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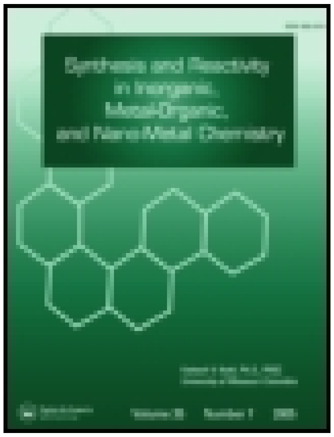

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Synthesis, Characterization, and Crystal Structure of a Novel Acetate-bridged Polynuclear Schiff Base Copper(II) Complex

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Synthesis, Characterization, and Crystal Structure of a Novel Acetate-bridged Polynuclear Schiff Base Copper(II) Complex

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A novel acetate-bridged polynuclear Schiff base copper(II) complex, $[CuL(CH_3COO)]_n$ (L = 4-nitro-2-[(2-methylaminoethylimino)methyl]phenol), has been synthesized and characterized by elemental analysis, IR spectrum and single crystal X-ray diffraction. Each Cu atom in the complex is five-coordinate in a trigonal-bipyramidal configuration, with one imine N atom and two acetate O atoms defining the basal plane, and one phenolate O and one amine N atoms occupying the axial positions. The [4-nitro-2-[(2-methylaminoethylimino)methyl]phenolato]copper(II) units are linked by the bridging acetate ligands, forming polymeric chains running along the *c* axis.

Keywords synthesis, crystal structure, Schiff base, copper complex, polynuclear complex

INTRODUCTION

Polynuclear complexes play an important role in the development of coordination chemistry related to magnetism and molecular architectures.[1–5] The prime strategy for designing these molecular materials is to use suitable bridging ligands that determine the nature of the magnetic interactions.[6–9] One to the versatile coordination modes of the acetate ligand and the wide range of magnetic coupling mediated by the acetate bridges, this ligand has become one of the most extensively studied building blocks in the field.[10–12]

In this paper, the author designed and synthesized the flexible tridentate Schiff base ligand 4-nitro-2-[(2-methylaminoethylimino)methyl]phenol (L). The complexes derived from the Schiff base ligand 2-[2-(methylamino)ethyliminomethyl]phenol[13] as well as its derivatives[14,15] have been widely studied; however, to our knowledge those from the similar Schiff base ligand L have never been reported so far. The acetate ligand readily bridges different metal ions through the O atoms. We report herein the synthesis, characterization and crystal structure of a novel acetate-bridged polynuclear Schiff base copper(II) complex $[CuL(CH_3COO)]_n$.

EXPERIMENTAL

Materials and Measurements

Commercially available 5-nitrosalicylaldehyde and *N*-methylethane-1,2-diamine were purchased from Sigma and used without further purification. Other solvents and reagents were made in China and used as obtained. C, H and N elemental analyses were performed with a Perkin-Elmer 240C elemental analyzer. The IR spectra were measured with a FT-IR 170-SX (Nicolet) spectrophotometer.

Synthesis of L

The ligand L was prepared by the condensation of 5-nitrosalicylaldehyde (1.0 mmol, 167.1 mg) with *N*-methylethane-1,2-diamine (1.0 mmol, 74.1 mg) in methanol (30 mL) at room temperature. Anal. Calcd. for $C_{10}H_{13}N_3O_3$ (FW 223.2): C, 53.81; H, 5.87; N, 18.82. Found: C, 53.60; H, 5.95; N, 18.73%. Yield, 171.0 mg (76.7% on the basis of 5-nitrosalicylaldehyde). Selected IR data (KBr, cm^{-1}): 3428 (m), 3217 (m), 2982 (m), 2937 (m), 2871 (m), 1655 (s), 1535 (s), 1354 (s), 1230 (m), 720 (m).

Synthesis of $[CuL(CH_3COO)]_n$

To a stirred methanol solution (10 mL) of L (0.1 mmol, 22.3 mg) was added an aqueous solution (3 mL) of $Cu(CH_3COO)_2 \cdot H_2O$ (0.1 mmol, 19.9 mg). The mixture was stirred for 30 min at room temperature to give a deep blue solution. Blue block-shaped crystals of the complex, suitable for X-ray single crystal analysis, were formed at the bottom of the vessel on slow evaporation of the solvent for a week. The isolated crystals were washed three times with cold methanol, and dried in a vacuum over anhydrous $CaCl_2$. Anal. Calcd. for $C_{12}H_{15}CuN_3O_5$ (FW 344.8): C, 41.80; H, 4.38; N, 12.19. Found: C, 42.05; H, 4.50; N, 12.03%. Yield, 18.0 mg (52.2% on the basis of L). Selected IR data (KBr,

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cm^{-1}): 3451 (m), 2982 (m), 2935 (m), 2872 (w), 1618 (s), 1573 (s), 1532 (s), 1408 (s), 1345 (s), 1180 (s), 623 (s).

DATA COLLECTION, STRUCTURAL DETERMINATION AND REFINEMENT

Crystal Structure Determination

Diffraction intensities for the complex were collected at 298(2) K using a Bruker SMART APEXII CCD area-detector with Mo$K\alpha$ radiation ($\lambda = 0.71073$ Å). The collected data were reduced using the SAINT program,[16] and multi-scan absorption corrections were performed using the SADABS program.[17] The structure was solved by direct method and refined against F^2 by full-matrix least-squares method using the SHELXTL program.[18] All of the non-hydrogen atoms were refined anisotropically. Atom H2 attached to N2 was located in a difference Fourier map and refined isotropically, with N-H distance restrained to 0.90(1) Å. All other H atoms in the complex were placed in calculated positions 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. Crystallographic data for the complex has been deposited with the Cambridge Crystallographic Data Centre (CCDC 637666).

TABLE 1
Crystallographic and experimental data for the complex

Formula	$C_{12}H_{15}CuN_3O_5$
FW	344.81
Crystal shape/colour	Block/blue
Crystal size/mm	0.30 × 0.23 × 0.22
Crystal system	Monoclinic
Space group	$P2_1/c$
a/Å	14.057(2)
b/Å	11.091(2)
c/Å	9.341(1)
β/°	92.149(2)
V/Å^3	1455.3(3)
Z	4
λ (Mo$K\alpha$)/Å	0.71073
T/K	298(2)
μ/mm^{-1} (Mo − K_α)	1.525
T_{min}	0.658
T_{max}	0.730
Reflections/parameters	3319/195
Independent reflections	2756
F(000)	708
Goodness of fit on F^2	1.046
R_1, wR_2 [$I \geq 2\sigma(I)$]^a	0.0356, 0.1069
R_1, wR_2 (all data)^a	0.0434, 0.1122

$^a R_1 = \sum||Fo| - |Fc||/\sum|Fo|$, $wR_2 = [\sum w(Fo^2 - Fc^2)^2/\sum w(Fo^2)^2]^{1/2}$.

TABLE 2
Selected bond lengths (Å) and bond angles (°) for the complex

Cu1-N1	2.062(2)	Cu1-N2	2.186(2)
Cu1-O1	2.068(2)	Cu1-O4	1.986(2)
Cu1-O5A	2.020(2)		
O4-Cu1-O5A	108.3(1)	O4-Cu1-N1	122.7(1)
O5A-Cu1-N1	128.7(1)	O4-Cu1-O1	95.3(1)
O5A-Cu1-O1	84.9(1)	N1-Cu1-O1	86.1(1)
O4-Cu1-N2	104.2(1)	O5A-Cu1-N2	92.2(1)
N1-Cu1-N2	80.5(1)	O1-Cu1-N2	160.2(1)

RESULTS AND DISCUSSION

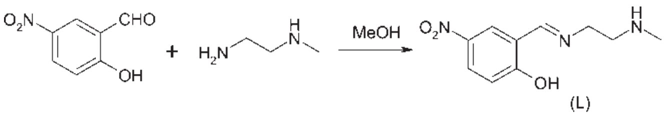
Preparation of the Ligand and the Complex

The author herein designed and synthesized the flexible Schiff base ligand L (as shown in Scheme 1). The acetate anion can bridge different metal ions through the two O atoms,[13−15] forming polynuclear structures. The copper(II) complex was synthesized according to the procedure as shown in Scheme 2.

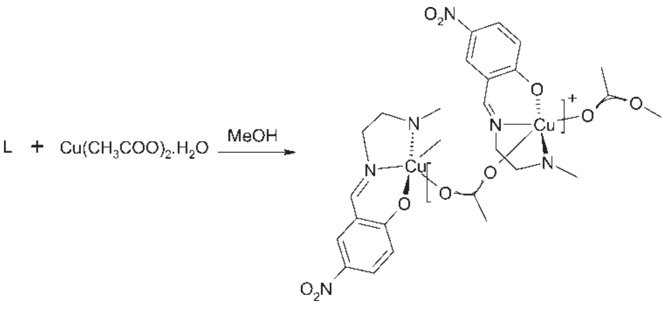
When compared to the structure the author had reported recently,[14] we can obviously found that the acetate anion is a good bridging group, and play an important role in the formation of the polymeric structure.

Stability in Air and Solubility in General Solvents

The Schiff base ligand L are yellow crystallite, stable in air at room temperature. It is soluble in polar organic solvents, such as MeOH, EtOH, MeCN and Me_2CO, but insoluble in water and Et_2O. The complex is also stable in air at room



SCH. 1.



SCH. 2.

temperature, soluble in DMF, DMSO, MeOH, EtOH and MeCN, insoluble in water and Et_2O.

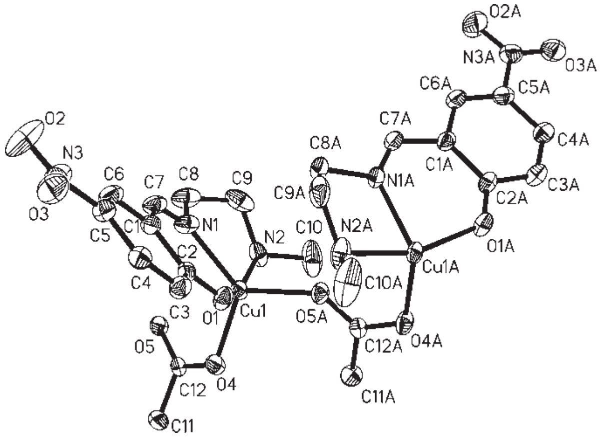


FIG. 1. The structure of the complex, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. H atoms have been omitted for clarity. Atoms labeled with the suffix A are at the symmetry positions x, $1/2-y$, $1/2+z$.

Structure Description of the Complex

The molecular structure and the molecular packing of the complex are shown in Figure 1 and Figure 2, respectively. The complex is a novel acetate-bridged polynuclear copper(II) compound. Each Cu atom in the complex is five-coordinate in a trigonal-bipyramidal configuration, with one imine N atom and two acetate O atoms defining the basal plane, and one phenolate O and one amine N atoms occupying the axial positions. The significant distortion of the trigonal-bipyramid is revealed by the bond angles between the axial and basal donor atoms. The O1-Cu1-N2 bond angle in the complex deviates from 180° by 19.8(1)°, as a result of the strain created by the five-membered chelate ring Cu1/N1/C8/C9/N2. The angles between the two axial donors and the three equatorial donor atoms range from 80.5(1)° for the N1-Cu1-N2 angle to 104.2(1)° for the O4-Cu1-N2 angle. The three equatorial angles range from 108.3(1)° for O4-Cu1-O5 to 128.7(1)° for O5-Cu1-N1, showing only slight differences from the ideal value of 120°. The bond lengths subtended at the metal centers are comparable to the corresponding values observed in other similar copper(II) complexes[19–21] and, as expected, the bonds involving amine N atoms are longer than those involving imine N atoms. The acetate anions act as bridging ligands and coordinate to the metals through the

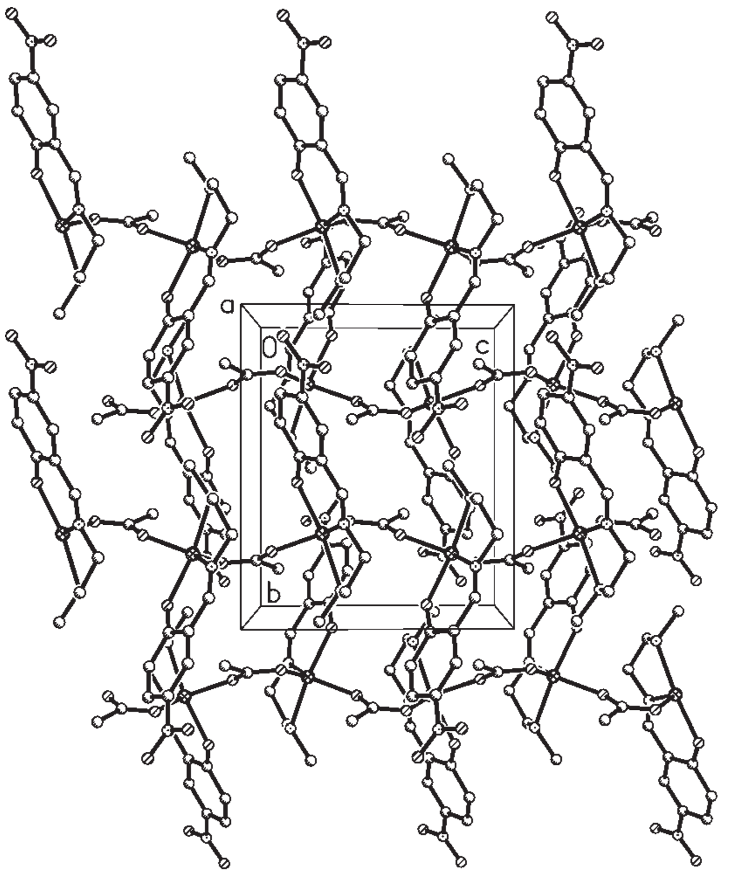


FIG. 2. The molecular packing of the complex, viewed along the a axis.

two O atoms. The deviation of atom Cu1 from the least-squares plane defined by the three basal donors is 0.054(1) Å.

In the crystal structure of the complex, the [4-nitro-2-[(2-methylaminoethylimino)methyl]phenolato]copper(II) units are linked by the bridging acetate ligands, forming polymeric chains running along the *c* axis.

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