Synthesis and Crystal Structure of a 4,4'-bipyridine Linked Dinuclear Copper(II) Complex Derived from 2-{[2-(2-hydroxyethylamino)ethylimino]methyl}-6-methylphenol

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Abstract
A novel 4,4'-bipyridine linked dinuclear copper(II) complex, [Cu2L2(bipy)](NO3)2·bipy (L = 2-{[2-(2-hydroxyethylamino)ethylimino]methyl}-6-methylphenol; bipy = 4,4'-bipyridine), was prepared and characterized by elemental analyses, IR spectroscopy, and single-crystal X-ray diffraction. The Cu···Cu distance is 11.129(2) Å. The CuII atom is coordinated by one phenolate O, one imine N, and one amine N atoms of a Schiff base ligand, and one N atom of the bridging 4,4'-bipyridine ligand, forming a square planar geometry. In the crystal structure of the complex, the dinuclear copper complex cations are linked by 4,4'-bipyridine molecules through intermolecular O–H···N hydrogen bonds, to form 1D chains running in the [2 0 −1] direction.

Keywords: Schiff base, Dinuclear structure, Copper complex, Crystal structure

1. Introduction
Molecular architectures, prepared by self-assembling of discrete coordination compounds, are attractive direction of modern inorganic and physico-inorganic chemistry, because cooperative behavior of linked units may lead to new properties.1 Transition metal complexes with Schiff base ligands have received considerable attention for their versatile structures and wide applications in coordination chemistry and biological areas.2–7 Among the complexes, those with polynuclear structures have been widely studied for their interesting magnetic properties.8,9 The building block method, because of its directive function of the target structures as well as the expected physical properties, has become one of the most important synthetic strategies for the preparation of polynuclear complexes. The prime method for designing polynuclear complexes is to use suitable bridging ligands, such as carboxylate anions, pseudohalide anions, etc.10–12 4,4'-Bipyridine and its analogs have proved especially useful as bridging ligands, resulting in a large number of polynuclear structures. However, to our knowledge, only 13 Schiff base copper complexes bearing 4,4'-bipyridine bridges have been reported so far.13–18 As a continuation of such work, we report here a new 4,4'-bipyridine bridged dinuclear copper(II) complex, [Cu2L2(bipy)](NO3)2·bipy (L = 2-{[2-(2-hydroxyethylamino)ethylimino]methyl}-6-methylphenol; bipy = 4,4'-bipyridine).

2. Experimental
2.1. Materials and Measurements
Commercially available 3-methylsalicylaldehyde, 2-(2-aminoethylamino)ethanol, and 4,4'-dipyridyl were purchased from Aldrich. Other solvents and reagents were made in China. All of the chemicals were used as received. C, H and N elemental analyses were performed with a Perkin-Elmer 240 elemental analyser. Infrared spectra were recorded on a Nicolet AVATAR 360 spectrometer 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.

2. 2. Synthesis of the Complex

3-Methylsalicylaldehyde (0.10 mmol, 13.6 mg) and hydroxyethylethylenediamine (0.10 mmol, 10.4 mg) were dissolved in methanol (10 mL). The mixture was stirred at room temperature for 10 min to give a yellow solution. To this solution was added with stirring a methanolic solution (10 mL) of Cu(NO₃)₂ · 3H₂O (0.10 mmol, 24.2 mg) and 4,4’-bipyridine (0.10 mmol, 15.6 mg). The mixture was stirred for another 10 min at room temperature. After keeping the filtrate on air for a few days, blue block-shaped crystals suitable for X-ray crystal structure determination, were formed at the bottom of the vessel. The crystals were isolated by filtration, washed three times with methanol and dried in a vacuum desiccator containing anhydrous CaCl₂. Yield 38% on the basis of copper salt. Analysis: Found: C 52.7, H 5.1, N 13.7%. Calculated for C₄₄H₅₀Cu₂N₁₀O₁₀: C 52.5, H 5.0, N 13.9%. IR data (KBr, cm⁻¹): 3437m, 3166m, 1637s, 1601m, 1548w, 1440m, 1416m, 1375s, 1322s, 1221w, 1074w, 1026w, 821m, 752w, 627w, 563w, 465w.

2. 3. X-ray Crystallography

Diffraction intensities for the complex were collected at 298(2) K using a Bruker D8 VENTURE PHOTON diffractometer with Mo Kα radiation (λ = 0.71073 Å). The collected data were reduced using SAINT program, and multi-scan absorption corrections were performed using SADABS program. Structure of the complex was solved by direct methods and refined against $F^2$ by full-matrix least-squares methods using SHELXTL. All of the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in idealized positions and constrained to ride on their parent atoms. Crystallographic data for the complex are summarized in Table 1. Selected bond lengths and angles are given in Table 2.

3. Results and Discussion

3. 1. General

The complex was prepared by the reaction of equimolar quantities of 3-methylsalicylaldehyde, hydroxyethylethylenediamine, 4,4’-bipyridine and Cu(NO₃)₂ · 3H₂O in methanol. Crystals of the complex are soluble in DMF, DMSO, methanol, ethanol, and acetonitrile.

3. 2. Crystal Structure Description of the Complex

Molecular structure of the complex is shown in Figure 1 together with the atom numbering scheme. X-ray crystallography indicates that the asymmetric unit of the complex contains a 4,4’-bipyridine bridged centrosymmetric dinuclear copper(II) complex cation, a hydrogen bonded 4,4’-bipyridine molecule, and two nitrate anions. The inversion center of the dinuclear complex cation is located at the midpoint of the 4,4’-bipyridine ligand. The Cu···Cu distance is 11.129(2) Å. The CuII atom is coordinated by one phenolate O, one imine N, and one amine N atoms of a Schiff base ligand, and one N atom of the bridging 4,4’-bipyridine ligand, forming a square planar geometry. The significant distortion of the square planar coordination is mainly revealed by the bond angles.

### Table 1. Crystallographic data and refinement parameters for the complex

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
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<tbody>
<tr>
<td>Chemical formula</td>
<td>C₄₄H₅₀Cu₂N₁₀O₁₀</td>
</tr>
<tr>
<td>M_r</td>
<td>1006.02</td>
</tr>
<tr>
<td>Crystal color, habit</td>
<td>Blue, block</td>
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<tr>
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<td>P–1</td>
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<tr>
<td>b (Å)</td>
<td>10.9261(7)</td>
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<tr>
<td>c (Å)</td>
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<tr>
<td>α (°)</td>
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<tr>
<td>β (°)</td>
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<tr>
<td>γ (°)</td>
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<tr>
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<td>Z</td>
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<tr>
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<tr>
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<tr>
<td>μ (mm⁻¹)</td>
<td>0.996</td>
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<td>F(000)</td>
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<td>Number of observed data [I &gt; 2σ(I)]</td>
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<tr>
<td>Number of parameters</td>
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<tr>
<td>R₁, wR₂ [I &gt; 2σ(I)]</td>
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<tr>
<td>R₁, wR₂ (all data)</td>
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<tr>
<td>Goodness of fit on $F^2$</td>
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### Table 2. Selected bond distances (Å) and angles (°) for the complex

<table>
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<tr>
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<td>Cu(1)–O(1)</td>
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<tr>
<td>Cu(1)–N(2)</td>
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<td>O(1)–Cu(1)–N(1)</td>
<td>93.34(7)</td>
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<tr>
<td>N(1)–Cu(1)–N(3)</td>
<td>164.99(8)</td>
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<tr>
<td>Cu(1)–N(1)</td>
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<td>Cu(1)–N(3)</td>
<td>2.035(2)</td>
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<td>O(1)–Cu(1)–N(2)</td>
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<td>N(1)–Cu(1)–N(2)</td>
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<tr>
<td>N(3)–Cu(1)–N(2)</td>
<td>95.44(7)</td>
</tr>
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N1–Cu1–N2 deviates from 90° by 5.81(7)°, which is due to the strain created by the five-membered chelate ring Cu1/N1/C8/C9/N2. The Cu–O and Cu–N bond lengths are comparable to the corresponding values observed in the Schiff base copper(II) complexes cited above. The dihedral angle between the planes defined by the bridging 4,4’-bipyridine ligand and the C1–C6 benzene ring is 31.8(3)°.

In the crystal structure the dinuclear copper complex cations are linked by 4,4'-bipyridine molecules through intermolecular O–H···N hydrogen bonds [O2–H2···N4: O2–H2 = 0.88 Å, H2···N4 = 1.90 Å, O2···N4 = 2.751(3) Å, O2–H2···N4 = 163°; N2–H2A···O5: N2–H2A = 0.89 Å, H2A···O5 = 2.12 Å, N2···O5 = 2.976(3) Å, N2–H2A···O5 = 160°], to form 1D chains running in the [2 0 –1] direction (Figure 2).

3. 3. IR Spectra

The bands in the range of 2850–2990 cm⁻¹ are characteristic of aliphatic ν(C–H) vibrations for the complex and the bands observed at 3030–3090 cm⁻¹ are attributed to the aromatic ν(C–H) vibrations. The medium and broad band centered at 3437 cm⁻¹ is assigned to the ν(O–H) vibration, while the medium and sharp band at 3166 cm⁻¹ is assigned to the ν(N–H) vibration. The strong absorption band at 1637 cm⁻¹ can be attributed to ν(C=–N). Nitrato complexes show IR bands in the range 1410–1448 (ν₁), 1290–1322 (ν₂), and 1073–1077 cm⁻¹ (ν₃) due to NO stretches. The value of Δ(ν₂ – ν₁), i.e., 102–131 cm⁻¹, suggests monodentate coordination. For monodentate coordination of NO₃⁻,

Figure 1. The structure of the complex, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. Unlabelled atoms are at the symmetry position (2 − x, 1 − y, − z).

Figure 2. The crystal packing of the complex, viewed along the b axis. Hydrogen bonds are shown as dashed lines.
the separation of first NO stretching vibrations is low (100–130 cm⁻¹), whereas these bands show larger separation (180–225 cm⁻¹) when NO₃ is bidentate.26 IR spectrum of the complex shows a band at 1375 cm⁻¹ due to ionic nitrate.27

3.4. Thermal Property

Thermal gravimetric analysis (TG) were conducted from 25 to 1000 °C under air atmosphere at a heating rate of 10 °C/min to examine the stability of the complex (Figure 3). The first step started at 202 °C and completed at 326 °C, probably corresponding to the loss of the coordinated and uncoordinated bipy ligands and methylbenzylidene moiety of the Schiff base ligands. The observed weight loss of 51.5% is close to the calculated value (52.3%). The second step, from 326 °C to 473 °C, probable corresponds to the loss of the remaining moieties of the Schiff base ligands and the nitrate anions, and the formation of the final product CuO. The total observed weight loss of 85.0% agrees well with the calculated value (84.1%).

Figure 3. TG curve of the complex.

4. Conclusions

A novel dinuclear copper(II) complex has been prepared and characterized by elemental analyses, IR spectroscopy, and single crystal X-ray diffraction. The Cu²⁺ atom is coordinated by one phenolate O, one imine N, and one amine N atoms of a Schiff base ligand, and one N atom of the bridging 4,4'-bipyridine ligand, forming a square planar geometry. Crystal structure of the complex are stabilized by intermolecular O–H···N hydrogen bonds. Thermal analysis indicates that the complex is stable up to 202 °C.

5. Supplementary Information

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre (CCDC-956327). Copy of this information can be obtained free of charge from CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk).

6. References

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