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Hydroxylation of isophthalic acid in the hydrothermal reaction of Cu^{II}-isophthalate system – Syntheses and crystal structures of two coordination polymers

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Abstract

The reaction of isophthalic acid (H_2ip) and copper nitrate under hydrothermal condition produced an in situ synthesized ligand 2-hydroxy isophthalic acid (or 2,6-dicarboxyl phenol, H_3ipO) derived from H_2ip without the presence of N-heterocyclic ligands. The hydroxylation was controlled by the temperature of hydrothermal synthesis. Two coordination polymers, $\{[Cu_5(OH)_2(ip)(ipO)_2]\cdot(H_2O)\}_n$ (**1**) and $[Cu_3(ipO)_2(H_2O)_2]_n$ (**2**) were synthesized and characterized by X-ray crystallography, IR spectra and elemental analyses. Complex **1** was assembled with both the original ligand and the in situ synthesized ligand.

Keywords: Hydrothermal synthesis; Cu^{II} complex; Isophthalic acid; Hydroxylation; Coordination polymer; Crystal structure

1. Introduction

The assembly of coordination polymers is now of great interest due to its importance both in chemistry and material science [1–11]. Among the approaches to coordination polymers, the assembly with metal ions and the in situ synthesized ligands is a striking method and a number of complexes with intriguing structures and properties have been prepared this way [5–11]. However, the ligands involved in in situ redox derivations are almost N-heterocyclic ligands such as phenanthroline, bipyridine and their derivatives [5,6]. There is only one example for non N-heterocyclic ligand yet in the presence of 4,4′-bipyridine [7]. Since it is well known that copper is a key cofactor in a vast range of chemical and biochemical catalytic systems [12–14], it is reasonable to presume that in the assembly of coordination polymers with Cu^{II} ions and appropriate ligands, e.g., isophthalic acid [15–18], the in situ derivation of ligands may occur even without the presence of N-heterocyclic ligands. As a part of our study on coordination polymers [19–23], we report here (1) the hydroxylation of isophthalic acid under Cu^{II}-isophthalate hydrothermal condition and (2) the formation of two coordination polymers: $\{[Cu_5(OH)_2(ip)(ipO)_2]\cdot(H_2O)\}_n$ (**1**) and $[Cu_3(ipO)_2(H_2O)_2]_n$ (**2**) (H_2ip = isophthalic acid, H_3ipO = 2-hydroxy isophthalic acid).

2. Experimental

2.1. Reagents and physical measurements

All reagents were commercially available and used without further purification. IR spectra were recorded

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on a Nicolet 740 FTIR spectrometer (wavelength range 4000–400 cm^{-1}, MCT-B detector, resolution 4 cm^{-1}) using KBr pellets. Analyses for C and H were performed on a CE instrument EA 1110 elemental analyzer.

*2.2. Synthesis of $\{[Cu_5(OH)_2(ip)(ipO)_2] \cdot (H_2O)\}_n$ (**1**)*

An aqueous mixture of copper nitrate trihydrate (0.24 g, 1 mmol), isophthalic acid (0.17 g, 1 mmol) and sodium hydroxide (0.08 g, 2 mmol) in 16 mL water was homogenized by stirring. The mixture was transferred into a 20-ml Teflon-lined bomb and heated to 180 °C and kept for 100 h. After cooling down to room temperature, bluish green sheet crystals of **1** were separated mechanically. FT-IR (KBr, cm^{-1}): 3638, 3443w, br, 1591vs, 1531s, 1444s, 1384vs, 1283, 1252, 1102, 1081, 762, 746s, 728, 635, 494.

*2.3. Synthesis of $[Cu_3(ipO)_2(H_2O)_2]_n$ (**2**)*

A synthesis process similar to **1** was used to prepare **2** except that the mixture was treated hydrothermally at 200 °C. Green block crystals of **1** were collected by filtration, washed with distilled water and dried in air. The yield of the product was about 25% based on Cu^{II}. Elemental analysis: *Anal.* Calc. for **2** $C_{16}H_{10}Cu_3O_{12}$: C, 32.86; H, 1.72. Found: C, 32.77; H, 1.80%. FT-IR (KBr, cm^{-1}): 3599w, 3183br, 1615vs, 1588s, 1557vs, 1447s, 1398w, 1375s, 1287, 758s, 635, 453w.

2.4. Determination of crystal structure

Single crystals of **1** and **2** were mounted on an Enraf–Nonius CAD4 diffractometer using graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) with ω scan mode and data were measured at 298 K. Structural solution and full-matrix least-square refinement based on F^2 were performed, respectively, with the SHELXS-97 [24] and SHELXL-97 [25] program packages. All the non-hydrogen atoms were refined anisotropically. Crystallographic data for **1** and **2** are summarized in Table 1. Selected bond lengths and angles for **1** and **2** are listed, respectively, in Tables 2 and 3.

Table 1
Crystallographic data for **1** and **2**

	1	**2**
Empirical formula	$C_{24}H_{14}Cu_5O_{17}$	$C_{16}H_{10}Cu_3O_{12}$
Formula weight	892.05	584.86
Crystal system	monoclinic	monoclinic
Space group	$P2_1/m$	$P2_1/c$
Unit cell dimensions		
a (Å)	5.340(1)	5.029(1)
b (Å)	21.213(4)	10.403(2)
c (Å)	11.630(2)	15.596(3)
β (°)	96.70(3)	91.97(3)
V (Å^3)	1308.6(5)	815.4(3)
Z	2	2
ρ (Mg m^{-3})	2.264	2.382
$F(0\,0\,0)$	878	578
μ(Mo Kα) (mm^{-1})	4.086	3.95
Crystal size (mm)	$0.18 \times 0.14 \times 0.03$	$0.40 \times 0.40 \times 0.18$
θ Range (°)	1.8–25.0	2.4–25.0
hkl ranges	$-6 \leqslant h \leqslant 0$, $-25 \leqslant k \leqslant 25$, $-13 \leqslant l \leqslant 13$	$-5 \leqslant h \leqslant 0$, $-12 \leqslant k \leqslant 0$, $-18 \leqslant l \leqslant 18$
Reflections collected	5142	1604
Independent reflections	2379	1430
R_{int}	0.085	0.014
Observed reflections [$I > 2\sigma(I)$]	1534	1326
Parameters	220	149
Goodness-of-Fit F^2	0.99	1.07
R_1 [$I > 2\sigma(I)$]	0.053	0.029
wR_2	0.118	0.078
R_1 (all data)	0.099	0.031
wR_2	0.138	0.081
Largest difference peak and hole (e Å^{-3})	0.76, −0.81	0.56, −0.55

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

Cu1–O1	1.934(5)	Cu3–O1d	2.476(6)
Cu1–O8	1.911(5)	Cu3–O2	1.929(6)
Cu2–O4b	1.876(6)	Cu3–O3	1.959(6)
Cu2–O5	1.884(6)	Cu3–O8	1.941(5)
Cu2–O6c	2.764(7)	Cu3–O8e	1.988(6)
Cu2–O7	1.895(6)	Cu3–O4	2.549(6)
Cu2–O7b	1.934(6)		
O1–Cu1–O1a	180.0(1)	O1d–Cu3–O2	113.0(2)
O1–Cu1–O8	92.5(2)	O1d–Cu3–O3	77.6(2)
O1–Cu1–O8a	87.5(2)	O1d–Cu3–O4	123.9(2)
O1a–Cu1–O8	87.5(2)	O1d–Cu3–O8	101.7(2)
O1a–Cu1–O8a	92.5(2)	O1d–Cu3–O8e	72.2(2)
O8–Cu1–O8a	180.0(1)	O2–Cu3–O3	92.2(2)
O4b–Cu2–O5	93.9(3)	O2–Cu3–O4	99.8(2)
O4b–Cu2–O6c	77.9(2)	O2–Cu3–O8	93.5(2)
O4b–Cu2–O7	170.7(3)	O2–Cu3–O8e	171.5(2)
O4b–Cu2–O7b	92.5(2)	O3–Cu3–O4	56.1(2)
O5–Cu2–O6c	95.5(2)	O3–Cu3–O8	174.1(2)
O5–Cu2–O7	94.2(3)	O3–Cu3–O8e	95.6(2)
O5–Cu2–O7b	171.4(3)	O4–Cu3–O8	121.0(2)
O6c–Cu2–O7	105.9(2)	O4–Cu3–O8e	81.8(2)
O6c–Cu2–O7b	91.4(2)	O8–Cu3–O8e	78.6(2)
O7–Cu2–O7b	79.0(3)		

Symmetry operation: (a) $-x, 1-y, 1-z$; (b) $1-x, 1-y, 2-z$; (c) $x-1, y, z$; (d) $x+1, y, z$; (e) $1-x, 1-y, 1-z$.

3. Results and discussion

3.1. Synthesis

The complexes $\{[Cu_5(OH)_2(ip)(ipO)_2] \cdot (H_2O)\}_n$ (**1**) and $[Cu_3(ipO)_2(H_2O)_2]_n$ (**2**) were synthesized with isophthalic acid and copper nitrate by hydrothermal reaction. In a typical hydrothermal synthesis, an aqueous mixture of copper nitrate, isophthalic acid and sodium hydroxide reacted at 180–200 °C for 100 h. During the synthe-