Structure and Magnetic Properties of a Single-strand Helical Cobalt(II) Coordination Polymer

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The one-dimensional helical chain-like coordination polymer $[Co(bpdc)(H_2O)_3]\cdot H_2O$ (**1**) has been synthesized by hydrothermal reaction of pdon with $Co(NO_3)_2\cdot 6H_2O$ and $Na_2B_4O_7$ (bpdc = 2,2′-bipyridyl-3,3′-dicarboxylate, pdon = 1,10-phenanthroline-5,6-dione). **1** crystallizes in the monoclinic space group $P2_1/n$ with the cell parameters: a = 9.987(1), b = 9.238(1), c = 16.080(2) Å, β = 97.471(1)°, V = 1471.0(3) Å^3, Z = 4. The bpdc ligand has resulted from an *in situ* carbon-carbon bond cleavage in the pdon ligand. The Co(II) atom is surrounded by two nitrogen atoms of the bpdc pyridyl groups and four O atoms, of which three belong to coordinated water molecules and one to a bpdc carboxylate group. The six-coordinated Co(II) atom adopts a distorted octahedral geometry. Compound **1** displays antiferromagnetic interactions. Above 30 K, χ_m^{-1} obeys the Curie-Weiss law with C = 3.12 cm^3 K mol^{-1} and Θ = −10.6 K.

Key words: Cobalt(II), Crystal Structure, Magnetic Properties

Introduction

1,10-Phenanthroline-5,6-dione (pdon), which is fairly distinct in its electronic character from 1,10-phenanthroline due to the two carbonyl groups, has been extensively used as a building block for the synthesis of supramolecular assemblies, since this ligand has the ability to form stable complexes with a wide variety of metal ions and carries an *o*-quinone moiety with pH-dependent electroactivity [1 – 4]. Remarkably, metal complexes of this ligand potentially allow for the variation and control of redox properties over a wide range as well as for a fine-tuning of the potential through pH changes [5, 6]. Furthermore, the diketone functionality can be easily transformed to other chelating groups such as a diamine or a dioxime or a large π-conjugated organic linker [7 – 10]. It is also relatively prone to unexpected reactions such as reduction, hydration or carbon-carbon bond cleavage, which is particularly attractive in synthetic chemistry [11, 12]. The carbon-carbon bond cleavage reactions under different conditions have attracted special attention. However, the exact carbon-carbon bond cleavage mechanism has not yet been established due to the few structurally characterized products in the literature [13, 14]. In this contribution, we present a single-strand helical coordination polymer, $[Co(bpdc)(H_2O)_3]\cdot H_2O$ (**1**), in which the bpdc ligand results from the *in situ* carbon-carbon bond cleavage of the pdon ligand under hydrothermal conditions.

Table 1. Crystal and refinement data for $[Co(bpdc)(H_2O)_3]\cdot H_2O$ (**1**).

Formula	$C_{12}H_{14}CoN_2O_8$
Mr	373.18
Crystal size, mm^3	$0.33 \times 0.12 \times 0.08$
Crystal system	monoclinic
Space group	$P2_1/n$
a, Å	9.987(1)
b, Å	9.238(1)
c, Å	16.080(2)
β, deg	97.471(1)
V, Å^3	1471.0(3)
Z	4
D_{calcd}, g cm^{-3}	1.69
μ(MoK_α), cm^{-1}	1.2
F(000), e	764
hkl range	$-13 \le h \le 12$, $-12 \le k \le 12$, $-21 \le l \le 21$
$((\sin\theta)/\lambda)$max, Å^{-1}	0.0339
Refl. measured	12922
Refl. unique	3610
R_{int}	0.0338
Param. refined	209
$R(F)$ / $wR(F^2)$[a] (all refls.)	0.0609 / 0.1151
A / B values for weighting scheme[b]	0.1 / 0.0000
GoF (F^2)[c]	1.139
$\Delta\rho_{fin}$ (max / min), e Å^{-3}	0.97 / −0.65

[a] $R1(F) = \||F_o| - |F_c|\|/\Sigma|F_o|$, $wR2(F^2) = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w\cdot(F_o^2)^2]^{1/2}$; [b] $w = [\sigma^2(F_o^2) + (AP)^2 + BP]^{-1}$, with $P = (\max\cdot(F_o^2,0) + 2F_c^2)/3$; [c] GoF$(F^2) = [\Sigma w(F_o^2 - F_c^2)^2/(n_{obs} - n_{param})]^{1/2}$.

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Co1–O7	2.065(2)	Co1–O3$^{\#1}$	2.0902	Co1–N1	2.152(2)
Co1–O6	2.076(2)	Co1–O5	2.1312	Co1–N2	2.118(2)
O4–C11	1.258(3)	O3–C11	1.241(3)	O2–C12	1.247(3)
O1–C12	1.260(3)	N1–C10	1.345(3)	N1–C6	1.351(3)
N2–C1	1.333(3)	N2–C5	1.352(3)	C5–C6	1.490(3)
O7–Co1–O6	97.64(1)	O6–Co1–N1	93.64(8)	O6–Co1–O3$^{\#1}$	89.33(7)
O7–Co1–N2	92.18(9)	O6–Co1–N2	169.82(8)	N2–Co1–O3$^{\#1}$	88.16(7)
O7–Co1–O5	91.42(8)	O6–Co1–O5	88.94(8)	O5–Co1–O3$^{\#1}$	178.24(7)
O7–Co1–N1	166.88(9)	N2–Co1–O5	93.49(8)	O7–Co1–O3$^{\#1}$	89.15(8)
O5–Co1–N1	95.48(8)	N2–Co1–N1	76.30(8)	N1–Co1–O3$^{\#1}$	84.29(8)
Hydrogen bonding contacts					
D–H···A	D–H	H···A	D···A	D–H···A	
O5–H5A···O4$^{\#2}$	0.90	2.4859	3.219(3)	138.89	
O5–H5B···O2$^{\#3}$	0.90	1.8740	2.734(3)	158.87	
O6–H6A···O1$^{\#2}$	0.90	1.7458	2.631(3)	167.36	
O6–H6B···O4$^{\#4}$	0.90	1.9282	2.724(3)	146.84	
O7–H7A···O8	0.90	1.7751	2.667(3)	172.48	
O7–H7B···O1$^{\#4}$	0.90	1.8128	2.704(3)	168.99	
O8–H7A···O2$^{\#2}$	0.90	1.9690	2.861(4)	174.39	
O8–H7B···O4$^{\#2}$	0.90	2.1550	2.1550	135.88	

Table 2. Selected interatomic distances (Å) and angles (deg) for **1**[a].

[a] Symmetry codes: $^{\#1}$ $-x+3/2$, $y+1/2$, $-z+1/2$; $^{\#2}$ $-1+x$, y, z; $^{\#3}$ $3/2-x$, $-1/2+y$, $1/2-z$; $^{\#4}$ $3/2-x$, $1/2+y$, $1/2-z$.

Experimental Section

Measurements of physical properties

All chemicals of p. a. grade were commercially available and used without further purification. The C, H and N microanalyses were performed with a Perkin-Elmer 2400-CHNS/O elemental analyzer. The FT-IR spectra were recorded from KBr pellets in the range 4000 – 400 cm^{-1} on a Shimadzu FT-IR-8900 spectrometer. The magnetic susceptibilities were measured using a SQUID magnetometer on crystalline samples in the temperature range of 2 to 300 K under 1 KOe.

*Preparation of [Co(bpdc)(H$_2$O)$_3$]·H$_2$O (**1**)*

A mixture of $Co(NO_3)_2 \cdot 6H_2O$ (0.291 g, 1.0 mmol), $Na_2B_4O_7 \cdot 10H_2O$ (0.381 g, 1.0 mmol), 1,10-phenanthroline-5,6-dione (0.228 g, 1.0 mmol), and 18 mL of H_2O was sealed in a 23 mL stainless-steel reactor with Teflon liner and kept under autogeneous pressure at 120 °C for 7 d. The mixture was cooled to r. t., and red crystals were obtained in 56 % yield (based on the initial amount of $Co(NO_3)_2{\cdot}6H_2O$). Anal. for $C_{12}H_{14}CoN_2O_8$: calcd. C 38.59, H 3.75, N 7.50; found C 38.55, H 3.64, N 7.38. – IR: ν = 3348s, 1586s, 1568s, 1438w, 1393s, 11153w, 1123w, 1097w, 831m, 781s, 753m, 698m, 662m, 603m cm^{-1}.

X-Ray structure analysis

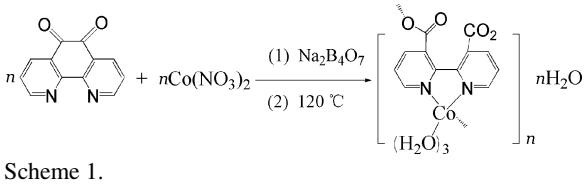
The reflection intensities of **1** were collected at 298(3) K using a Bruker SMART Apex II CCD area detector single crystal diffractometer, with graphite-monochromatized MoK_α radiation (λ = 0.71073 Å), using the $\varphi/2\vartheta$ scan mode. Absorption correction was applied using the program SADABS [15]. The structure was solved by Direct Methods using SHELXS-97 [16] and refined by full-matrix least-squares methods on F^2 using SHELXL-97 [17]. All hydrogen atoms attached to the carbon and nitrogen atoms were generated geometrically, and the hydrogen atoms of the water molecules were located from the difference Fourier syntheses. All non-hydrogen atoms were finally refined with anisotropic displacement parameters. H atoms attached to C atoms were positioned geometrically and treated as riding, with C–H = 0.93 Å. The H atoms of the water molecules were located in a difference map and refined with U_{iso}(H) = 1.5 U_{eq}(O). Pertinent crystal and structure determination data are summarized in Table 1. Selected interatomic distances and bond angles are given in Table 2.

CCDC 708833 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Results and Discussion

Synthesis and IR spectra

In the preparation of **1**, the bpdc ligand results from an *in situ* carbon-carbon bond cleavage of the pdon ligand under hydrothermal conditions, as shown in Scheme 1. Repeated experiments have indicated that



Scheme 1.

$Na_2B_4O_7$ plays a key role in the formation of crystalline products of **1**, which suggests that the carbon-carbon bond cleavage reaction is probably mediated by the alkalinity.

The IR spectrum of **1** shows the ν(O–H) stretching vibration of water molecules at 3348 cm^{-1}. The absorptions at 1586 and 1393 cm^{-1} can be assigned to the $\nu_{as}(CO_2^-)$ and $\nu_s(CO_2^-)$ stretching vibrations, respectively. A comparison with the characteristic carboxylate stretching vibrations of free 2,2′-bipyridyl-3,3′-dicarboxylic acid shows a significant blue-shift attributed to a coordination interaction. The strong absorptions located at 1568 and 1438 cm^{-1} may be assigned to pyridyl vibrations.

Structure description

Compound **1** crystallizes in the monoclinic space group $P2_1/n$, and is isostructural with the previously reported complex $[Ni(bpdc)(H_2O)_3]\cdot H_2O$ [14, 18]. The asymmetric unit of compound **1** contains one Co(II) atom, one bpdc ligand, three coordinated water molecules (O5 – O7) and one solvate water molecule (O8), as shown in Fig. 1. Each Co(II) atom is surrounded by two nitrogen atoms and four O atoms, of which three belong to the coordinated water molecules and one to a bpdc carboxylate group. The six-coordinated Co(II) atom adopts a distorted octahedral geometry. The Co–O and Co–N bond lengths are in the ranges from 2.063(2) to 2.1305(19) Å and from 2.118(2) to 2.152(2) Å, respectively, similar to those

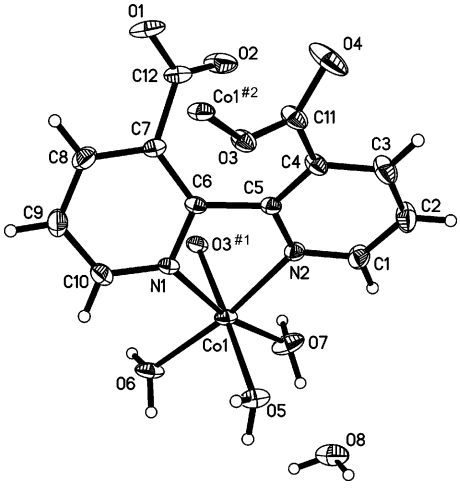


Fig. 1. ORTEP view of the coordination mode with atomic labelling for **1** (the displacement ellipsoids are drawn at the 30 % probability level).

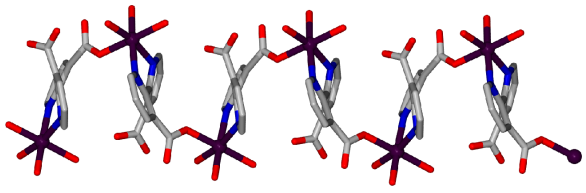


Fig. 2. The single-strand helical chain of **1**.

found in the complex of $[Co(bpdc)(H_2O)_2]$ [14]. The Co atoms are linked by the bpdc ligands into single-strand helical chains (Fig. 2), and the chains are further interlinked by strong hydrogen bonds *via* the coordinated water molecules donating hydrogen atoms to the uncoordinated carboxylate oxygen atoms (O4 and O7), to form a 2D supramolecular structure. The resulting layers are arranged in an $\cdots$ABAB$\cdots$ fashion with hydrogen bonding interactions between the coordinated water molecules (O3) and the uncoordinated carboxylate oxygen atoms (O6). Within each layer, all helical chains have the same chirality. However, helical chains of opposite chiralities construct adjacent layers, and thus **1** crystallizes in a centrosymmetric space group [14].

Magnetic properties

The magnetic susceptibilities were measured on crystalline samples of complex **1** in the temperature range from 2 to 300 K under 1 KOe using a SQUID magnetometer. Above 30 K, the reciprocal molar susceptibility χ_m^{-1} of **1** obeys the Curie-Weiss law with C = 3.12 cm^3 K mol^{-1} and Θ = −10.6 K. The negative Weiss constant indicates that antiferromagnetic exchange interactions are dominant in the helical chains.

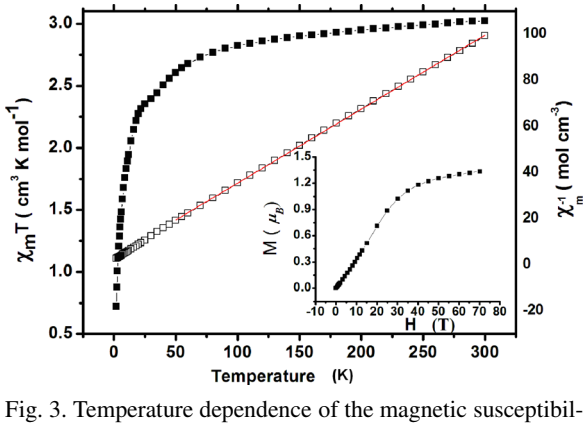


Fig. 3. Temperature dependence of the magnetic susceptibilities of **1**.

Upon lowering the temperature, the product $\chi_m T$ (at 300 K, the $\chi_m T$ value is 3.02 cm^3 K mol^{-1} corresponding to one Co(II) with $g = 2.53$) decreases gradually in the temperature range of 300 to 30 K and then abruptly reaches a value of 0.72 cm^3 K mol^{-1} at 2 K, indicating an overall weak antiferromagnetic coupling of the Co(II) ions (Fig. 3). The weak antiferromagnetic interaction has been confirmed by magnetization measurements at 2 K up to an external field strength of 8 T. At higher field, the reduced magnetization is non-saturated for a $S = 3/2$ system. The overall shape of the plot indicates a very slow decrease of the magnetization values consistent with a weak antiferromagnetic interaction.

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