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# Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry

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Crystal Structures and Electrochemical Property of Two Novel Complexes  $[Cu(o-phth)(H_2O)]_n$  and  $[Co(3-nitro-phth)(4,4'-bipy)_2(H_2O)_3]_n$ 

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#### Synthesis and Reactivity in Inorganic, Metal-Organic and Nano-Metal Chemistry, 35:627–632, 2005 Copyright © 2005 Taylor & Francis, Inc. ISSN: 0094-5714 print/1532-2440 online DOI: 10.1080/15533170500225219



## Crystal Structures and Electrochemical Property of Two Novel Complexes [Cu(*o*-phth)(H<sub>2</sub>O)]<sub>n</sub> and [Co(3-nitro-phth)(4,4'-bipy)<sub>2</sub>(H<sub>2</sub>O)<sub>3</sub>]<sub>n</sub>

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A copper(II) complex with *o*-phthalate acid  $[Cu(o-phth)-(H_2O)]_n$  (1) and a cobalt(II) complex with 3-nitro-phthalic acid and 4,4'-bipyridine  $[Co(3-nitro-phth) (4,4'-bipy)_2(H_2O)_3]_n$  (2) have been synthesized. These two novel complexes were characterized by IR, X-ray crystallography diffraction. Complex 1 belongs to monoclinic crystal with C2 (1)/c space group, the complex 2 triclinic crystal with P-1. Also, electrochemical properties of these complexes and thermal decomposition process of complex 1 were investigated.

**Keywords** 4,4'-bipy, *o*-phthalate, Co(II), Cu(II), hydrogen bond

#### INTRODUCTION

In 1994, Constable introduced the term metallosupramolecular chemistry to describe the use of odd combinations of metal ions and polydentate organic ligands for the controlled assembly of large molecular structures held together by metal-ligand interactions (Christopher, 2000; Ruiz–Pérez and Sanchiz, 2000; Liu et al., 2004). The construction of metal supramolecular structures with interesting properties in catalysis, electrical conductivities and molecular-based magnets have attracted considerable attention in recent years (Ruiz-Pérez and Hernández, 2000a, 2000b; Wei and Zhang, 1996). Organic carboxylate compounds were excellent bridging ligands due to their strong coordinative capacity (bidentate through two carboxylate–oxygen and different carboxylate-bridging modes) (Moghimi et al., 2002; Liu et al., 2004). In the interest of studying coordination ability and configuration of carboxylate–oxygen with transition metals, a copper(II) complex with *o*-phthalate  $[Cu(o-phth)(H_2O)]_n$  and a cobalt(II) complex with both 3-nitro-phthalic acid and 4,4'-bipyridine  $[Co(3-nitro-phth)-(4,4'-bipy)_2(H_2O)_3]_n$  were synthesized. The crystal structures and electrochemical properties of these two complexes are discussed.

#### **RESULTS AND DISCUSSION**

The crystal data and structural determination summary for complexes 1, 2 are shown in Table 1. Their selected bond distances and bond angles are listed Tables 2 and 3 respectively.

#### **Crystal Structure of Complex 1**

Two copper atoms are all four coordination in crystal unit, but have different coordination environments (Figure 1). Four oxygen atoms from four *o*-phthalate groups coordinate to the Cu (1) center and build a nearly square geometry, which is shown in such angle data: O(4A)-Cu(1b)-O(4G) = 85.7 $(2)^{\circ}$ , O(4A)-Cu(1B)-O(1B) = 92.04 (17)^{\circ}, O(4A)-Cu(1B)- $O(1H) = 170.25 (17)^{\circ}$ . The values of the copper-oxygen bond lengths differ from each other [1.939 Å for Cu(1B)–O(4A) and Cu(1B) - O(4G), 1.949 Å for Cu(1B) - O(1B) and Cu(1B) - O(1B)O(1H)]. The angle deviation of Cu(1) from the plane is 0.1258°. Two water molecules and two oxygen atoms from two o-phthalates, each of which supplies one carboxylateoxygen, bond with Cu(2B) and form parallelogram geometry. The bond angle data include: Cu(2B) - O(5E) = 1.950 (5) Å, Cu(2B) - O(2K) #3 = 1.963 (4) Å and O(5E) - Cu(2B) - Cu(2B) $O(2H) = 89.9 \quad (2)^{\circ}, \quad O(5B) - Cu(2B) - O(2H) = 90.1 \quad (2)^{\circ}.$ Two adjacent benzene ring planes of C(2K), C(3K), C(4K), C(5K), C(6K), C(7K) and C(2H), C(3H), C(4H), C(5H), C(6H), C(7H) are parallel, the distance between two planes is 3.47 A, which shows strong  $\pi - \pi$  interaction existing in stacking crystals with the other benzene ring at an angle of 31.4°.

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	Complex 1	Complex 2	
Formula	C <sub>32</sub> H <sub>24</sub> Cu <sub>4</sub> O <sub>20</sub>	C <sub>28</sub> H <sub>25</sub> CoN <sub>5</sub> O <sub>9</sub>	
Crystal system	Monoclinic	Triclinic	
Space group	C2 (1)/c	P-1	
a/Å	26.143 (5)	7.4264 (2)	
b/Å	6.6868 (13)	11.224 (2)	
c/Å	9.823 (2)	12.836 (3)	
$\alpha/^{\circ}$	90	79.89 (3)	
$\beta/^{\circ}$	94.11	70.76 (3)	
$\gamma/^{\circ}$	90	86.07 (3)	
$V/Å^3$	1712.7 (6)	1403.2 (5)	
$Dc/Mg m^{-3}$	1.905	1.502	
Z	2	2	
$\mu/\mathrm{mm}^{-1}$	2.540	1.443	
Reflens collected	2543/1444[R(int) = 0.1305]	5066/5066[R(int) = 0.0000]	
Data/restraints	1444/0/138	5066/0/413	
R <sup>a</sup>	0.0796	0.0447	
R <sup>b</sup> <sub>w</sub>	0.1992	0.1062	
Goodness of fit on $F^2$	1.032	1.075	
$\Delta ho_{ m min}$ and $\Delta ho_{ m max}/{ m e}{ m \AA}^{-3}$	0.794  and  -1.109	0.588 and $-0.530$	

 TABLE 1

 Crystallographic data and structure refinement for complexes 1, 2

Hydrogen bond is exhibited in the crystal structure, with two hydrogen atoms in coordinating water, bond to carboxylate oxygen. The crystal structure is stabilized by weak hydrogen bond interactions and strong  $\pi - \pi$  interactions (Figure 2).

Eight Cus constitute a parallelogram unit, Cu(1A)– Cu(1D) = 20.061 Å, Cu(1A)–Cu(1E) = 11.942 Å, Cu(1D)– Cu(1A)–Cu(1E) = 24.28°, as shown in Figure 4.

#### **Crystal Structure of Complex 2**

The cobalt ion has a coordination geometry that approximates an octahedron. Each Co(II) coordinated by one nitrogen atom from 4,4'-bipyridyl, one oxygen of 3-nitro-phthalic acid and two water molecules, in the equatorial plane, while the other nitrogen atom of other 4,4'-dipyridyl and one water molecular oxygen occupy the two axial sites of the octahedron. Four Co–O bonds with approximate lengths of 2.10 Å are shorter than the other two Co–N bonds with lengths of 2.150 Å. The equatorial plane including Co(1A), O(8A), O(4A), O(9A) and N(2A) is a distorted square plane, as shown in Figure 3. The axial plane is approximately vertical to it (at an angle 91.6°). The angle:  $O(7A)-Co(1A)-N(4A) = 172.08^{\circ}$ , which shows the octahedron being asymmetric. In 4,4'-bipyridyl, two pyridine cycles are distorted with 18.6 Å, which is less space resistance. With this distortion, the

 TABLE 2

 Selected bond distances (Å) and angles (deg) for complex 1

Cu(1B)-O(4A)	1.939 (4)	Cu(1B)-O(4G)	1.939 (4)	
Cu(1B)–O(1B)	1.949 (4)	Cu(1B)-O(1H)	1.949 (4)	
Cu(2B)-O(5B)	1.950 (5)	O(1H) - C(1H)	1.267 (7)	
Cu(2B)-O(2H)	1.963 (4)	O(3H)-C(8H)	1.235 (7)	
C(2K)-C(7K)-C(8K)	123.7 (6)	C(1H)-O(1H)-Cu(1H)	131.2 (4)	
O(4A) - Cu(1B) - O(1B)	92.04 (17)	O(5E)-Cu(2B)-O(2H)	89.9 (2)	
O(4A)-Cu(1B)-O(1H)	170.25 (17)	O(5B)-Cu(2B)-O(2K)	89.9 (2)	
O(4G) - Cu(1B) - O(1B)	161.38 (7)	O(2K)-Cu(2B)-O(2H)	180.00 (15)	
O(4G)-Cu(1B)-O(4A)	85.7 (2)	O(1H)-Cu(1B)-O(1B)	91.7 (3)	

Symmetry transformations used to generate equivalent atoms: #1 - x + 1, y - 1, -z + 1/2; #2 x, y - 1, z; #3 - x + 1, y, -z + 1/2; #4 - x + 1, -y + 1, -z + 1; #5 x, -y + 1, z + 1/2; #6 x, y + 1, z.

Co(1A)-O(8A)	2.094 (2)	Co(1A)-N(2A)	2.148 (2)	
Co(1A)-O(7A)	2.105 (2)	Co(1A)-N(4A)	2.150 (2)	
Co(1A) - O(4A)	2.099 (2)	O(1A)-C(7A)	1.234 (4)	
O(8A)-Co(1A)-O(4A)	83.70 (9)	O(8A) - Co(1A) - O(7A)	97.80 (10)	
O(7A)-Co(1A)-O(9A)	91.14 (10)	O(4A)-Co(1A)-N(2A)	98.75 (9)	
O(7A)-Co(1A)-N(2A)	85.89 (10)	N(2A)-Co(1A)-N(4A)	87.19 (9)	
O(4A)-Co(1A)-O(9A)	168.09 (9)	O(8A)-Co(1A)-N(4A)	89.27 (9)	
O(8A) - Co(1A) - O(7A)	88.97 (9)	O(9A)-Co(1A)-N(4A)	93.08 (9)	
C(23A)-N(4A)-C(19A)	116.4 (3)	C(23A) - N(4A) - Co(1A)	122.06 (19)	
C(4A) - C(3A) - N(1A)	116.6 (3)	C(9A)-N(2A)-Co(1A)	122.0 (2)	
C(19A) - N(4A) - Co(1A)	121.51 (19)	C(28A)-N(5A)-C(24A)	116.3 (4)	

 TABLE 3

 Selected bond distances (Å) and angles (deg) for complex 2

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

4,4'-dipyridyl forms a dibridge framework (Figure 4). The selected bond distances and angles are shown in Table 3.

There are strong  $O-H\cdots O$  and  $O-H\cdots N$  hydrogen bonds in the crystal structure.  $O(7A)-H(7E)\cdots O(5A)$  in the crystal structure shows a 4,4'-dipyridyl coordinating to a water molecule weakly by a hydrogen bond (Figure 5). The bond lengths and angles are shown in Table 4. The structure of Co framework in complex 2, shown in Figure 6, adopts a chair conformation (Bhubon Singh et al., 2001).

#### **IR Spectra**

In the IR spectra of complex 1, a strong and broad band (O–H stretching vibration) in the  $3500-3000 \text{ cm}^{-1}$  region indicates the presence of coordinated water molecule; the medium intensity peaks at 1564, 1537 and 1488 cm<sup>-1</sup> are consistent with the existence of a benzene cycle. The other strong peaks at 1618 and  $1538 \text{ cm}^{-1}$ , and 1413 and  $1366 \text{ cm}^{-1}$  can be attributed to  $v_{as}$  COO,  $v_s$  COO, respectively. In the IR spectra of complex 2, the presence of H<sub>2</sub>O accounts



FIG. 1. The crystal structural unit of complex 1.



FIG. 2. The crystal cell structure of complex 1.

for the strong and broad band (O–H stretching vibration) in the  $3600-2800 \text{ cm}^{-1}$  region. Strong peaks at 1614 and  $1603 \text{ cm}^{-1}$  are for  $v_{as}COO$ , medium intensity peaks at 1397 and  $1382 \text{ cm}^{-1}$  are for  $v_sCOO$ , and two strong peaks at 1539 cm<sup>-1</sup> are attributed for  $v_{as}$  NO<sub>2</sub>. Additional peaks at 1344 and 1517 cm<sup>-1</sup> are attributed for  $v_sNO_2$  and C=N, respectively.



FIG. 3. The crystal structural unit of complex 2.



FIG. 4. The crystal cell structure of complex 2.

#### **Thermal Analysis**

Thermogravimetric analysis of complex 1 reveals that a weak endothermal peak appears at 149.6 °C. The whole weight loss is about 6.8% (calculated 7.3%), which suggests loss of one water molecule. A strong exothermal peak appears from 212 °C to 432 °C with weight loss of 62%, corresponding to *o*-phthalate decomposition (calculated 65%), the residue is 25.2% corresponding to CuO and organic remains.

#### **Electrochemical Analysis**

A cyclic voltammogram (CV) obtained at 0.1 V/s using 0.1 M KCl as supporting electrolyte is shown in Figure 7. The copper complex shows one pair of well-defined and stable redox waves in the potential range of  $0.8 \sim -0.1$  V and two irreversible broad waves in the range of  $-0.2 \sim -0.8$  V, whereas the sharp anodic peak observed at 0.02 V is typical



FIG. 5. The structure of metal framework in complex 1.

D–H···A	D(D-H)	$D(H \cdots A)$	$D(D \cdots A)$	<dha< th=""></dha<>
$O(8) - H(8F) \cdots O(2)$	0.78 (4)	1.93 (4)	2.700 (3)	168 (4)
$O(7) - H(7E) \cdots N(5)$	0.92 (4)	1.85 (5)	2.776 (4)	177 (4)
$O(7) - H(7F) \cdots O(3)$	0.86 (4)	1.81 (4)	2.640 (3)	162 (4)
$O(9) - H(9F) \cdots N(3)#3$	0.80 (4)	2.00 (4)	2.794 (4)	173 (4)
$O(8) - H(8E) \cdots O(2) #4$	0.95 (4)	1.77 (4)	2.713 (3)	171 (4)
$O(9) - H(9E) \cdots O(1) #4$	0.94 (5)	1.79 (5)	2.731 (3)	174 (4)
S		1 .		2

 TABLE 4

 Hydrogen bonds for complex 2 [Å and deg.]

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

for a species stripped from the electrode surface (Beatriz et al., 2001).

The effects of scan rates (v) on the peak potentials and the peak currents were investigated for the first redox couple between 0.1 to 0.5 V/s over a reduced potential range (+0.8 to -0.1 V). The values of the formal potential  $\text{E}^{0}$  $(E_{CuL_1}^0 = 0.143 \text{ V})$ , taken as the average of  $E_{pa}$  and  $E_{pc}$ , and the potential separation  $\Delta E = E_{pa} - E_{pc}(\Delta E_{CuL_1} = 137 \text{ mV})$ for the copper complex is very different due to the difference of space circumstance. The deviation from this value of  $\Delta E$ is scan-rate dependent. The variations of  $i_{\rm pa}/i_{\rm pc}$  as a function of the scan rate were analyzed, showing the current ratio change from 1.0 to 1.5 with the increase of v. The results indicate that the species undergoes a quasi-reversible redox process. In addition, it was found that ip is linearly proportional to  $v^{1/2}$ , confirming the reversible diffusion-controlled process for the electrochemical system. From the experiment, the electrode reactions are very complex, indicating that the electrode

response can be assigned to the oxidation-reduction of copper in the complexes (Hong and You, 2004).

Figure 6b shows the CV of Co(L) on the glassy carbon. The complexes produce the irreversible cathodic wave at -0.559, moreover the peak currents decrease with succeeding potential scans, suggesting an adsorbed species formation on the electrode surface. However, the process at 0.505 V is also a successive reaction, which was confirmed by performing the scan from 0.80 V to 0.20 V, and there is no wave, whereas the anodic wave is still present. The electrode reactions may be attributed to the cobalt of the complexes (Kumita et al., 1998; Desiraju, 1996).



FIG. 6. The structure of metal framework in complex 2.



FIG. 7. Cyclic voltammogram of complex 1, 2; (a) the cyclic voltammogram of complex 1 (CuL<sub>1</sub>); and (b) the cyclic voltammogram of complex 2 (CoL<sub>2</sub>).

#### EXPERIMENTAL

#### **Equipment and Measurements**

The chemicals for the syntheses of the compounds were all of analytical pure grade, purchased from Zhengzhou Chemical Reagent Company and used without further purification. IR spectra were recorded on a Nicolt IR-470 spectrophometer as KBr pellets in the range 4000–400 cm<sup>-1</sup>. Single crystal structure was measured on a Rigaku-Raxis-IV X-ray diffractometer and thermal analyses were done with a NETZCH DSC in air atmosphere from room temperature to 700°C. Cyclic voltammogram was electroanalysized with CHI650 (SHANGHAI CHENHUA).

#### Syntheses of Complexes 1, 2

Complex 1: 2 ml (0.5 M) aqueous solution of CuCl<sub>2</sub> was added to the aqueous solution containing *o*-phthalic anhydride (0.07 g, 0.5 mmol), then neutralized to pH  $\approx$  7 using 0.5 M KOH solution with stirring. The resulting mixture was run into a small vial and allowed to slowly evaporate at room temperature. A blue massive crystal suitable for single crystal X-ray diffraction analysis was obtained in one month and filtered, washed with anhydrous ethanol, and dried naturally.

With the same method mentioned above, purple crystals of complex 2 is synthesized in about one month.

#### X-Ray Crystallography

Intensity data of complexes 1, 2 were measured with a Rigaku-Raxis-IV X-ray diffractometer using monochromated Mo Ka ( $\lambda = 0.71073$  Å) radiation at 291 K. Raw data were corrected and the structure was solved using the SHELX-97 program. Non-hydrogen atoms were located by direct phase determination and subjected to anisotropic refinement. The full-matrix least-squares calculation on F<sup>2</sup> were applied on the final refinement. The refinement converged at R1 = 0.0722, wR2 = 0.1925 values for reflection with I > 2\sigma for complex 1, and R1 = 0.0447, wR2 = 0.1062 values for reflection with I > 2\sigma for complex 2. Details of crystal structure determination are summarized in Table 1. Full atomic data are available as a file in CIF format.

#### Supplementary Material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 237171, 249824 for compounds 1 and 2, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 -1223-336033; email: deposit@ccdc.cam.ac.uk.)

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