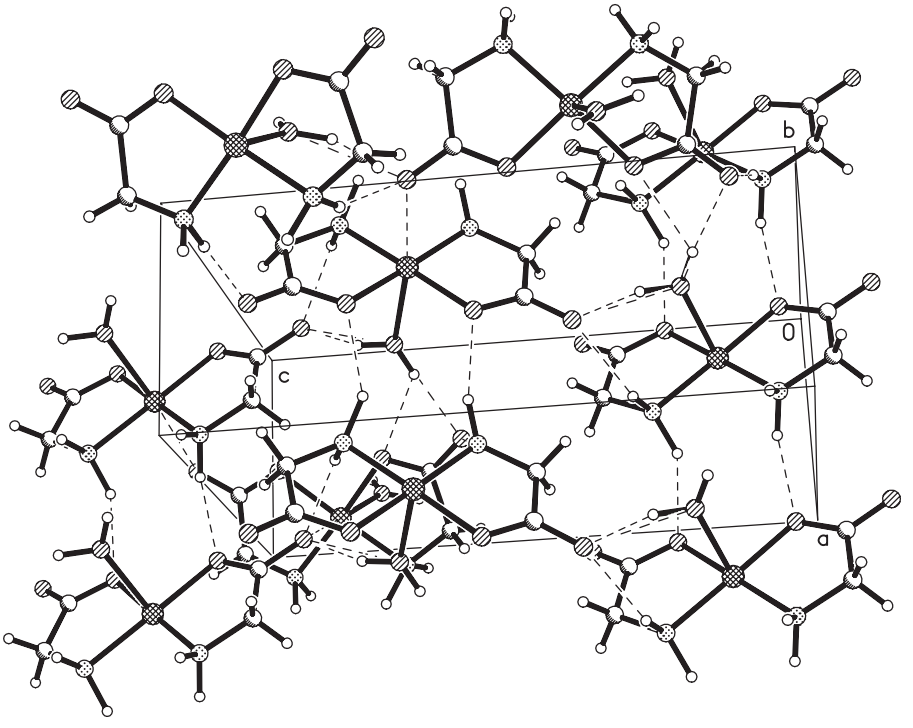

Figure 2. Unit cell packing of **1** showing hydrogen-bonding interactions.

ligands, the remaining oxygen from one water, and two nitrogens from two glycine ligands. The coordination environment of Co1 is slightly distorted square-pyramidal. In the basal positions, the four coordinating atoms are approximately coplanar, with an average deviation of 0.031 (4) Å; Co1 lies 0.045(2) Å above this plane and the two *trans* angles O3–Co1–N1 and O1–Co1–N2 deviate from the ideal angle of 180° by 5.20(2) and 2.00(2)°, respectively. Other angles around Co deviate from 90°, ranging from 84.62(18) to 97.06(19)°, consistent with slightly distorted square-pyramidal coordination of Co1. The same character is also revealed by the torsion angles in the structure (table 2).

In the crystal structure, molecules are linked via three intermolecular N–H···O and two O–H···O hydrogen bonds, forming a three-dimensional network (details given in table 3 and figure 2).

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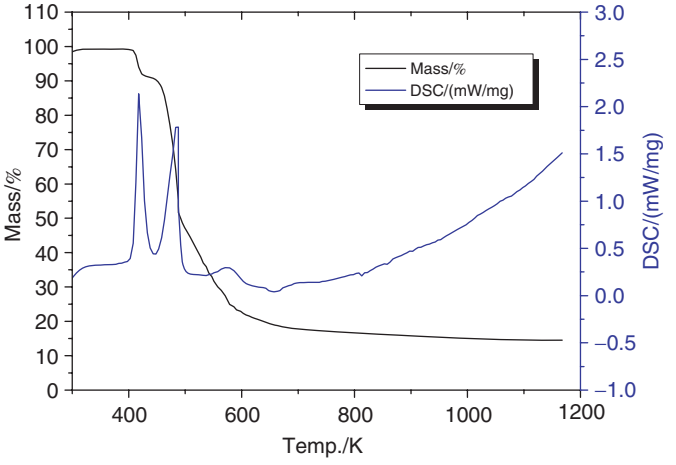

Figure 3. The TG-DTG curves of **1**.

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3.2. *IR spectra*

In free glycine acid a band at 3167 cm^{-1} is assigned to ν(N–H), which is almost identical for the glycine polymorphs [18, 19]. However, it shifts to 3317 cm^{-1} in **1**, and a ν(Co–N) appears at 541 cm^{-1}, indicating that glycine acid coordinates to Co. The spectrum closely matches previously reported spectra of amino acid complexes of other transition metals [20, 21]. The absorptions due to carboxylate of free glycine are observed at 509, 897 and 1600 cm^{-1}; in **1**, these peaks are shifted to 511, 1037 and 1700 cm^{-1}, respectively. Similarly, the absorptions due to NH_3^+ of free glycine at 1109, 1129 and 1516 cm^{-1} are shifted to 1087, 1146 and 1538 cm^{-1}, respectively. A strong and broad band at 3340 cm^{-1} is assigned to ν(OH) absorption with the hydrogen bonds or water molecules [22].

3.3. *TG-DTG properties*

In the TG-DTG of **1** (figure 3), there are two main mass loss stages. The first of 8.10% starts at 372.5 K and ends at 423.5 K while reaching its highest rate at 418.6 K, attributed to loss of coordinated H_2O (Calcd about 8.00%). The last weight loss stage with 74.55% starts at 423.5 K and ends at 685.5 K. The residue is 19.15% of the total mass.

3.4. *Magnetic properties of 1*

Magnetic susceptibility measurements of **1** were performed on crushed crystals of the compound. The results are shown in figure 4.

The value of $\chi_M T$ at 300 K is 3.4 emu mol^{-1} K, in good agreement with the expected value for isolated high spin Co(II) ions with an orbital contribution ($S = 3/2$ and $g = 2.8$) in a magnetically dilute sample. The $\chi_M T$ value continuously decreases from room temperature and reaches a value of 1.6 emu mol^{-1} K at 2 K. The temperature dependence of χ^{-1} between 300 and 50 K approximates Curie–Weiss behavior with

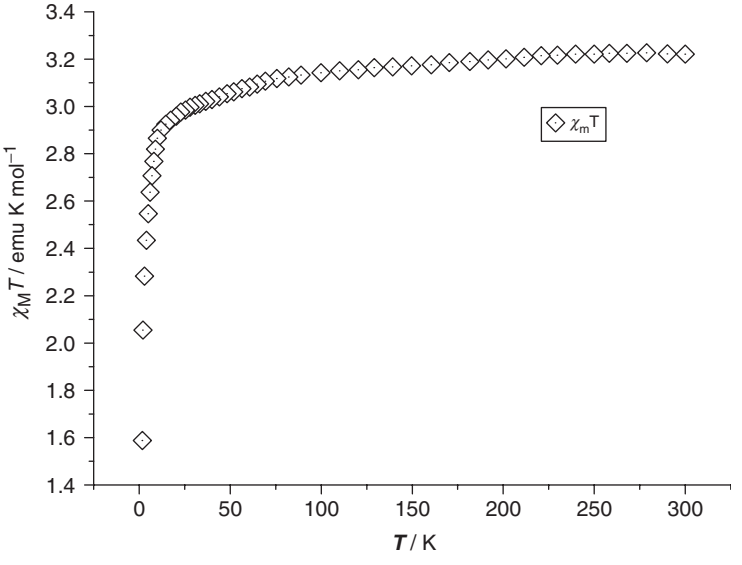

Figure 4. Plots of $\chi_M T$ *vs.* T for $Co(C_2H_4NO_2)_2 \cdot H_2O$.

$C = 3.8\,\text{emu mol}^{-1}\,\text{K}$ and $\theta = -38\,\text{K}$, the negative Curie–Weiss constant indicates dominant spin-orbit coupling effects for Co(II).

4. Summary and conclusions

A new coordination polymer has been prepared and the structure and magnetic properties determined. Cobalt(II) coordinates two glycine ligands, chelating via nitrogen and oxygen in a square-pyramidal geometry. Hydrogen bonding leads to a three-dimensional network.

Supplementary data

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre CCDC: (**1**) 680091. Copies of this information may be obtained free of charge from The Director, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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