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The Unexpected Synthesis, Crystal Structure, and Thermal Stability of a Copper(II) Complex Derived from 2-[(2-Phenylaminoethylimino)methyl]benzoic Acid

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The Unexpected Synthesis, Crystal Structure, and Thermal Stability of a Copper(II) Complex Derived from 2-[(2-Phenylaminoethylimino)methyl]benzoic Acid

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A new mononuclear copper(II) complex, [Cu(PIBA)₂(OH₂)], where PIBA is the anionic form of 2-(1-phenylimidazolidin-2yl)benzoic acid, has been unexpectedly obtained from the reaction of 2-formylbenzoic acid, *N*-phenylethane-1,2-diamine, and copper perchlorate in methanol. The complex was characterized by elemental analysis, infrared spectrum, and single-cyrstal X-ray diffraction. The complex crystallizes in the triclinic space group *P*-1, with unit cell dimensions a = 11.812(2) Å, b = 11.884(2) Å, c = 22.799(3) Å, $\alpha = 89.168(2)^\circ$, $\beta = 87.290(2)^\circ$, $\gamma = 88.604(2)^\circ$, V = 3195.5(10) Å³, Z = 4, $R_1 = 0.0775$, and $wR_2 = 0.1647$. The Cu atom in the complex is five-coordinated in a square pyramidal geometry by two carboxylate O and two imidazolidine N atoms from two PIBA ligands, and by one water O atom. The thermal stability of the complex has also been determined.

Keywords copper(II) complex, crystal structure, synthesis, thermal stability

INTRODUCTION

Metal complexes containing Schiff bases have been of great interest for a long time due to their importance in the fields of coordination chemistry related to catalysis and enzymatic reactions, magnetism and molecular architectures.^[1–5] In recent years, a large number of copper(II) complexes with Schiff bases derived from salicylaldehyde and its derivatives have been reported.^[6–9] 2-Formylbenzoic acid is a structurally similar compound to salicylaldehyde, however, no complexes with the Schiff bases derived from 2-formylbenzoic acid have been reported so far. As an exploration of the work on the preparation of the complexes with such ligands, in the present paper, a new mononuclear copper(II) complex, [Cu(PIBA)₂(OH₂)], where PIBA is the anionic form of 2-(1-phenylimidazolidin-2-yl)benzoic acid (HPIBA; Scheme 1), has been unexpectedly obtained from the reaction of 2-formylbenzoic acid, *N*-phenylethane-1,2-diamine, and copper perchlorate in methanol.

SCH. 1. The ligand HPIBA

OH



Materials and Measurements

Commercially available 2-formylbenzoic acid and *N*-phenylethane-1,2-diamine were purchased from Aldrich (Shanghai, China) and used without further purification. Other solvents and reagents were made in China and used as received. C, H, and N elemental analyses were performed with a Perkin-Elmer elemental analyzer (Nanjing University, China). The infrared spectra were recorded on a Nicolet AVATAR 360 spectrometer (Liaoning Normal University, China) as KBr pellets in the 4000–400 cm⁻¹ region. Thermal stability analysis was performed on a Perkin-Elmer Pyris Diamond TG-DTA thermal analyses system (Nanjing University, China).

Synthesis of the Complex [Cu(PIBA)₂(OH₂)]

2-Formylbenzoic acid (1.0 mmol, 0.150 g), NEt₃ (1.0 mmol, 0.101 g), and *N*-phenylethane-1,2-diamine (1.0 mmol, 0.136 g) were dissolved in methanol (20 mL) with stirring. The mixture was stirred for 30 min at room temperature. To the above mixture was added with stirring a methanol solution (10 mL) of copper perchlorate (1.0 mmol, 0.373 g). The final mixture was further stirred for 1 h, and filtered. Green block-shaped single crystals of the complex were formed by slow evaporation of the solution. Yield: 63% on the basis of 2-formylbenzoic acid. Anal. Calcd. for $C_{32}H_{32}CuN_4O_5$ (FW 616.2): C, 62.4; H, 5.2; N, 9.1. Found: C, 62.2; H, 5.4; N, 9.0%.

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 TABLE 1

 Crystallographic and experimental data for the complex

Formula	C ₃₂ H ₃₂ CuN ₄ O ₅		
FW	616.2		
Crystal shape/color	block/green		
Crystal size/mm	$0.25 \times 0.23 \times 0.23$		
Crystal system	Triclinic		
Space group	<i>P</i> -1		
a/Å	11.812(2)		
b/Å	11.884(2)		
c/Å	22.799(3)		
$\alpha /^{\circ}$	89.168(2)		
β /°	87.290(2)		
γI°	88.604(2)		
V/Å ³	3195.5(10)		
Ζ	4		
T/K	298(2)		
$\mu/\text{mm}^{-1}(\text{Mo-K}\alpha)$	0.727		
$D_c/\mathrm{g~cm}^{-3}$	1.281		
Reflections/parameters	13628/781		
Restraints	10		
Observed reflections $[I \ge 2\sigma(I)]$	4823		
<i>F</i> (000)	1284		
T _{min}	0.8391		
T _{max}	0.8506		
Goodness of fit on F^2	0.941		
$R_1, wR_2 \ [I \ge 2\sigma(I)]^{\mathrm{a}}$	0.0775, 0.1647		
R_1 , wR_2 (all data) ^a	0.2313, 0.2290		

 ${}^{a}R_{1} = \sum ||F_{o}| - |F_{c}|| / \sum |F_{o}|, wR_{2} = [\sum w(F_{o}^{2} - F_{c}^{2})^{2} / \sum w(F_{o}^{2})^{2}]^{1/2}.$

Diffraction intensities for the complex were collected at

298(2) K using a Bruker SMART 1K area detector (Shan-

dong University of Technology, China) with MoK α radiation

 $(\lambda = 0.71073 \text{ Å})$. The collected data were reduced using the

SAINT program,^[10] and multiscan absorption corrections were

performed using the SADABS program.^[11] The structure was

solved by direct methods and refined against F^2 by full-matrix least-squares methods using the SHELXTL program.^[12] All of

the non-hydrogen atoms were refined anisotropically. The water

and amino H atoms in the complex were located in a difference

Fourier map and refined isotropically, with O-H, N-H, and

H...H distances restrained to 0.85(1), 0.90(1), and 1.37(2) Å,

respectively. All other H atoms were placed in idealized posi-

Data Collection, Structural Determination,

and Refinement

 TABLE 2

 Selected bond lengths (Å) and angles (°)

Bond lengths			
Cu1–O2	1.947(4)	Cu1–O3	1.947(5)
Cu1–N1	2.043(6)	Cu1–N3	2.039(6)
Cu1–O9	2.306(5)	Cu2–O5	1.954(4)
Cu2–O7	1.954(4)	Cu2–N5	2.034(6)
Cu2–N7	2.024(6)	Cu2-O10	2.340(5)
Bond angles			
O3–Cu1–O2	178.9(2)	O3-Cu1-N3	89.5(2)
O2-Cu1-N3	90.3(2)	O3-Cu1-N1	89.8(2)
O2-Cu1-N1	90.3(2)	N3-Cu1-N1	177.7(2)
O3–Cu1–O9	91.3(2)	O2-Cu1-O9	89.8(2)
N3-Cu1-O9	90.0(2)	N1-Cu1-O9	92.2(2)
O7–Cu2–O5	178.9(2)	O7-Cu2-N7	90.8(2)
O5-Cu2-N7	90.0(2)	O7-Cu2-N5	90.9(2)
O5-Cu2-N5	88.3(2)	N7-Cu2-N5	177.3(2)
O7-Cu2-O10	87.1(2)	O5-Cu2-O10	93.7(2)
N7-Cu2-O10	92.1(2)	N5-Cu2-O10	90.1(2)

tions and constrained to ride on their parent atoms. The crystallographic data for the complex are summarized in Table 1. Selected bond lengths and angles are given in Table 2. Hydrogen bonding information is given in Table 3. Crystallographic data for the complex have been deposited with the Cambridge Crystallographic Data Center (CCDC 867495).

RESULTS AND DISCUSSION

Synthesis of the Complex

The complex was prepared by the reaction of 2formylbenzoic acid, NEt₃, *N*-phenylethane-1,2-diamine, and copper perchlorate in ethanol, as shown in Scheme 2. It is interesting that the formyl group of 2-formylbenzoic acid linked to both the amine and the imine N atoms of *N*-phenylethane-1,2-diamine during the reaction, which was seldom seen for the preparation of complexes with Schiff bases derived from other aldehydes.

Structure Description of the Complex

The asymmetric unit of the complex contains two independent mononuclear copper(II) complex molecules, as shown in Figures 1 and 2, respectively. The Cu atom in each molecule is in a square pyramidal coordination, with two carboxylate O and two imidazolidine N atoms from two PIBA ligands defining the



SCH. 2. Preparation of the complex.



FIG. 1. The Cu1 complex molecule of the complex at 30% probability displacement. The carbonyl H atoms have been omitted for clarity.

TABLE 3 Hydrogen-bond geometry for the complex (Å, $^{\circ}$)						
<i>D</i> –H…A	D–H	Н…А	D····A	D–H…A		
010–H10D…O8 ⁱ	0.85(1)	2.06(3)	2.868(9)	158(7)		
N7–H7A…O8 ⁱ	0.90(1)	2.14(4)	2.950(7)	149(6)		
O10-H10C…O6 ⁱⁱ	0.85(1)	2.55(6)	2.948(8)	110(5)		
N5–H5A…O6 ⁱⁱ	0.90(1)	2.13(2)	3.028(7)	171(7)		
O9–H9D…O1 ⁱⁱⁱ	0.85(1)	2.23(5)	2.800(7)	125(5)		
N1-H1A…O1 ⁱⁱⁱ	0.90(1)	2.22(3)	3.050(7)	154(6)		
N3–H3A…O4 ^{iv}	0.90(1)	2.29(4)	3.081(7)	147(6)		
O9–H9C…O4 ^{iv}	0.85(1)	2.04(3)	2.811(8)	149(6)		

Symmetry codes: (i) 1 - x, 2 - y, 2 - z; (ii) 1 - x, 1 - y, 2 - z; (iii) 1 - x, 1 - y, 1 - z; (iv) 2 - x, 1 - y, 1 - z.

basal plane, and with one water O atom occupying the apical position. The angles between the apical and the four basal donor atoms range from 89.8(2) to $92.2(2)^{\circ}$ for Cu1 and from 87.1(2) to $93.7(2)^{\circ}$ for Cu2, and the perpendicular angles of the basal plane range from 89.5(2) to $90.3(2)^{\circ}$ for Cu1 and from 88.3(2) to $90.9(2)^{\circ}$ for Cu2, indicating the difference from the ideal values of 90° . The apical bonds are much longer than the basal bonds. The Cu atoms deviate from the least-squares planes defined by the basal donor atoms by 0.029(1) Å for Cu1, and 0.025(1) Å for Cu2, toward the apical donor atoms. Within the ligands PIBA, the dihedral angles between the two benzene rings C1-C6 and C11-C16, C17-C22 and C27-C32, C33-C38 and C43-C48, and C49-C54 and C59 and C64 are 90.7(3)°, 88.1(3)°, 91.9(3)°, and $92.5(3)^{\circ}$, respectively. The imidazolidine groups adopt envelope shape, with the secondary amino N1, N3, N5, and N7 atoms deviate from the least-squares planes defined by the remaining four atoms by 0.509(2) Å, 0.523(2) Å, 0.533(2) Å, and 0.499(2) Å, respectively. The dihedral angles between the carboxylate



FIG. 2. The Cu2 complex molecule of the complex at 30% probability displacement. The carbonyl H atoms have been omitted for clarity.



FIG. 3. The crystal structure of the complex, viewed along the c-axis. Hydrogen bonds are shown as dashed lines.

planes with the benzene rings they attached are in the range $52.3(3)-54.7(3)^{\circ}$.

The coordination number 5 for copper(II) complexes is very common and usually presents either a square pyramidal or a trigonal bipyramidal geometry, or any of the distorted intermediate geometries. For a pentacoordinated metal center, the distortion of the coordination environment from square pyramidal to trigonal bipyramidal can be calculated from the Addison distortion index, τ , which defined as $\tau = (\beta - \alpha)/60$, where α and β are the two largest coordinate angles, and $\tau = 0$ represents perfect square pyramidal, $\tau = 1$ represents perfect trigonal bipyramidal.^[13] In the present complex, the calculated τ values are 0.020 for Cu1 and 0.027 for Cu2, suggesting they are square pyramidal geometry, instead of trigonal bipyramidal.



FIG. 4. DT-TGA curve of the complex.

IR Spectrum

The O–H and N–H vibrations are observed as weak bands at 3468 and 3136 cm⁻¹, respectively. The characteristic feature of the infrared spectrum of the complex is the positions of the ν_{as} (COO) and ν_{s} (COO) bands at 1594 and 1380 cm⁻¹, respectively. Their difference, $\Delta = 214$ cm⁻¹, is characteristic of the monodentate coordination mode of the carboxylate groups.^[14] The weak bands located at the low numbers may be assigned to the ν (Cu–O) and ν (Cu–N).

Thermal Stability

Differential thermal (DT) and thermal gravimetric analyses (TGA) were conducted to examine the stability of the complex. The first step started at about 100°C and was completed at 130°C, corresponding to the loss of the coordinated water molecule. The observed weight loss of 3.1% is close to the calculated value of 2.9%. The second step, from 164° C to 412° C, corresponds to the loss of the benzene and the benzoate groups of the ligands. The observed weight loss of 63.3% is close to the calculated value of 64.0%. The last step, from 412° C to 654° C, corresponds to the loss of the imidazolidine groups, and the formation of the final product (CuO). The observed weight loss of 19.0% in this step is close to the calculated value of 20.5%. The total weight loss of 85.3% is close to the calculated value (87.0%).

CONCLUSION

A new mononuclear copper(II) complex has been unexpectedly obtained from the reaction of 2-formylbenzoic acid, *N*phenylethane-1,2-diamine, and copper perchlorate in methanol. The crystal structure of the complex was determined. The formyl group of 2-formylbenzoic acid linked to both the amine and the imine N atoms of *N*-phenylethane-1,2-diamine during the reaction.

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