

A Novel Ni(II) Coordination Polymer Constructed From Organic Acid and Bis(imidazol) Ligand: Hydrothermal Synthesis, Crystal Structure, and Electrochemical Properties

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A novel coordination polymer, $[Ni(BDC)(bix)(H_2O)](H_2BDC =$ 1,4-benzenedicarboxylic; bix = 1,4-bis(imidazol-1-ylmethyl) benzene), has been synthesized under hydrothermal conditions and structurally characterized by elemental analyses, IR spectroscopy, and single X-ray diffraction. Ni(II) ion in a distorted octahedral coordination environment and bix plays a bidentate bridging ligand to conform the 2D square grid structure which is expands to the 3D structure through the hydrogen bonds. The thermal and electrochemical properties of complex were investigated as well.

Keywords crystal structure, electrochemical properties, Ni(II) coordination polymer, 1, 4-benzenedicarboxylic, 1, 4bis(imidazol-1-ylmethyl)benzene

INTRODUCTION

The rational design and synthesis of new discrete or polymeric metal-organic coordination architectures have received intense interest not only owing to their variety of intriguing architectures and topologies but also their potential application, such as catalysis, nonlinear optics, magnetism, and electric conductivity.^[1–12] Rational control in the construction of polymeric network remains a great challenge in crystal engineering.^[13,14] The generation of supermolecule framework rests on various factors, while the regulation and design of the ligand are the most important.

As a kind of versatile ligand, carboxylate ligands have been widely used in the construction of coordination polymers with desired structure and properties, for example rigid polycarboxylate ligands, such as benzenepolycarboxylates, pyridinepolycar-

boxylates, and flexible polycarboxylate ligands.^[15-19] On the other hand, imidazole-class ligands have been growing concern by people in the ligand design process.^[12,20-24] The ligand bix(1,4-bis(imidazole-1-ylmethyl)benzene) was an important imidazole ligand and used to construct structures for the following merit: the bis(imidazole) groups can afford two N donors to bridge metal centers, the spacer -(CH₂)- can afford flexible sites and the rigid phenyl ring spacer reduces the flexibility of the bix ligand. So the bix ligand possesses the combination rigidness and flexibility. While compared with aforementioned cased, mixed-ligand coordination polymers with aromatic carboxylates and bix have been rarely presented.^[23,24] Herein, we report the synthesis, crystal structure, thermal behaviors, and electrochemical properties of a novel polymer [Ni(BDC)(bix)(H₂O], which was constructed from the reaction of Ni(II) with mixed ligands of polycarboxylates and bix.

EXPERIMENTAL

Material and Methods

All chemicals were of reagent-grade quality obtained from commercial sources and used without further purification.

IR spectra were recorded on a Nicolet NEXUS 470-FTIR spectrophotometer (USA) as KBr pellets in the 400–4000 cm⁻¹ region. Elemental analyses (C, H, and N) were carried out on a FLASH EA1112 elemental analyzer (USA). TG-DSC measurements were performed by heating the sample from 20 to 800°C at a rate of 10°C/min on a NETZSCH STA 409PC differential thermal analyzer (Germany). Cyclic voltammetry of complex was investigated on a CHI-660B electrochemistry workstation. The surface-modified Glassy carbon electrode (GCE) was prepared as follows: 5 mg compound 1 accurately weighed was dissolved in 2 mL Nafion solution, followed by ultrasound for 15 min, and then the suspension solutions were prepared. Using a microinjector, 5 μ L suspension solutions was packed to the GCE surface, dried with infrared lamp, washed with

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TABLE 1	
Crystallographic data for complex	1

Empirical formula	C22H20N4NiO5
Formula weight	479.13
T(K)	298(2)
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P2(1)/c
a (Å)	15.5099(17)
b (Å)	6.4975(6)
c (Å)	20.2737(18)
α (°)	90.00
eta (°)	97.2180(10)
γ (°)	90.00
V (Å ³)	2026.9(3)
Z	4
$Dc (mg/m^3)$	1.570
F(000)	992
Crystal size (mm ³)	$0.44 \times 0.40 \times 0.30$
Reflections collected / unique	9830/3554 [R(int) = 0.0318]
Max. and min. transmission	0.7531 and 0.6669
Data/restraints/parameters	3554/0/362
Goodness-of-fit on F^2	1.038
Final R indices	$R_1 = 0.0336, wR2 = 0.0777$
[I > 2 sigma(I)]	
R indices (all data)	$R_1 = 0.0484, wR2 = 0.0863$

water and dried with nitrogen, and then surface-modified working electrode was obtained.

Syntheses of bix

The bis(imidazole) ligands were prepared as previously described.^[25] A solution containing imidazole (6.8 g, 100 mmol) and α, α' -dichloro-p-xylene (1.75 g, 10 mmol) in methanol (100 mL) was heated under reflux for 30 h. Removal of most of the solvent at reduced pressure gave a light yellow syrup, which was dissolved in 100 mL of aqueous K₂CO₃(13.50g). This solution upon standing yielded a crystalline of 1,4-bix, which was recrystallized from water. Anal. Calcd. for C₁₄H₁₄N₄.2H₂O: C, 61.3; H, 6.6; N, 20.4. Found: C, 61.2; H, 6.5; N, 20.3.



FIG. 1. The coordination environments for Ni ions in complex 1.

Synthesis of complex

A mixture of NiSO₄·6H₂O (0.25 mmol, 0.1315 g), H₂BDC (0.25 mmol 0.084 g), bix (0.25 mmol, 0.143 g), and NaOH (0.5 mmol, 0.02 g) and 8 mL deionized water were sealed in 25 mL Teflon-lined bomb and heated at 180°C for 72 h, then cooled to room temperature at a rate of 10°C/h. Suituable green crystals from 1 were filtered off, washed with water, and dried in air. Crystals of 1 are stable in the air. Yield: 72.6%. Anal. Calcd. for C₂₂ H₂₀ N₄ O₅ Ni (%): C: 55.10, H: 4.17, N: 11.69. Found (%): C: 54.65, H: 5.04, N: 11.95.

X-Ray Crystallography

Crystal data and experimental details for compound 1 are shown in Table 1. A green single crystal of the title compound $(0.44 \text{ mm} \times 0.40 \text{ mm} \times 0.30 \text{ mm})$ was selected and mounted on a glass fiber. All measurements were made on a Bruker Smart 1000 diffractometer (Germany) with a graphite monochromated MoK α radiation ($\lambda = 0.71073$ A). All data were collected at 298(2) K using the ω -2 θ scan mode and corrected for Lorenz polarization effects. A total of 9830 reflections in the range of $0.97 \le \theta \le 25.50$ (h: -10~10, k: -7~7, l: -23~22) and 3554 unique ones ($R_{int} = 0.0416$) were collected. The empirical

Selected bond distances (Å) and angle (°) for complex 1							
Ni(1)-O(3)	2.0236(17)	Ni(1)-N(4)	2.066(2)	Ni(1)-N(2)	2.069(2)		
Ni(1)-O(1)	2.0893(17)	Ni(1)-O(5)	2.0981(18)	Ni(1)-O(2)	2.2589(18)		
O(3)-Ni(1)-N(4)	88.16(8)	O(5)-Ni(1)-O(2)	163.00(7)	O(3)-Ni(1)-N(2)	91.36(8)		
N(4)-Ni(1)-N(2)	177.74(9)	O(3)-Ni(1)-O(1)	162.43(7)	N(4)-Ni(1)-O(1)	90.90(8)		
N(2)-Ni(1)-O(1)	88.89(7)	O(1)-Ni(1)-O(5)	102.47(7)	N(4)-Ni(1)-O(5)	87.49(8)		

TABLE 2



FIG. 2. (A) 2D rectangular structure from complex 1 at the *b*-axis. (B) Hydrogen bonds for complex 1 along the *a*-axis (bix are omitted for clarity).

absorption corrections by SADABS were carried out (University of Göttingen, Germany).

The structure was solved by direct methods and expanded by Fourier technique with SHELX-97 program (University of Göttingen, Germany).^[26] The non-hydrogen atoms were refined with anisotropic thermal parameters. The N3 and C8-C14 are disorders and the position occupancy is 0.52. The hydrogen atoms bound to carbon were placed geometrically. The selected bond distances and angles are presented in Table 2.

RESULTS AND DISCUSSION

The single-crystal structure shows that compound 1 crystallizes in group P2(1)/c. As shown in Figure 1, the fundamental unit of complex 1 is composed of a Ni(II) atom, a BDC^{2–} anion, a bix, and a water molecule. The geometry around Ni(II)

TABLE 3ydrogen bonds for complex 1							
D-H	d(D-H)	d(HA)	<dha< th=""><th>d(DA)</th><th>А</th></dha<>	d(DA)	А		
O(5)- H(5B)	0.850	1.972	138.11	2.666	O(4)		
O(5)- H(5C)	0.850	2.094	145.89	2.838	O(2) [x, y + 1, z]		

is six-coordinated in the distorted octahedron environment. For a six-coordinate Ni(II) atom, the equatorial plane is defined by three carboxylate oxygen atoms (O1, O2, and O3) from BDC^{2–} units and one oxygen atom from water molecule (the mean

FIG. 3. The 3D structure for complex $\mathbf{1}$ (dotted lines represent the hydrogen bonds).

deviation from the plane is 0.1017 Å), and the axial positions are occupied by two nitrogen atoms from imidazoles of different bix ligands. The Ni-O distances fall in the range 2.0238–2.2589 Å while the Ni-N₂ and Ni-N₄ distances are 2.069(2) Å and 2.066(2) Å, respectively (Table 2). The bond angles around central Ni ion vary from 60.84(6)° to 177.74(9)° compared with from 90° or 180° for an ideal octahedral structure.

The BDC^{2–} ligand exhibits two types of coordination modes: one carboxylate acts as a bidentate bridging ligand to chelate four-membered ring while the other shows monodentate coordination. BDC^{2–} acts as a bridging ligand and propagates the chain in a zigzag manner along 001 direction and make the angle 139° (Figure 2). The bix ligand is present in an anti conformation and bridges the Ni(II) of the adjacent sheets to conform 2D square grid structure to get two quadrangle channels at 1.08*0.55 nm² and 1.08*0.39 nm² (Figure 2).

The coordinated water molecule, O(5), acts as hydrogenbond donors to O₄ and O₂ of carboxylic ion, O(5)-H(5)...O(4) (2.666Å) and O(5)-H(5)C...O(2) (2.838Å; Table 3). The 2D square grid structure conforms to 3D structure through the hydrogen bond (Figure 3)

IR and Thermal Analysis

The IR analysis of the complex is consistent with their crystal analysis. The band attributable to H_2O occurs at 3384 cm⁻¹. For the complex, the 1564 cm⁻¹ and 1379 cm⁻¹ are the *vas*(OCO) and *vs*(OCO) stretch vibration, respectively. The undeprotonated carboxyl group of free H_2BDC at 1680 cm⁻¹ disappear. The absorption bands at 1513 cm⁻¹ and 1422 cm⁻¹ can be assigned to the vibrations of the C=N and C=C in the imidazole ring.

The TG curve (Figure 4) shows that there two weight-loss processes. The one (3.85%) below 281°C is attributed to the loss of one coordinated water molecule (calcd. 3.75%). From 396 to 4566°C there is a sharp weight-loss step that can be attributed

FIG. 4. Thermogravimetric curve of complex 1.

FIG. 5. Cyclic voltammogram of complex 1 at 20 mVs⁻¹ scan rates.

to the decomposition of organic ligands. Then to 800° C, there is NiO left (found 16.13%, calcd. 15.59%).

Electrochemical Properties

The complex electrochemical behaviors were investigated in a three-electrode system, using a surface-modified glassy carbon electrode(GCE; φ 3 mm) working electrode, a Pt wire auxiliary electrode, and a saturated calomel electrode as the reference electrode.

Surface-modified GCE by complex **1** was used to study its redox properties in the solid state by cyclic voltammetry, and the result obtained is shown in Figure 5. The electrochemical behaviors were studied in phosphate buffer solution (pH = 8). In the potential range of +1.5V to -1.2V with 20 mVs⁻¹ scan rate, there is a pair of redox peaks corresponding to the redox couple of Ni(II)/Ni (Epa = -0.241 V and Epc = -0.691 V). The half-wave potentials potential (E $\frac{1}{2} = (E_{pa} + E_{pc})/2)$ is -0.466 V.The peak-to-peak separation (ΔE) is 0.450 V and the i_{pc}/i_{pa} is 9.48, exhibiting a quasireversible electrode process. The cathode peak is higher than the anode peak which shows that the Ni(II) is reduced easily and oxidized hardly.

SUPPLEMENTARY MATERIALS

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC No.826989 for compound 1. 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; E-mail: deposit@ccdc.cam.ac.uk or www: http:// www.ccdc.cam.ac.uk).

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