

Hydrothermal *in situ* Ligand Synthesis from 1,10-Phenanthroline-5,6-dione and Characterization of 1D Coordination Polymers [Co(bpdc)(H₂O)₃] · H₂O and [Cu(bpy)V₂O₆]*

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Received Aug. 14, 2006

Hydrothermal treatment of MCl₂ (M = Co or Cu), NH₄VO₃, and 1,10-phenanthroline-5,6-dione (pdon) resulted in the formation of a duplex coordination polymer [Co(bpdc)(H₂O)₃] · H₂O (bpdc = 2,2'-bipyridine-3,3'-dicarboxylate) and a chain-like coordination polymer [Cu(bpy)V₂O₆] (bpy = 2,2'-bipyridine). X-ray single-crystal structural analysis shows that under hydrothermal conditions and in the presence of different transition metals, the organic reagent pdon was transformed *in situ* into bpdc and bpy, respectively. Mechanism of the *in situ* ligand synthesis reaction has been discussed.

Keywords Hydrothermal synthesis; *In situ*; Ligand synthesis; Coordination polymer; Mechanism

Introduction

In situ ligand synthesis has received considerable interest in coordination chemistry and organic chemistry for preparing crystalline coordination complexes, discovering new organic reactions, and understanding their mechanisms^[1–18].

Considerable attention has been paid to study the reactivity of chelate ligands such as 2,2'-bipyridine (bpy) and 1,10-phenanthroline under hydrothermal conditions and their hydroxylation reactivities were promoted by transition metal cations, especially copper (II) ions^[4–8,19,20]. 1,10-Phenanthroline-5,6-dione (pdon), which is regarded as a bis-chelate bridging ligand that incorporates the orthoquinone and α -diimine moieties has been widely studied^[21–23]. However, the study on the *in situ* ligand synthesis of bpdc from pdon is very limited^[8,24]. To our great surprise, it was observed that the hydrothermal treatment of pdon results in the formation of not only bpdc but also bpy.

This study reports the *in situ* hydrothermal syntheses of bpdc and bpy from pdon and their coordination polymers: a new duplex coordination polymer [Co(bpdc)(H₂O)₃] · H₂O (1) and a chain-like complex [Cu(bpy)V₂O₆] (2) that is similar to the compound reported by DeBord *et al.*^[25], but synthesized using a different method. The mechanism of the *in situ* ligand synthesis reactions is also reported.

Experimental

1 Chemical Reagents and Apparatus

All the chemicals purchased were of reagent grade and used without further purification. The ligand pdon was synthesized by following the method described in the literature^[26]. Elemental analyses (C, H, and N) were carried out on a Perkin Elmer 2400 CHN elemental analyzer. The crystal data were obtained using a Bruker Smart Apex II CCD diffractometer.

2 Synthesis of {[Co(bpdc)(H₂O)₃] · H₂O} (1)

A mixture of CoCl₂ · 6H₂O (23.8 mg, 0.1 mmol), pdon (21.0 mg, 0.1 mmol), NH₄VO₃ (11.7 mg, 0.2 mmol), HCl (1 mL, 0.1 mmol), and water (15 mL) was stirred for 20 min, then transferred to a 25 mL Teflon-lined stainless steel container, which was then sealed and heated to 160 °C for 72 h. After cooling to room temperature at a rate of 5 °C/h, the resulting solution was filtered and the filtrate was allowed to stand in air at room temperature for several days, yielding the red crystals of complex 1 (32% yield based on Co). Elemental anal. (%) calcd. for C₁₂H₁₄CoN₂O₈: C 38.65, H 3.78, N 7.51; found: C 38.60, H 3.82, N 7.44.

3 Synthesis of [Cu(bpy)V₂O₆] (2)

A mixture of CuCl₂ · 2H₂O (17.0 mg, 0.1 mmol), pdon (21.0 mg, 0.1 mmol), NH₄VO₃ (11.7 mg, 0.2 mmol), HCl (1 mL, 0.1 mmol), and water (15 mL) was stirred for 20 min, then transferred into a

* Supported by Natural Science Foundation of Liaoning Province (No. 20061073) and Education Committee Foundation of Liaoning Province (No. 2004F023).

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25 mL Teflon-lined stainless steel container, which was then sealed and heated to 160 °C for 72 h. After cooling to room temperature at a rate of 5 °C/h, the well blocked-shaped green crystals of complex 2 were obtained (43% yield based on V). Elemental anal. (%) calcd. for $C_{10}H_8CuN_2O_6V_2$: C 28.73, H 1.92, N 6.71; found: C 28.70, H 1.90, N 6.68.

4 X-Ray Crystallographic Analyses of Complexes 1 and 2

Structural measurements of both the complexes were carried out on a computer controlled Bruker Smart Apex II CCD diffractometer equipped with graphite-monochromated $Mo K\alpha$ radiation at radiation wavelength of 0.071073 nm using the ω scan technique. The structures were resolved by direct methods and refined with the full-matrix least-squares on F^2 using the SHELXS-97 and SHELXL-97 programs^[27,28]. All the non-H atoms were refined anisotropically, and the H atoms attached to C atoms were added at the calculated positions with the distance 0.093–0.096 nm.

Table 1 shows the crystal data and details of the collection and the refinement for complexes 1 and 2.

Tables 2 and 3 show the selected bond parameters of complexes 1 and 2.

Table 4 shows the hydrogen-bonding parameters of complexes 1 and 2, respectively.

Table 1 Crystal data and details of collection and refinement for complexes 1 and 2

Complex	1	2
Empirical formula	$C_{12}H_{14}CoN_2O_8$	$C_{10}H_8CuN_2O_6V_2$
Formula weight	373.18	417.61
Temperature/K	293(2)	293(2)
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/n$	$P\bar{1}$
a/nm	0.99822(8)	0.5826(3)
b/nm	0.92287(8)	1.0189(5)
c/nm	1.60500(13)	1.0914(5)
$\alpha/(\circ)$	90.00	89.499(6)
$\beta/(\circ)$	97.4940(10)	85.254(5)
$\gamma/(\circ)$	90.00	78.892(6)
Volume/ nm^3	1.4659(2)	0.6335(5)
Z	4	2
$D_{Calc.}/(g \cdot cm^{-3})$	1.691	2.189
$F(000)$	764.0	410.0
θ range/ (\circ)	2.28–29.03	1.87–29.22
Reflections collected	8889	3958
Independent reflections	3563	2919
Goodness-of-fit on F^2	0.933	0.945
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0377$ $wR_2 = 0.1169$	$R_1 = 0.0422$ $wR_2 = 0.1223$
R indices (all data)	$R_1 = 0.0510$ $wR_2 = 0.1302$	$R_1 = 0.0562$ $wR_2 = 0.1360$

Table 2 Selected bond lengths (nm) and bond angles (\circ) for complex 1*

Co—O1	0.2059(2)	Co—O4	0.2071(2)
Co—O3#1	0.2088(2)	Co—N2	0.2116(2)
Co—O2	0.2126(2)	Co—N1	0.2149(2)
O1—Co—O4	97.41(11)	O1—Co—N2	92.41(10)
O1—Co—O3#1	89.27(8)	O3#1—Co—N2	88.17(7)
O4—Co—N2	169.87(9)	O4—Co—O2	88.77(9)
O1—Co—O2	91.38(10)	N2—Co—O2	93.49(8)
O3#1—Co—O2	178.19(7)	O4—Co—N1	93.83(8)
O1—Co—N1	166.95(9)	N2—Co—N1	76.13(7)
O3#1—Co—N1	84.22(7)	O4—Co—O3#1	89.47(8)
O2—Co—N1	95.47(9)		

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

Table 3 Selected bond lengths (nm) and bond angles (\circ) for complex 2

Cu—O2	0.1943(3)	Cu—O3	0.1946(3)
Cu—N2	0.1984(4)	Cu—N1	0.1986(4)
Cu—O1	0.2251(4)		
O2—Cu—O3	91.88(13)	O2—Cu—N2	92.50(14)
O3—Cu—N2	163.63(15)	O2—Cu—N1	172.20(13)
O3—Cu—N1	92.93(14)	N2—Cu—N1	81.22(15)
O2—Cu—O1	95.41(13)	O3—Cu—O1	95.90(14)
N2—Cu—O1	99.38(15)	N1—Cu—O1	90.20(14)

Table 4 Hydrogen-bonding parameters (nm, \circ) for complexes 1 and 2

Comp.	D—H...A	$d(D-H)$	$d(H...A)$	$d(D...A)$	$\angle(DHA)$
1	OW—HWA...O5	0.064	0.202	0.285	171
	O4—H4B...O6	0.088	0.177	0.263	165
	OW—HWB...O7	0.099	0.209	0.287	135
	O1—H1B...OW	0.072	0.195	0.267	175
2	C4—H4A...O4	0.093	0.242	0.335	173
	C7—H7A...O4	0.093	0.248	0.339	166

Results and Discussion

1 Crystal Structure

As shown in Fig. 1, all the atoms are located at general positions in complex 1. The Co(II) site shows a distorted octahedral geometry and is ligated by two nitrogen atoms of one bpdc in a chelate mode, one carboxylate oxygen atom (O3A), from another bpdc ligand

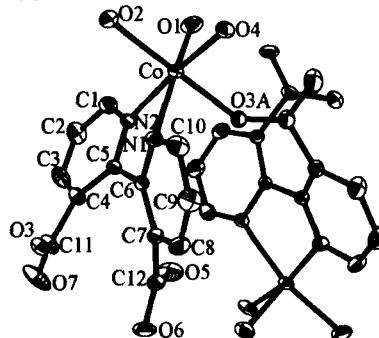


Fig. 1 Local coordination environment of cobalt (II) atom in complex 1

A: $-x - 1/2, y + 1/2, -z + 3/2$.

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