

Two-dimensional Coordination Polymers of Copper(II) with Oxalate: Lattice Water Control of Structure

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Three oxalate copper(II) complexes, $[\text{Cu}(\text{bipy})(\text{C}_2\text{O}_4)(\text{H}_2\text{O})] \cdot 2\text{H}_2\text{O}$ (**1**), $[\text{Cu}(\text{nphen})(\text{C}_2\text{O}_4)(\text{H}_2\text{O})] \cdot 2\text{H}_2\text{O}$ (**2**), and $[\text{Cu}(\text{phen})(\text{C}_2\text{O}_4)(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}$ (**3**) (bipy = 2,2'-bipyridine, nphen = 5-nitro-1,10-phenanthroline and phen = 1,10-phenanthroline), have been synthesized and their crystal structures have been determined. Compound **1** crystallizes in the triclinic space group $P\bar{1}$ with $a = 7.2554(10)$ Å, $b = 10.5712(14)$ Å, $c = 10.8178(15)$ Å, $\alpha = 62.086(2)^\circ$, $\beta = 77.478(3)^\circ$, $\gamma = 81.773(3)^\circ$, and $Z = 2$. Compound **2** crystallizes in the triclinic space group $P\bar{1}$ with $a = 9.582(2)$ Å, $b = 10.086(2)$ Å, $c = 10.592(2)$ Å, $\alpha = 64.18(3)^\circ$, $\beta = 79.47(3)^\circ$, $\gamma = 60.06(3)^\circ$, and $Z = 2$. Compound **3** crystallizes in the monoclinic space group $P2(1)/n$ with $a = 8.4655(7)$ Å, $b = 9.7057(8)$ Å, $c = 17.4572(14)$ Å; $\beta = 103.865(2)^\circ$, and $Z = 4$. The crystal structures of all complexes consist of neutral $[\text{Cu}(\text{L})(\text{C}_2\text{O}_4)(\text{H}_2\text{O})]$ (L = bipy, nphen, and phen) units and one or two lattice water molecules in the unit cell. Each copper atom in **1**, **2**, and **3** involves a five-coordinate $\text{CuN}_2\text{O}_2\text{O}'$ environment, with a distorted square-pyramidal structure. In **1** and **2**, two lattice water molecules are around each unit of $[\text{CuL}(\text{C}_2\text{O}_4)(\text{H}_2\text{O})]$ (L = bipy and nphen) and form two-dimensional networks. Only one lattice water molecule is found in the unit cell of **3** and the two-dimensional structure is different from **1** and **2**. The extended three-dimensional structure is formed through π - π interactions between layers. The influences of hydrogen bonds and the sizes and Lewis basicity of ligands to the structures were discussed.

Introduction

The coordination ability of the oxalate anion has been widely investigated in the past two decades. Considerable attention has been devoted to the oxalate ligand as a structure unit in the preparation of ordered polymetallic chains in the context of low-dimensional electronic and magnetic systems.^{1–5} Since the oxalate group can function as a bidentate ligand, coordination to two metal ions affords a wide variety of polynuclear complexes, a characteristic particularly well-documented for copper-oxalate chemistry.^{1,4,6–11} Oxalato-bridged oligonuclear complexes are also useful models for theoretical and experimental investigation of the factors governing the magnitude of the exchange interactions between adjacent metal atoms.^{12–14}

Furthermore, such complexes could have potential application as precursors for the synthesis of, for instance, copper-containing superconducting ceramics.¹⁵

Self-assembly of metal compounds by hydrogen bonds into one-, two-, and three-dimensional supramolecular architectures connects with biological chemistry, material chemistry (such as organic film¹⁶ and magnetic material^{17–20}), and supramolecular chemistry.^{21–23} Hydrogen bonds play vital roles in highly efficient and specific biological reactions and are essential for molecular recognition and self-organization of molecules in supramolecular chemistry. Hydrogen-bond assembled molecular

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materials are of considerable attention and the incorporation of a transition metal ion into hydrogen-bond systems is important in the crystal engineering of nonlinear optical, conducting, and ferromagnetic materials.¹⁸

In the present work, we report the synthesis, structure, and spectroscopic properties of three oxalate copper(II) complexes, [Cu(bipy)(C₂O₄)(H₂O)]·2H₂O (**1**), [Cu(nphen)(C₂O₄)(H₂O)]·2H₂O (**2**), and [Cu(phen)(C₂O₄)(H₂O)]·H₂O (**3**) (bipy = 2,2'-bipyridine, nphen = 5-nitro-1,10-phenanthroline and phen = 1,10-phenanthroline). The crystal structures of complexes **1**, **2**, and **3** consist of neutral [CuL(C₂O₄)(H₂O)] (L represents the bidentate ligand bipy, nphen and phen) units and one or two lattice water molecules in the unit cell. Adjacent neutral units are linked by hydrogen bonds to form two-dimensional structures. The structures described demonstrate that intermolecular hydrogen bonds have potentials for assembling multidimensional systems in which the subunits are metal complexes. Complex **1** was determined rashly previously and the hydrogen-bonding network that developed was not observed.⁸ Among the three complexes, hydrogen-bonding networks are different with the change in size of the ligands and the number of lattice water molecules. The influences of hydrogen bonds and the size of the ligands to the structures of the complexes were discussed.

Experimental Section

Materials. Starting materials were purchased from the Aldrich Company. The mononuclear precursor K₂[Cu(ox)₂]·2H₂O was prepared by the literature method.²⁴

Synthesis of [Cu(bipy)(C₂O₄)(H₂O)]·2H₂O (1**).** An ethanol solution (10 mL) of 2,2'-bipyridine (62.5 mg, 0.4 mmol) was added to a solution of K₂[Cu(C₂O₄)₂]·2H₂O (141.5 mg, 0.4 mmol) dissolved in 15 mL water. The resulting mixture was stirred and refluxed for 5 h, then filtered off. The filtrate was evaporated at room temperature. Azure crystals suitable for X-ray analysis were obtained in a few weeks. Yield: 38%. Anal. Calcd for C₁₂H₁₄N₂O₇Cu (**1**): C, 39.80; H, 3.82; N, 7.74. Found: C, 39.95; H, 3.90; N, 7.68.

Synthesis of [Cu(nphen)(C₂O₄)(H₂O)]·2H₂O (2**).** The synthetic method of **2** is similar to that of **1** except that 2,2'-bipyridine was replaced by 5-nitro-1,10-phenanthroline. After a few weeks, blue crystals suitable for X-ray analysis were obtained. Yield: 40%. Anal. Calcd for C₁₄H₁₃N₃O₉Cu (**2**): C, 39.00; H, 3.02; N, 9.75. Found: C, 38.49; H, 2.66; N, 10.13.

Synthesis of [Cu(phen)(C₂O₄)(H₂O)]·H₂O (3**).** The synthetic method of **3** is similar to that of **1** except that 2,2'-bipyridine was replaced by 1,10-phenanthroline. Blue crystals suitable for X-ray analysis were obtained in a week. Yield: 30%. Anal. Calcd for C₁₄H₁₂N₂O₆Cu (**3**): C, 45.68; H, 3.26; N, 7.61. Found: C, 45.14; H, 3.02; N, 7.38.

Physical Measurements. Elemental analyses for C, H, and N were obtained at the Institute of Elemental Organic Chemistry, Nankai University. IR spectra were recorded in KBr disks on a Shimadzu IR-408 infrared spectrophotometer in the 4000–600 cm⁻¹ region. UV–vis spectra were recorded on a Shimadzu UV-2101PC UV–vis scanning spectrophotometer. X-band EPR spectra were recorded on a Bruker ER 200 D-SRC ESR spectrometer. Thermogravimetric analysis was carried out at the Tianjin Institute of Chemical Engineering by using Shimadzu simultaneous TA-50I in a helium atmosphere. All the complexes were heated from 25 to 500 °C at a heating rate of 5 °C/min.

Crystallographic Studies. An azure single crystal of **1** having the approximate dimensions 0.20 mm × 0.15 mm × 0.10 mm was mounted on a glass fiber. Determination of the unit cell and data collection were performed with MoKα radiation (λ = 0.71073 Å) on a BRUKER SMART 1000 diffractometer equipped with a CCD camera. Cell parameters were determined from a least-squares refinement on the

Table 1. Crystallographic Data for **1**, **2**, and **3**

	1	2	3
formula	C ₁₂ H ₁₄ CuN ₂ O ₇	C ₁₄ H ₁₃ CuN ₃ O ₉	C ₁₄ H ₁₂ CuN ₂ O ₆
fw	361.79	430.81	367.80
space group	P $\bar{1}$ (2)	P $\bar{1}$ (2)	P2(1)/n
a (Å)	7.2554 (10)	9.582 (2)	8.4655(7)
b (Å)	10.5712 (14)	10.086 (2)	9.7057(8)
c (Å)	10.8178 (15)	10.592 (2)	17.4572(14)
α (deg)	62.086 (2)	64.18 (3)	90
β (deg)	77.478 (3)	79.47 (3)	103.865(2)
γ (deg)	81.773 (3)	60.06 (3)	90
Z	2	2	4
μ/mm ⁻¹	1.565	1.4275	1.604
V/Å ³	714.90 (17)	797.7 (4)	1392.6 (2)
ρ _c (g/cm ³)	1.681	1.794	1.754
T (K)	293 (2)	299(1)	298(2)
R1	0.0407	0.076	0.0325
wR2 ^{a,b}	0.1063 ^a	0.079 ^b	0.0795 ^a

^a [I > 2σ(I)] for **1** and **3**, [I ≥ 3σ(I)] for **2**. ^b R1 = Σ||F_o - |F_c|| / Σ|F_o|, wR2 = (Σ[w(F_o² - F_c²)²] / Σ(F_o²)²)^{1/2} for **1** and **3**, R1 = Σ||F_o - |F_c|| / Σ|F_o|, wR2 = [Σw(|F_o - |F_c||)² / ΣwF_o²]^{1/2} for **2**. w = 1/[σ²(F_o²) + (0.0756P)² + 0.0237P] and P = (F_o² + 2F_c²) / 3 for **1**, w = 1/[σ²(F_o²) + 0.0001F²] for **2**, w = 1/[σ²(F_o²) + (0.0468P)² + 0.3389P] and P = (F_o² + 2F_c²) / 3 for **3**.

setting angles from 25 centered reflections in the range 2.16° < θ < 26.36° at 293(2) K. The intensities of the ±hkl reflections were measured up to θ_{max} = 26.36°; the ω-2θ scan technique was employed. The index range is -9 ≤ h ≤ 6, -13 ≤ k ≤ 12 and -13 ≤ l ≤ 9. No absorption correction was made during processing. Crystal parameters and structure refinements are summarized in Table 1. The structure of **1** was solved primarily by direct method and second by Fourier difference techniques and refined by the full-matrix least-squares method on F² for 223 refined parameters. The computations were performed with the SHELXL-97 program.²⁵ All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were set in calculated positions and refined as riding atoms with a common fixed isotropic thermal parameter. The residual maximum and minimum in the final Fourier-difference maps were 0.514 and -0.624 eÅ⁻³. The value of the goodness-of-fit is 1.039. Final atomic coordinates and average temperature factors are listed in Table 2.

A blue single crystal of **2** having the approximate dimensions 0.30 × 0.35 × 0.50 mm, was mounted on a glass fiber. Determination of the unit cell and data collection were performed with MoKα radiation (λ = 0.71073 Å) on an ENRAF-NONIUS CAD4 diffractometer equipped with a graphite monochromator. Cell parameters were determined from a least-squares fit of the setting angles of 25 reflections with θ range from 7.91° < θ < 12.31° at 299(1) K. The intensities of the ±hkl reflections were measured up to θ_{max} = 25; the ω-2θ scan technique was employed. The ω-2θ width was equal to (0.7 + 0.35*^atan θ)° and the scan speed 0.92–5.49° min⁻¹. Three standard reflections monitored every 60 min showed no intensity variation during the data collection. An empirical absorption correction was applied using the routine DIFABS program.²⁶ Crystal parameters and structure refinements are summarized in Table 1. The structure of **2** was solved by direct methods (MULTAN 82) and refined by the full-matrix least-squares method on F. The method of locating and refining H atoms is added theoretically and refined with riding model position parameters and fixed isotropic thermal parameters. The other non-hydrogen atoms were determined with successive difference Fourier syntheses. The final full-matrix least-squares refinements minimizing Σw(|F_o - |F_c||)² converged at the values of R₁ and R₂ listed in Table 1. The residual maximum and minimum in the final Fourier-difference maps were 0.71 and -0.88 eÅ⁻³. All calculations were performed on a PDP 11/44 computer using these SDP-PLUS program system. Final atomic coordinates and average temperature factors are listed in Table 3.

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Table 2. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for **1**

atoms	x	y	z	U(eq) ^a
Cu(1)	-1332(1)	-3619(1)	3648(1)	29(1)
O(1)	-542(3)	-4663(2)	2514(2)	35(1)
O(2)	-2291(3)	-5435(2)	5131(2)	37(1)
O(3)	-1080(4)	-6735(2)	2608(2)	46(1)
O(4)	-2993(3)	-7525(2)	5366(2)	38(1)
O(5)	-4015(3)	-2642(3)	2571(2)	43(1)
O(6)	4627(4)	3752(3)	-741(3)	60(1)
O(7)	-2085(3)	-5692(3)	-30(3)	50(1)
N(1)	117(3)	-1868(3)	2412(3)	29(1)
N(2)	-2149(3)	-2599(2)	4825(2)	27(1)
C(1)	1396(4)	-1650(3)	1240(3)	35(1)
C(2)	2317(4)	-383(4)	448(3)	40(1)
C(3)	1886(5)	693(3)	854(3)	42(1)
C(4)	556(4)	475(3)	2059(3)	36(1)
C(5)	-277(4)	-827(3)	2828(3)	28(1)
C(6)	-1611(4)	-1234(3)	4196(3)	27(1)
C(7)	-2240(4)	-329(3)	4814(3)	35(1)
C(8)	-3441(5)	-848(4)	6109(4)	39(1)
C(9)	-3980(5)	-2246(4)	6762(3)	40(1)
C(10)	-3322(4)	-3084(3)	6084(3)	36(1)
C(11)	-1212(4)	-5912(3)	3138(3)	30(1)
C(12)	-2274(4)	-6362(3)	4685(3)	28(1)

^a U(eq) is defined as one-third of the trace of the orthogonalized Uij tensor.

Table 3. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for **2**

atoms	x	y	z	U(eq) ^a
Cu(1)	2712(1)	-4232(1)	632(1)	36(1)
O(11)	747(7)	-4019(7)	2171(5)	47(3)
N	6779(8)	-12442(8)	3793(7)	43(3)
O(1)	6818(10)	-12911(9)	2904(8)	72(4)
O(2)	7339(9)	-13349(8)	4983(7)	70(4)
O(3)	1303(7)	-3017(7)	-1025(6)	46(3)
O(4)	2627(6)	-2119(7)	198(5)	39(3)
O(5)	-66(8)	-454(9)	-2587(6)	56(4)
O(6)	1255(7)	548(7)	-1254(5)	43(3)
N(1)	4473(7)	-5602(7)	2115(6)	35(3)
N(2)	3158(8)	-6470(9)	851(6)	42(4)
C(1)	861(9)	-1497(10)	-1540(7)	35(4)
C(2)	1605(8)	-900(9)	-847(7)	31(3)
C(11)	5041(9)	-5054(10)	2759(9)	44(4)
C(12)	6198(10)	-6163(11)	3861(8)	47(5)
C(13)	6767(9)	-7820(10)	4333(8)	41(4)
C(14)	6188(8)	-8456(10)	3696(7)	35(4)
C(15)	6689(9)	-10148(9)	4073(8)	36(3)
C(16)	6072(9)	-10627(9)	3419(7)	35(4)
C(17)	4815(8)	-9436(10)	2294(7)	34(4)
C(18)	4013(10)	-9829(11)	1599(9)	45(4)
C(19)	2840(9)	-8529(12)	567(8)	47(5)
C(20)	2505(8)	-6896(10)	241(8)	38(4)
C(21)	4337(8)	-7784(8)	1908(7)	29(3)
C(22)	5000(8)	-7211(9)	2592(7)	31(3)
O(21)	-1028(10)	2866(9)	-4209(7)	70(4)
O(22)	257(9)	-6739(11)	3177(8)	74(5)

^a U(eq) is defined as one-third of the trace of the orthogonalized Uij tensor.

A blue single crystal of **3**, having the approximate dimensions 0.10 mm \times 0.15 mm \times 0.20 mm, was mounted on a glass fiber. Determination of the unit cell and data collection were performed with Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) on a BRUKER SMART 1000 diffractometer equipped with a CCD camera. Cell parameters were determined from a least-squares refinement on the setting angles from 25 centered reflections in the range $2.40 < \theta < 25.03^\circ$ at 298(2) K. The intensities of the $\pm hkl$ reflections were measured up to $\theta_{\max} = 25.03^\circ$; the ω - 2θ scan technique was employed. Index range is $-7 \leq h \leq 10$, $-11 \leq k \leq 11$ and $-20 \leq l \leq 19$. No absorption correction was made during processing. Crystal parameters and structure refine-

Table 4. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for **3**

atom	x	y	z	U(eq) ^a
Cu(1)	6447(1)	196(1)	1542(1)	29(1)
N(1)	7339(3)	-1201(2)	911(1)	29(1)
N(2)	6558(3)	1416(3)	626(1)	30(1)
O(1)	5119(3)	1447(2)	1985(1)	34(1)
O(2)	5933(3)	-1140(2)	2276(1)	39(1)
O(3)	3552(3)	1420(3)	2836(1)	50(1)
O(4)	4635(3)	-1227(3)	3237(2)	58(1)
O(5)	8784(3)	906(3)	2316(2)	52(1)
O(6)	3883(3)	4230(3)	1764(2)	47(1)
C(1)	7730(4)	-2506(3)	1083(2)	37(1)
C(2)	8399(4)	-3335(4)	588(2)	40(1)
C(3)	8668(4)	-2807(3)	-95(2)	37(1)
C(4)	8283(4)	-1424(3)	-289(2)	31(1)
C(5)	8569(4)	-739(4)	-972(2)	36(1)
C(6)	8193(4)	601(4)	-1113(2)	36(1)
C(7)	7470(3)	1392(3)	-593(2)	30(1)
C(8)	7030(4)	2786(3)	-707(2)	38(1)
C(9)	6376(4)	3433(4)	-169(2)	43(1)
C(10)	6158(4)	2734(3)	499(2)	38(1)
C(11)	7193(3)	749(3)	85(2)	27(1)
C(12)	7617(3)	-665(3)	240(2)	26(1)
C(13)	4499(4)	883(3)	2506(2)	33(1)
C(14)	5048(4)	-635(3)	2703(2)	34(1)

^a U(eq) is defined as one-third of the trace of the orthogonalized Uij tensor.

ments are summarized in Table 1. The structure of **3** was solved primarily by direct method and second by Fourier difference techniques and refined by the full-matrix least-squares method on F^2 for 256 refined parameters. The computations were performed with SHELXL-97 program.²⁵ All non-hydrogen atoms were treated anisotropically. The hydrogen atoms were set in calculated positions and refined as riding atoms with a common fixed isotropic thermal parameter. The residual maximum and minimum in the final Fourier-difference maps were 0.285 and -0.429 e\AA^{-3} . The value of the goodness-of-fit is 1.017. Final atomic coordinates and average temperature factors are listed in Table 4.

Results and Discussion

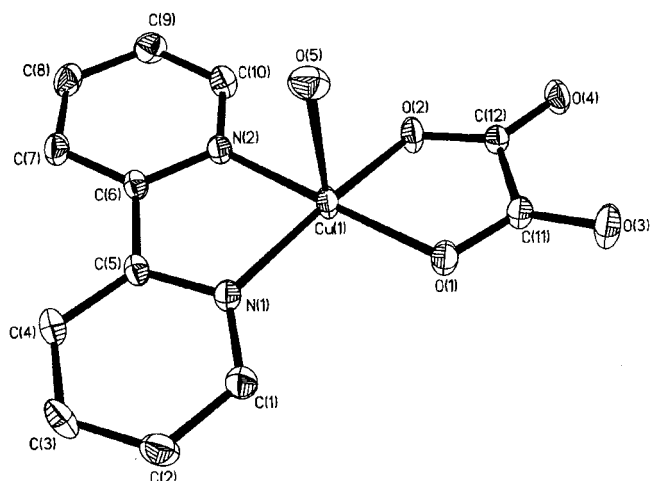
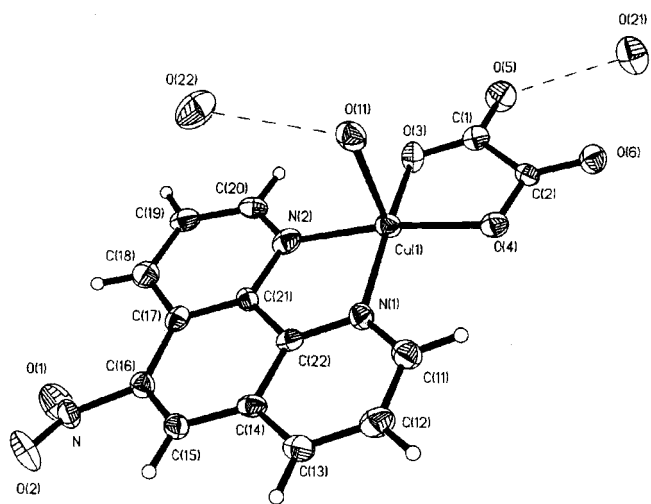
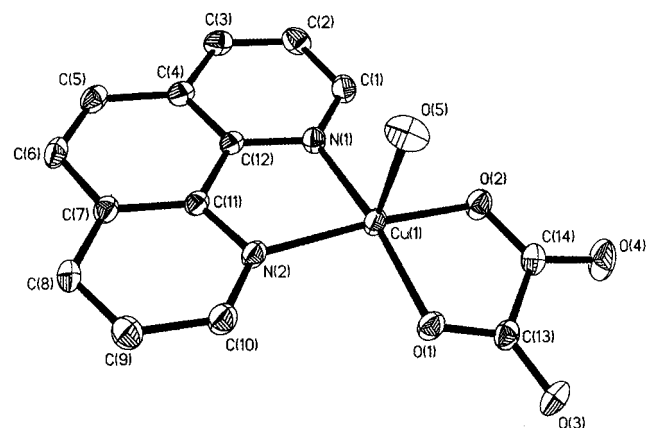
Structures. Selected bond distances and angles for **1–3** are listed in Table 5. The ORTEP drawings of the complexes [Cu(bipy)(C₂O₄)(H₂O)] \cdot 2H₂O (**1**), [Cu(nphen)(C₂O₄)(H₂O)] \cdot 2H₂O (**2**), and [Cu(phen)(C₂O₄)(H₂O)] \cdot H₂O (**3**) are shown in Figures 1–3, respectively. The crystal structures of all complexes consist of neutral [Cu(L)(C₂O₄)(H₂O)] (L = bipy, nphen and phen) units in the unit cell. Each copper atom in **1**, **2**, and **3** involves a five-coordinate CuN₂O₂O' environment, with a distorted square-pyramidal structure. In **1**, the bipy and oxalate anion are both asymmetrically coordinated to the copper atom (mean Cu(1)–N(1) 1.987 Å, Cu(1)–N(2) 1.978 Å, Cu(1)–O(1) 1.958 Å, Cu(1)–O(2) 1.938 Å) in the plane of the square pyramid with a water molecule occupying the fifth coordinated position at a distance of 2.344 Å. The dihedral angle between the pyridine ring [N1C1C2C3C4C5] (mean plane I) and [N2C6C7C8C9C10] (mean plane II) is 6.02(0.16)° and that between mean plane II and the [N1N2O1O2] mean plane is 6.27(0.12)°. The Cu atom lies 0.1132 Å above the [N1N2O1O2] mean plane toward the coordinated water molecule. Another example of oxalate-bipy compound is [Cu(bipy)(ox)] \cdot 2H₂O.^{7,8} No water molecules were found to coordinate to copper ions. The crystal structure was composed of polymeric chains of [Cu(bipy)]²⁺ ions bridged by oxalato anions. Compared with the 2,2'-bipyridine (bipy), 4,4'-pyridine (4,4'-bipy) has a tendency to coordinate to metal ions in bridged mode. This feature of 4,4'-bipy is widely used in the design and preparation of multidimensional mixed-ligand

Table 5. Selected Bond Lengths (Å) and Angles (deg) for **1**, **2**, and **3**

Complex 1			
Cu(1)–O(2)	1.938(2)	Cu(1)–O(1)	1.958(2)
Cu(1)–N(2)	1.978(2)	Cu(1)–N(1)	1.987(2)
Cu(1)–O(5)	2.344(2)		
O(2)–Cu(1)–O(1)	84.55(8)	O(2)–Cu(1)–N(2)	94.36(9)
O(1)–Cu(1)–N(2)	178.91(8)	O(2)–Cu(1)–N(1)	166.34(9)
O(1)–Cu(1)–N(1)	99.36(9)	N(2)–Cu(1)–N(1)	81.69(9)
O(2)–Cu(1)–O(5)	99.45(9)	O(1)–Cu(1)–O(5)	90.67(9)
N(2)–Cu(1)–O(5)	89.55(9)	N(1)–Cu(1)–O(5)	93.62(9)
C(11)–O(1)–Cu(1)	112.06(17)	C(12)–O(2)–Cu(1)	113.00(18)
C(1)–N(1)–C(5)	119.2(3)	C(1)–N(1)–Cu(1)	126.3(2)
C(5)–N(1)–Cu(1)	114.56(19)	C(10)–N2–C(6)	119.0(2)
C(10)–N(2)–Cu(1)	126.1(2)	C(6)–N(2)–Cu(1)	114.50(18)
Complex 2			
Cu(1)–O(11)	2.242(6)	Cu(1)–O(3)	1.936(6)
Cu(1)–O(4)	1.935(7)	Cu(1)–N(1)	1.993(6)
Cu(1)–N(2)	1.988(9)		
O(11)–Cu(1)–O(3)	95.9(2)	O(11)–Cu(1)–O(4)	97.3(2)
O(3)–Cu(1)–O(4)	85.3(3)	O(11)–Cu(1)–N(1)	93.9(2)
O(3)–Cu(1)–N(1)	769.9(3)	O(4)–Cu(1)–N(1)	95.7(3)
O(11)–Cu(1)–N(2)	93.6(3)	O(3)–Cu(1)–N(2)	94.6(3)
O(4)–Cu(1)–N(2)	169.1(2)	N(1)–Cu(1)–N(2)	82.5(3)
Cu(1)–O(3)–C(1)	112.6(7)	Cu(1)–O(4)–C(2)	111.9(7)
Cu(1)–N(1)–C(11)	127.7(5)	Cu(1)–N(1)–C(22)	114.0(7)
C(11)–N(1)–C(22)	117.9(11)	Cu(1)–N(2)–C(20)	131.2(5)
Cu(1)–N(2)–C(21)	112.8(7)	C(20)–N(2)–C(21)	115.9(8)
Complex 3			
Cu(1)–O(1)	1.9370(19)	Cu(1)–O(2)	1.944(2)
Cu(1)–N(1)	2.005(2)	Cu(1)–N(2)	2.011(2)
Cu(1)–O(5)	2.221(2)		
O(1)–Cu(1)–O(2)	84.97(9)	O(1)–Cu(1)–N(1)	166.90(9)
O(2)–Cu(1)–N(1)	94.83(9)	O(1)–Cu(1)–N(2)	95.17(9)
O(2)–Cu(1)–N(2)	167.86(10)	N(1)–Cu(1)–N(2)	82.28(10)
O(1)–Cu(1)–O(5)	94.61(10)	O(2)–Cu(1)–O(5)	96.53(10)
N(1)–Cu(1)–O(5)	98.42(10)	N(2)–Cu(1)–O(5)	95.56(10)
C(1)–N(1)–C(12)	118.5(3)	C(1)–N(1)–Cu(1)	128.9(2)
C(12)–N(1)–Cu(1)	112.48(19)	C(10)–N(2)–C(11)	118.1(3)
C(10)–N(2)–Cu(1)	129.9(2)	C(11)–N(2)–Cu(1)	111.98(19)
C(13)–O(1)–Cu(1)	113.07(19)	C(14)–O(2)–Cu(1)	112.64(19)
N(1)–C(1)–C(2)	121.8(3)		

coordination systems. Recently, Li et al. reported a new type of two-dimensional metal oxalate-4,4'-bipy coordination polymer $2_{\infty}[\text{M}(\text{ox})(4,4'\text{-bipy})]$ ($\text{M} = \text{Fe}(\text{II}), \text{Co}(\text{II}), \text{Ni}(\text{II}), \text{Zn}(\text{II})$).²⁷ Both oxalate and 4,4'-bipy act as bridged ligands and form a two-dimensional layered network. The copper(II) complex, however, is not reported in this series. Instead, the two- and three-dimensional Cu-X-4,4'-bipy compounds $2_{\infty}[\text{Cu}_2\text{X}_2(4,4'\text{-bipy})]$ ($\text{X} = \text{Cl}, \text{Br}$) and $3_{\infty}[\text{CuBr}(4,4'\text{-bipy})]$ were obtained when the oxalato anions were replaced by chloride or bromide ions.²⁸ Similarly, the three-dimensional manganese(II) systems containing both N_3 - and 4,4'-bipy were reported.²⁹ Although the 2,2'-bipyridine is likely to link the metal centers in terminal mode, the two- and three-dimensional coordination systems can be constructed based on the metal ions and other bridged ligands.³⁰

In **2**, the nphen and oxalate anion are both symmetrically coordinated to the copper atom (mean Cu(1)–N 1.993 Å, Cu(1)–O 1.936 Å) in the plane of the square pyramid with a

**Figure 1.** ORTEP drawing (30% of thermal ellipsoid probability) of **1**.**Figure 2.** ORTEP drawing (30% of thermal ellipsoid probability) of **2**.**Figure 3.** ORTEP drawing (30% of thermal ellipsoid probability) of **3**.

water molecule occupying the fifth coordinated position at a distance of 2.344 Å. N(1), N(2), O(3), and O(4) are basically located in a plane. For the complex **3**, the phen and oxalate anion are both asymmetrically coordinated to the copper atom (mean Cu(1)–N(1) 1.987 Å, Cu(1)–N(2) 1.978 Å, Cu(1)–O(1) 1.958 Å, Cu(1)–O(2) 1.938 Å) in the plane of the square pyramid with a water molecule occupying the fifth coordinated position at a distance of 2.221 Å. The dihedral angle between

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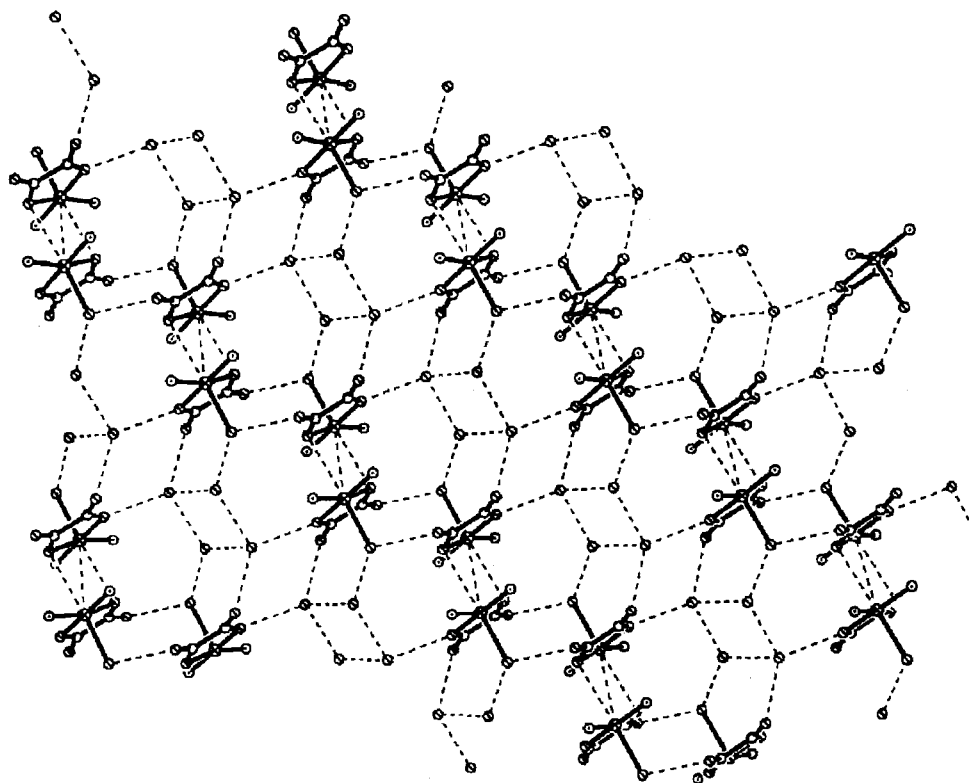


Figure 4. The two-dimensional structure of **1**.

the pyridine ring of 1,10-phenanthroline is $5.41(0.11)^\circ$. The Cu atom lies 0.2156 \AA above the $[\text{N1N2O1O2}]$ mean plane toward the coordinated water molecule.

The significant difference among the three complexes is the number of lattice water molecules. Both **1** and **2** contain two lattice water molecules in the unit cell. In **1**, the two lattice water molecules involve a relatively short $\text{H}_2\text{O}(6)\text{---H6A}\cdots\text{O}(7)$ contact of 2.872 \AA and a $\text{H}_2\text{O}(6)\text{---H6B}\cdots\text{O}'(7)$ contact of 2.855 \AA , suggesting hydrogen bonding. The distances of $\text{H}_2\text{O}(5)\text{---H5A}\cdots\text{O}'4$ and $\text{H}_2\text{O}(5)\text{---H5B}\cdots\text{O}(6)$ are 2.808 and 2.863 \AA , respectively. The lattice water molecule $\text{H}_2\text{O}(7)$ has hydrogen bonds with O(3) and O(1) ($\text{O7}\text{---H7B}\cdots\text{O3}$, 2.760 \AA ; $\text{O7}\text{---H7A}\cdots\text{O1}$, 2.835 \AA). A parallelogram is formed in the four adjacent lattice water molecules by hydrogen bonds. The whole molecules are organized in wave layers in which the two-dimensional structure is formed and shown in Figure 4. Further nonbonding contacts ($1-x$, $1-y$, $-z$) yield a weak dimer with a $\text{Cu}\cdots\text{Cu}$ distance of 3.696 \AA . The two-dimensional structure of the **2** is a little different from **1** and shown in Figure 5. In **2**, the hydrogen bond length between two lattice water molecules is 2.761 \AA . The distances between the lattice $\text{H}_2\text{O}(11)$ and the adjacent coordinated $\text{H}_2\text{O}(22)$ and the distances between the lattice $\text{H}_2\text{O}(21)$ and O(5) of the oxalate group are 2.727 and 2.739 \AA , respectively. The distance of $\text{Cu}\text{---}\text{Cu}$ is 4.037 \AA , which is so long that no dimer is formed. The distances between Cu and O(5) and O(6) of oxalate group in the adjacent molecule are 3.887 and 3.885 \AA , respectively. The whole molecules are also organized in the two-dimensional plane structure.

The difference of two-dimensional structures between **1** and **2** is mainly due to the sizes of bipy and nphen ligands. The steric effect of bipy is smaller than that of nphen and the lattice water molecules are a short distance from being linked by hydrogen bonds to form a parallelogram. Compound **1** forms wavelike layers in space and the parallelograms linked by lattice

water molecules are stacked to form channels. In **2**, the two lattice water molecules linked by hydrogen bonds have no interaction with adjacent two lattice water molecules because of long distance between them. The whole structure of complex **2** in space is a two-dimensional plane. There is no $\pi\text{---}\pi$ stacking interaction in the molecular structures of **1** and **2** because the phenyl rings of bipy and nphen are staggered.

Compared with **1** and **2**, only one lattice water molecule of **3** is involved in the unit cell. This fact can be explained by the Lewis basicity of the ligands. When the number of phenyl rings increases, the Lewis basicity also increases. Since the nitro group of the ligand in **2** decrease the Lewis basicity, the Lewis basicity of the ligand in **3** is the strongest among the three ligands. In **3**, the hydrogen bonds between O5 and the lattice water molecule and between O5 and O2' of the oxalate group in the adjacent $[\text{Cu}(\text{phen})(\text{C}_2\text{O}_4)(\text{H}_2\text{O})]$ unit with the distances of 2.758 and 2.950 \AA have been observed. The distances of $\text{H}_2\text{O}(5)$ and O1 of the adjacent $[\text{Cu}(\text{phen})(\text{C}_2\text{O}_4)(\text{H}_2\text{O})]$ unit is 2.888 \AA . The one-dimensional chain structure is formed by these hydrogen bonds. The distances of the lattice water molecule and O3, O4 of the oxalate group in adjacent chains are 3.154 and 3.011 \AA , respectively. The interchain hydrogen bonds are weaker than intrachain hydrogen bonds. The whole molecules are organized in two-dimensional layers by hydrogen bonds which is shown in Figure 6. Furthermore, the rings of 1,10-phenanthroline are parallel in the crystal cell. The distances of C4A and C5A to the adjacent ring of 1,10-phenanthroline are 3.405 and 3.377 \AA and the distances of C10B and N1B to the adjacent ring of *o*-phenanthroline are 3.555 and 3.552 \AA , respectively. They are short enough to have $\pi\text{---}\pi$ interactions. The two types of $\pi\text{---}\pi$ interactions are shown in Figure 7 and the three-dimensional structure through $\pi\text{---}\pi$ interactions is shown in Figure 8. Unlike the parallel overlap of phenanthroline of **3**, the phenyl rings are alternate between layers in **1** and **2**. The $\pi\text{---}\pi$ interactions of **1** and **2** are much weaker than that of **3**. The two- and three-

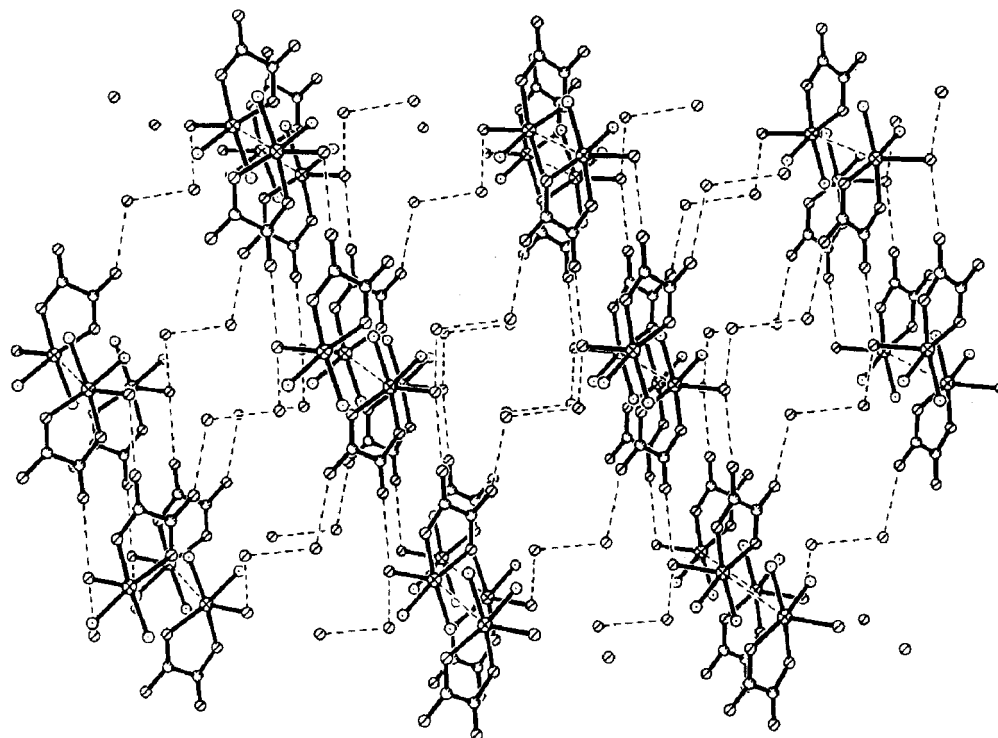


Figure 5. The two-dimensional structure of 2.

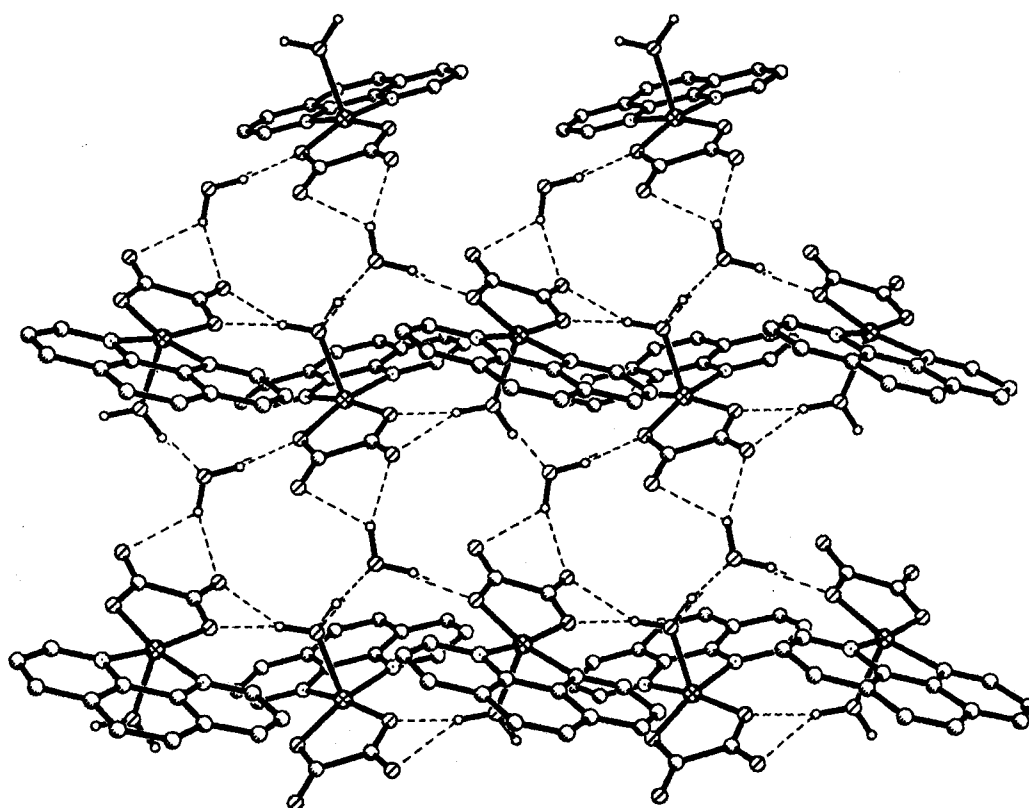


Figure 6. The two-dimensional structure of 3.

dimensional structures of 3 are stabilized by hydrogen bonding and $\pi-\pi$ interactions. In 1 and 2, the two-dimensional structures formed by strong hydrogen bonds are stable.

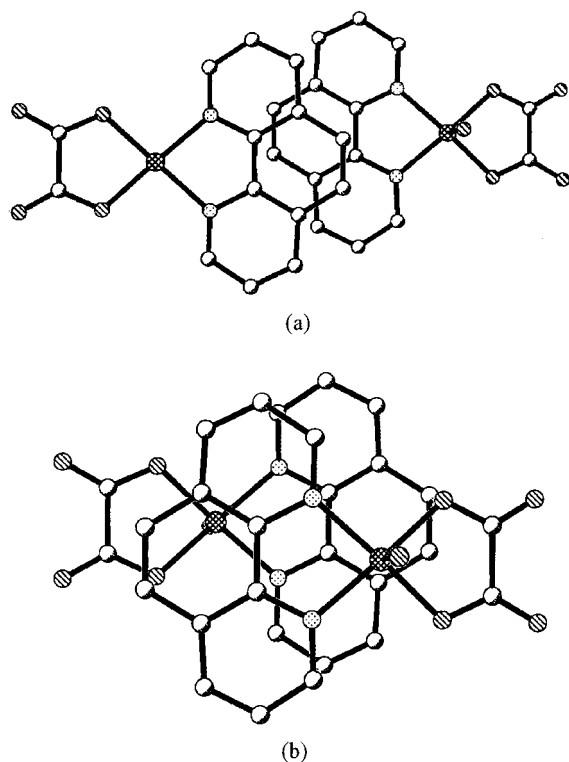
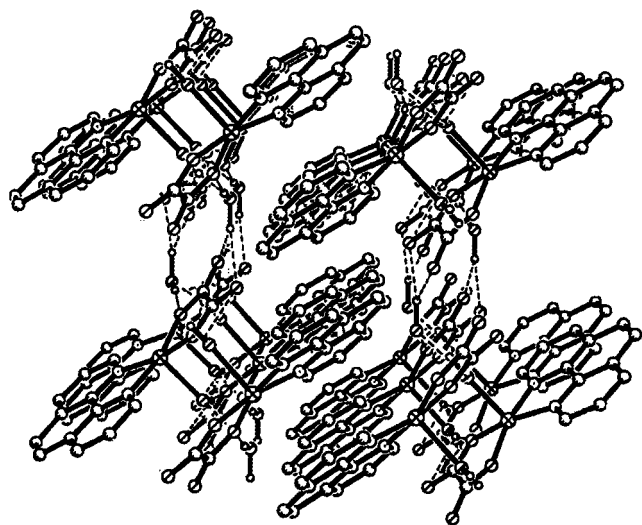
Spectroscopic Studies. The IR spectra of the three complexes show strong and broad bands in the $3610-3280\text{ cm}^{-1}$ range assignable to $\nu(\text{OH})$ stretching vibrations of lattice and/or coordinated water molecules.³¹ The observed position of the

$\nu(\text{OH})$ bands is in agreement with the participation of water molecules in strong hydrogen bonds. For the oxalate ligand, various coordination modes via one, two, three, or four oxygen atoms have been previously characterized.^{27,32-36} The absorption

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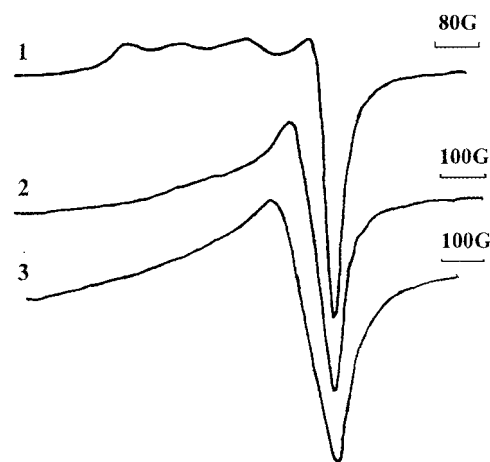
Table 6. Spectroscopic Data for **1**, **2**, and **3**

complex	IR/cm ⁻¹				UV-vis/cm ⁻¹			EPR			
	$\nu_{\text{as}}(\text{COO}^-)$	$\nu_{\text{s}}(\text{COO}^-)$	$\nu(\text{C}-\text{O})$	$\delta(\text{COO}^-)$	CT transition	$d-d$ transition		$g_{\parallel}(\text{RT})$	$g_{\parallel}(\text{LT})$	$g_{\perp}(\text{RT})$	$g_{\perp}(\text{LT})$
1	1670(s)	1380(s)	1240(m)	790(s)	33300	16020	14300(sh)	2.207	2.199	2.060	2.069
2	1670(s)	1395(s)	1335(m)	790(s)	36400	15770	14140(sh)	2.220	2.222	2.068	2.066
3	1650(s)	1400(s)	1255(m)	790(s)	37040	15920	14280(sh)	2.115	2.112	2.057	2.064

**Figure 7.** The two types of $\pi-\pi$ interactions in **3**.**Figure 8.** The three-dimensional structure of **3**.

bands which appeared in the region of 1670 to 790 cm^{-1} for three complexes are listed in Table 6 and can be assigned to

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**Figure 9.** The X-band EPR spectra of polycrystalline samples of **1**, **2**, and **3** at 77 K.

$\nu_{\text{as}}(\text{COO}^-)$, $\nu_{\text{s}}(\text{COO}^-)$, $\nu(\text{C}-\text{O})$, and $\delta(\text{COO}^-)$, respectively. It shows that the oxalate anion behaves as a bichelating oxygen-donor ligand and is in agreement with the result of the X-ray analysis.

The diffuse reflectance spectra of compounds **1**, **2**, and **3** exhibit more intense bands centered at 33 300, 36 400, and 37 040 cm^{-1} , which can be assigned to π (bipy, nphen and phen) \rightarrow Cu(II) ($d_{x^2-y^2}$, d_{z^2}), LMCT, and internal ligand $\pi \rightarrow \pi^*$ transitions, respectively. In the visible region, three complexes exhibit essentially similar patterns. The broad absorption at ca. 15870 cm^{-1} with a shoulder peak at ca. 14280 cm^{-1} has been observed. This is consistent with a five-coordinated copper(II) chromophore.^{8,37}

The X-band EPR spectra of the polycrystalline powder of **1**, **2**, and **3**, have been recorded at both room temperature and 77 K. The EPR spectra at room temperature and low temperature are quite similar for each complex and the latter are shown in Figure 9. The EPR parameters obtained from the spectra are listed in Table 6. The solid spectra is axial with $g_{\parallel} > g_{\perp} > 2.0$. These g -values are consistent with the distorted square pyramidal $\text{CuN}_2\text{O}_2\text{O}'$ chromophores present in the complexes and indicate a basically $d_{x^2-y^2}$ ground state for the Cu(II) ion. The apparent superhyperfine splitting was observed for **1**. The values of A_{\parallel} are obtained to be 112 and 116 G from room temperature and 77 K spectra, respectively.

Thermal Analysis. The crystal samples of all the complexes were heated from 25 to 500 $^{\circ}\text{C}$. For **1** and **2**, TGA showed that the weight loss occurred from 50 $^{\circ}\text{C}$ through 101 $^{\circ}\text{C}$. The estimated weight losses were 9.32% for **1** and 8.19% for **2**, respectively, corresponding to the loss of two lattice water molecules (calcd 9.96% for **1** and 8.36% for **2**, respectively). The coordinated water molecules and other ligands for both **1** and **2** were lost gradually since 195 $^{\circ}\text{C}$. The thermal decomposition behavior of **3** is a little different from that of **1** and **2**. When the crystal samples of **3** were heated, the weight loss of 9.62% was observed from 77 to 117 $^{\circ}\text{C}$, which is attributed to the release of both lattice and coordinated water molecules (calcd

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9.80%). The other parts of the complex were lost gradually after 170 °C.

Acknowledgment. This work was supported by the National Natural Science Foundation of China (No. 29971017) and the Teaching and Research Award Program for Outstanding Young Teachers in Higher Education Institutions of MOE, P. R. C.

Supporting Information Available: Tables of crystallographic data, structure solutions and refinements, atomic coordinates, interatomic bond distances and angles, and anisotropic thermal parameters for complexes **1**, **2**, and **3**. This material is available free of charge via the internet at <http://pubs.acs.org>.

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