

UDC 548.73:541.49:546.56

STRUCTURE AND CHARACTERIZATION OF A 1D DOUBLE CHAIN COPPER (II) COMPLEX $\{[\text{Cu}(\text{BIX})_2(\text{H}_2\text{O})_2](\text{PhCOO})_2\}_n$ **G.-H. Cui, J.-C. Geng, T.-F. Liu, X. Peng, C.-H. He, C.-H. Jiao***College of Chemical Engineering, Hebei United University, Tangshan, Hebei, P. R. China,
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A novel copper(II) complex $\{[\text{Cu}(\text{BIX})_2(\text{H}_2\text{O})_2](\text{PhCOO})_2\}_n$ (**1**) (BIX = 1,4-bis(imidazole-1-methyl)benzene) is synthesized and characterized by elemental analysis, IR, TG, and single crystal X-ray diffraction. Complex **1** crystallizes in the triclinic crystal system with the *P*-1 space group, $Z = 1$, $a = 9.465(2) \text{ \AA}$, $b = 9.703(2) \text{ \AA}$, $c = 12.060(2) \text{ \AA}$, $\alpha = 77.26(3)$, $\beta = 70.37(3)$, $\gamma = 67.14(3)^\circ$, and $V = 956.1(3) \text{ \AA}^3$. The crystal structural analysis of complex **1** shows that the copper center is six-coordinated in an elongated octahedral geometry by four N atoms from four different BIX and two O atoms from two water molecules; two neighboring Cu(II) cations are bridged by two BIX extending into an infinite 1D double chain structure.

Key words: 1,4-bis(imidazole-1-methyl)benzene, benzoate, coordination polymers, copper complex.

INTRODUCTION

In the past decade, coordination polymers constructed by metal ions and organic linkers have attracted great interest not only due to their variable topological structures, but also their intriguing potential applications such as ion exchange, catalysis, nonlinear optics, and gas sorption [1, 2]. However, the structure of a coordination polymer may be affected by many factors, such as coordinated geometry of metal, solvent system, counterions, bridged ligands, and so on, in which the selection of organic bridged ligands is the key factor to influence the architectures and properties of resulting coordination polymers [3, 4]. Thus, the studies in this field focus on the preparation of bridged ligands with novel structures and the examination of the relationship between the structures of ligands and the structures and functionalities of the corresponding coordination polymers.

At present, the design and construction of coordination polymers with flexible bridged ligands have attracted great attention. Due to their structural sensitivity and diversification, these flexible bridged ligands can afford good opportunities to investigate the details of the self-assembly process and provide more information on the predicted structures with tailored functions of coordination polymers [5].

We have been interested in the preparation of coordination polymers with flexible imidazole-containing ligands for several years [6]. Some complexes of the BIX ligand with a variety of architectures such as interpenetrating 1D or 2D coordination motifs, interpenetrating 2D networks, and 3D α -Po-type nets have been reported in the literature [7–12]. In this paper, we present the novel 1D double chain copper(II) complex $\{[\text{Cu}(\text{BIX})_2(\text{H}_2\text{O})_2](\text{PhCOO})_2\}_n$ **1**. Its crystal structure was determined by the single crystal X-ray diffraction analysis. The elemental analysis, IR, TG were also used to investigate complex **1**.

EXPERIMENTAL

Materials and physical measurements. Commercially available starting materials of analytical grade were used as received. The BIX ligand was prepared according to the description in the literature [13]. Elemental analyses were taken on a Perkin-Elmer 240C analyzer. IR spectra (KBr pellets) were obtained on a FT-IR 170 SX (Nicolet) spectrometer. Thermal stability (TG) studies were carried out on a NETZSCH TG 209 thermal analyzer from room temperature to 800° under N₂ with a heating rate of 10°/min.

Synthesis of complex 1. Copper(II) hydroxide (97.5 mg, 1 mmol) and benzoic acid (244 mg, 2 mmol) in 30 ml of the methanol/water (1:1) mixed solvent were heated under reflux conditions for 1 h, when filtered gave the blue solution. A methanol solution of BIX (476 mg, 2 mmol) was added to the above blue solution; the final mixture was stirred for 20 min. The resultant clear blue-violet solution was allowed to stand at room temperature. After one month, blue crystals suitable for the single crystal X-ray diffraction analysis were obtained. Yield: 607 mg (*ca* 74.2 % based on copper(II) hydroxide). Anal. calc. for CuC₄₂H₄₂N₈O₆: C 61.64; H 5.17; N 13.69; found: C 62.45; H 5.24; N 13.52 %. IR (KBr pellets, cm⁻¹): 3359(s), 3129(s), 1690(m), 1600(s), 1375(s), 1245(s), 1106(s), 1012(m), 946(m), 832(m), 728(s), 656(s), 609(m), 469(w).

Table 1

Crystal data and structure refinement details for complex 1

| | |
|------------------------------------------------------------------------------------------------|--------------------------------------------------------------------|
| Complex | 1 |
| Empirical formula | CuC ₄₂ H ₄₂ N ₈ O ₆ |
| Formula weight | 818.39 |
| Temperature, K | 293(2) |
| Wavelength, Å | 0.71073 |
| Crystal colour | Blue block |
| Crystal size, mm | 0.24×0.23×0.16 |
| Crystal system | Triclinic |
| Space group | <i>P</i> -1 |
| Unit cell dimensions: <i>a</i> , <i>b</i> , <i>c</i> , Å; α , β , γ , deg. | 9.465(2), 9.703(2), 12.060(2); 77.26(3), 70.37(3), 67.14(3) |
| Volume, Å ³ | 956.1(3) |
| <i>Z</i> | 1 |
| Calculate density, Mg/m ³ | 1.421 |
| Absorption coefficient, mm ⁻¹ | 0.632 |
| <i>F</i> (000) | 427 |
| θ range for data collection, deg. | 3.41 to 25.02 |
| Index ranges | $-11 \leq h \leq 10$, $-11 \leq k \leq 11$, $-14 \leq l \leq 14$ |
| Reflections collected | 7742 |
| Independent [<i>R</i> _{int}] | 3285 |
| Completeness to $\theta = 25.02$ | 97.5 % |
| Refinement method | Full-matrix least-squares on <i>F</i> ² |
| Data / restraints / parameters | 3285 / 0 / 267 |
| Goodness-of-fit on <i>F</i> ² | 1.066 |
| Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)] | <i>R</i> ₁ = 0.0303, <i>wR</i> ₂ = 0.0787 |
| <i>R</i> (all data) | <i>R</i> ₁ = 0.0332, <i>wR</i> ₂ = 0.0803 |
| Largest diff. peak and hole, e ⁻ ·Å ³ | 0.199 and -0.277 |

$$R_1 = \frac{\sum ||F_0| - |F_c||}{\sum |F_0|}; \quad wR_2 = \left\{ \frac{\sum [w(F_0^2 - F_c^2)]}{\sum [w(F_0^2)]} \right\}^{1/2}.$$

X-Ray crystallography. A suitable single crystal of the title complex was mounted on the top of a glass fiber with epoxy cement for the X-ray measurement. The crystallographic data collections for complex **1** were carried out on a Bruker Smart 1000 CCD diffractometer with graphite-monochromatized MoK α radiation ($\lambda = 0.71073 \text{ \AA}$) and ω -2 θ scan mode at 293 K. All absorption corrections were applied using the SADABS program [14]. The structure was solved by direct methods and refined anisotropically by the full-matrix least-squares technique using the Bruker's SHELXTL program package [15]. All non-hydrogen atoms were refined with anisotropic displacement parameters. The H atoms of water were located on a difference Fourier map, while other H atoms were included in the calculated positions and refined with anisotropic thermal parameters riding on the corresponding parent atoms. Details of the data collection and structure refinement for the crystals of **1** are summarized in Table 1.

RESULTS AND DISCUSSION

Synthesis and general characterization. The single crystal of complex **1** was obtained by the reaction of copper(II) hydroxide, benzoic acid, and BIX at the 1:2:2 molar ratio in the methanol/water system by slow volatilization of the solvent. The results of elemental analysis for complex **1** are highly consistent with the theoretical requirements of their compositions (X-ray analysis results). The title compound is stable in air. In the IR spectra of complex **1**, a broad strong band observed at 3359 cm^{-1} is assigned to the stretching vibrations of the hydroxyl group in water molecules; the value is much smaller than that of crystalline water (near 3500 cm^{-1}), owing to the participation of water molecules with strong hydrogen bonds in coordination with metal ion in complex **1**. The absorption peaks of 1509 cm^{-1} , 1245 cm^{-1} , and 1106 cm^{-1} show the presence of the imidazole ring, and strong sharp bands at 3129 cm^{-1} and 728 cm^{-1} further indicate the C—H stretching and bending frequencies of the imidazole ring. The characteristic bands of the carboxylate group are observed at 1690 cm^{-1} for the anti-symmetric vibration and at 1375 cm^{-1} for the symmetric vibration. The antisymmetric and symmetric stretching vibrations of the carboxylate group of benzoate in complex **1** are slightly shifted in contrast with those of free benzoic acid, indicating that the carboxylate group is not coordinated to the metal ion in complex **1**, which is in good agreement with the observed X-ray structure.

Crystal structure of complex 1. The structure of **1** consists of 1D cationic polymeric chains $\{[\text{Cu}(\text{BIX})_2(\text{H}_2\text{O})_2]^{2+}\}_n$ and uncoordinated PhCOO^- anions. The coordination environment of the Cu(II) center is depicted in Fig. 1, and the selected bond lengths and angles are listed in Table 2. From the structural data of complex **1**, we can see that the Cu1 center is six-coordinated by four N atoms from four different BIX ligands with Cu1—N distances of $2.003(15) \text{ \AA}$ and $2.006(16) \text{ \AA}$ and two O atoms from two different water molecules with Cu1—O distances of $2.718(2) \text{ \AA}$ to form an elongated octahedral geometry. The four *cis*-coordination angles vary from $88.08(7)^\circ$ to $95.60(8)^\circ$, and all the three *trans*-coordination angles are 180° . It is noteworthy that Cu—O coordination bonds are very weak; the distance is much longer than that of Cu—N in complex **1**. Four N donors from BIX

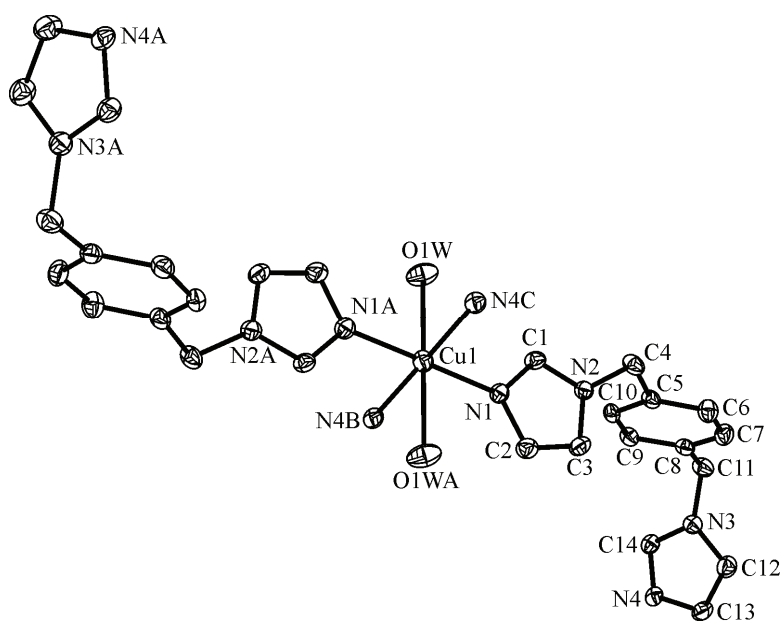


Fig. 1. Coordination environment around the Cu(II) center in **1** at 30% probability

Table 2

Selected bond lengths (Å) and bond angles (deg.) for complex 1

| | | | | | |
|---------------|----------|----------------------|------------|---------------------|-----------|
| Cu(1)—N(1) | 2.003(2) | O(1W)—Cu(1)—N(1) | 89.49(7) | O(1W)—Cu(1)—N(4)#2 | 84.41(8) |
| Cu(1)—N(4)#2 | 2.006(2) | O(1W)—Cu(1)—N(4)#3 | 95.60(8) | O(1W)—Cu(1)—O(1W)#1 | 180.00(9) |
| Cu(1)—O(1W) | 2.718(2) | O(1W)—Cu(1)—N(1)#1 | 90.51(7) | N(1)—Cu(1)—N(4)#2 | 88.08(7) |
| Cu(1)—N(1)#1 | 2.003(2) | N(1)—Cu(1)—N(4)#3 | 91.92(7) | N(1)—Cu(1)—O(1W)#1 | 90.51(7) |
| Cu(1)—N(4)#3 | 2.006(2) | N(1)—Cu(1)—N(1)#1 | 180.00(9) | N(4)#2—Cu(1)—N(4)#3 | 180.00(9) |
| Cu(1)—O(1W)#1 | 2.718(2) | N(4)#2—Cu(1)—O(1W)#1 | 95.60(8) | N(4)#2—Cu(1)—N(1)#1 | 91.92(7) |
| | | N(4)#3—Cu(1)—O(1W)#1 | 84.41(8) | N(4)#3—Cu(1)—N(1)#1 | 88.08(7) |
| | | O(1W)#1—Cu(1)—N(1)#1 | 89.49(7) | Cu(1)—N(1)—C(1) | 123.50(1) |
| | | Cu1—N(1)—C(2) | 130.18(12) | | |

Symmetry codes: #1, $-x+1, -y+2, -z-1$; #2, $x+1, y, z-1$; #3, $-x, -y+2, -z$.

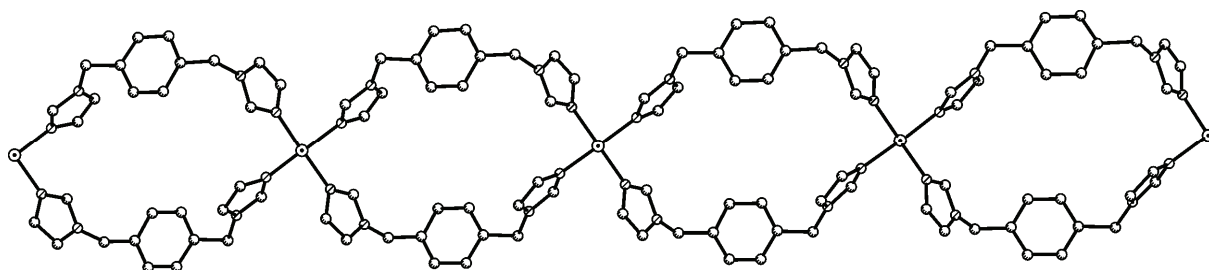


Fig. 2. Cationic double chain of the complex with 28-membered macrometallacyclic repeating units

ligands are located in the basal plane, and two O donors are in the axial position. On the equatorial plane, four Cu—N bond lengths and four *cis* N—Cu—N angles are so close that we can take the basal position as a square plane. The BIX ligand in **1** adopts *cis*-coordinated conformation with the dihedral angle of the two adjacent imidazole rings being 62.4°; the two neighboring Cu atoms are bridged by two BIX ligands through Cu—N bonds to form a 28-membered macrocycle with the Cu···Cu distance of 12.583 Å. This 28-membered macrocyclic unit is constantly repeated, resulting in a 1D infinite double-chain structure (Fig. 2).

In the complex **1** unit there are two uncoordinated benzoic acid anions that play two roles. One is to keep the system charge balance, another is to form hydrogen bonding interactions with the coordinated water molecules and imidazole rings of BIX ligands to extend and stabilize the crystal structure of **1**. The O atom of the carboxylate group of the benzoic acid anion can form two hydrogen bonding interactions between two coordinated water molecules (O1w—H1wA···O2 and O1w—H1wB···O2) with O1w···O2 distances of 2.907(3) Å and 2.789(3) Å respectively. Another O atom of the carboxylate group of the free benzoic acid anion forms two weak hydrogen bonding interactions with two C

Table 3

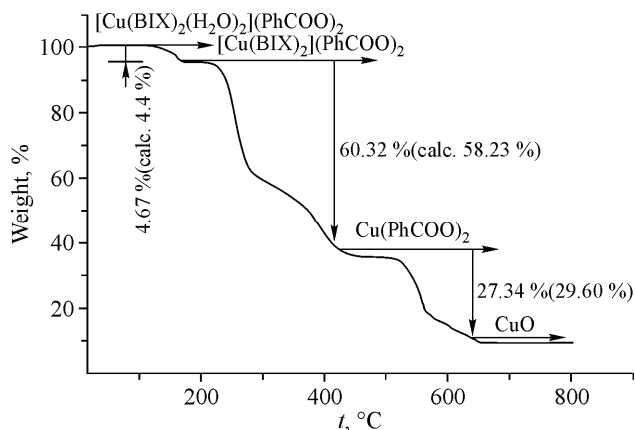
Hydrogen bond lengths (Å) and angles (deg.) for complex 1

| D—H···A | Dist. (D—H) | Dist. (H···A) | Dist. (D···A) | Angle (D—H···A) |
|---------------|-------------|---------------|---------------|-----------------|
| O1W—H1WA···O2 | 0.75(4) | 2.16(4) | 2.907(3) | 169(4) |
| O1W—H1WB···O2 | 0.79(4) | 2.01(4) | 2.789(3) | 170(3) |
| C2—H2A···O1 | 0.93(4) | 2.42(4) | 3.299(3) | 157(4) |
| C14—H14A···O1 | 0.93(4) | 2.22(4) | 3.109(3) | 160(3) |

Fig. 3. TGA curve of **1**

atoms of two imidazole rings coordinated to the same metal ion (C2—H2A···O1 and C14—H14A···O1) with C2···O1 distances of 3.299(3) Å and C14···O1 distances of 3.109(3) Å respectively. The hydrogen bonding interactions as listed in Table 3.

TG analysis. From the TG curve observed, we can find three weight loss processes of complex **1** between 128.6° to 650°. The first weight loss of 4.67 % from 128.6° to 163.8° corresponds to a gradual release of coordinated water molecules (calc. 4.40 %). The second weight loss appeared from 163.9° to 430.5°, implying the loss of two BIX ligands in the crystal unit (observed 60.32 %, calc. 58.23 %). The last temperature range of the decomposition of complex **1** is from 430.5° to 650.1°, corresponding to the loss of two benzoic acid anions, resulting in copper(II) oxide where the weight loss is 27.34 % (calc. 29.60 %). After 650.1°, the curve is relatively flat to 800°.



CONCLUSIONS

Novel 1D double chain coordination polymer **1** was synthesized by the solvent-volatile method and structurally determined by the single crystal X-ray diffraction analysis. The element and IR analyses were in good agreement with the theoretical requirements of their compositions. The thermal stability of **1** is also investigated by the TG analysis.

Acknowledgements. X-ray diffraction file for **1** in CIF format has been submitted to the Cambridge Crystallographic Data Center as the supplementary publication, CCDC No. 771099. This data can be freely obtained from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk or on the web <http://www.ccdc.cam.ac.uk>.

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