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Synthesis and Crystal Structure of a Trinuclear Copper(II) Complex Derived from N,N'-Bis(4-Methoxysalicylidene)-1,3-Pentanediamine[1]

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Abstract—A trinuclear copper(II) complex $[Cu_3Cl_2L_2]$, where L is the dianionic form of N,N'-bis(4-methoxysalicylidene)-1,3-pentanediamine, has been synthesized and characterized by means of spectroscopic methods and single crystal X-ray structure determination. The complex crystallizes in the orthorhombic space group *Pnma* with unit cell dimensions $a = 15.301(2)$, $b = 23.226(2)$, $c = 12.089(1)$ Å, $V = 4296.2(8)$ Å^3, $Z = 4$, $R_1 = 0.0682$, and $wR_2 = 0.1590$. The molecule of the complex possesses a crystallographic mirror plane symmetry with the mirror plane passes through the three Cu atoms and the two Cl atoms. The two terminal Cu atoms adopt distorted square pyramidal coordination, and the middle one adopts square planar coordination. The intramolecular Cu···Cu distances are 2.900(1) and 2.916(1) Å. The complex was tested for its antibacterial activity to assess its inhibiting potential.

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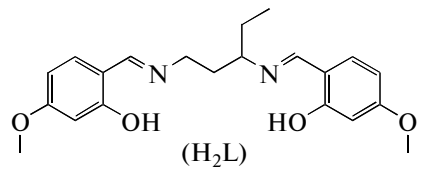
INTRODUCTION

Schiff bases have often been used as versatile chelating ligands in coordination chemistry. Schiff bases with donors, such as O, N, and S, have structure similarities with neutral biological systems and due to presence of imine groups are utilized in elucidating the mechanism of transformation of rasemination reaction in biological system [1–3]. The Schiff bases preprared from salicylaldehyde and its derivatives are interesting and have received considrable attention not only for their application in coordination chemistry [4–6] but also for their importance in medicinal and pharmaceutical fields. Most Schiff bases and their complexes show biological activities including antibacterial [7–9], antifungal [9, 10], antitumor [11], anticancer [10], anticorrosion and anti-inflammatory activities. As a continuation of the biological activities of Schiff base complexes, in the present article, the author reports the synthesis and structure of a new Schiff base trinuclear copper complex with the new Schiff base ligand N,N'-bis(4-methoxysalicylidene)-1,3-pentanediamine (H_2L). The antibacterial activity of the complex was evaluated.



(H_2L)

[1] The article is published in the original.

EXPERIMENTAL

Material and methods. All materials were obtained from commercial sources and used as received. Copper chloride was prepared by the reaction of basic cupric carbonate with chloric acid in distilled water. Infrared spectra were collected on a Nicolet 5SXC FT-IR spectrometer as KBr pellets. Microanalyses for C, H, and N were performed on a PerkinElmer 2400 CHNS/O Elemental Analyzer.

Synthesis of H_2L. To a methanolic solution (20 mL) of 4-methoxysalicylaldehyde (0.30 g, 2 mmol) was added dropwise a methanolic solution (10 mL) of pentane-1,3-diamine (0.10 g, 1 mmol). The reaction mixture was gently heated at 50°C for 30 min while stirring and the compound precipitated was recrystallized from ethanol, yielding yellow product of H_2L. The yield was 81%. IR (KBr; ν, cm^{-1}): 1639 (C=N).

For $C_{21}H_{26}N_2O_4$			
anal. calcd., %:	C, 68.1;	H, 7.1;	N, 7.6.
Found, %:	C, 67.9;	H, 7.1;	N, 7.5.

Synthesis of the copper complex. To a methanolic solution (10 mL) of the Schiff base ligand (37 mg, 0.1 mmol) was added a methanolic solution (5 mL) of copper chloride (35 mg, 0.2 mmol). The reaction mixture was gently heated at 50°C for 30 min to give a blue solution. Blue block-shaped single crystals of the complex were formed when slow evaporation of the solu-

Table 1. Crystal data and structure refinement for the complex

Parameter	Value
M	990.3
Crystal size, mm	0.23 × 0.20 × 0.20
Temperature, K	298(2)
Crystal system	Orthorhombic
Space group	*Pnma*
a, Å	15.301(2)
b, Å	23.226(2)
c, Å	12.089(1)
V, Å^3	4296.2(8)
Z	4
ρ_{calcd}, g cm^{-3}	1.531
$F(000)$	2020
μ, mm^{-1}	1.652
Max/min transmission	0.702/0.733
θ Range for data collection, deg	2.3–28.0
Index ranges h, k, l	$-18 \le h \le 15$, $-28 \le k \le 20$, $-14 \le l \le 14$
Reflections collected	19918
Independent reflections (R_{int})	3961 (0.0802)
Observed reflections	2451
Parameters refined	297
R_1, wR_2 ($I > 2\sigma(I)$)	0.0682, 0.1590
R_1, wR_2 (all data)	0.1257, 0.2079
Goodness-of-fit on F^2	1.112
Largest diff. peak and hole, e Å^{-3}	1.835, −0.766

tion in air for a few days. The yield was 37%. IR (KBr; ν, cm^{-1}): 1610 (C=N).

For $C_{42}H_{40}Cl_2Cu_3N_4O_8$			
anal. calcd. %:	C, 50.9;	H, 4.1;	N, 5.7.
Found, %:	C, 50.7;	H, 4.2;	N, 5.7.

X-ray structure determination. Crystal data, data collection and refinement parameters for the complex are listed in Table 1. Data were obtained on a Bruker Apex II diffractometer equipped with graphite monochromated MoK_α (λ = 0.71073 Å) radiation. The structure of the compound was solved by direct methods and refined on F^2 by full-matrix least-squares using SHELX-97 [12]. All non-hydrogen atoms were refined anisotropically. All hydrogens were placed in calculated positions, assigned fixed isotropic thermal parameters at 1.2 or 1.5 times the equivalent isotropic U of the atoms to which they are attached and allowed to ride on their respective parent atoms. The contributions of these hydrogen atoms were included in the structure factor calculations. Selected bond lengths and angles are listed in Table 2.

Supplementary material for the complex has been deposited with the Cambridge Crystallographic Data Centre (no. 868925; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

Antibacterial activities. Antibacterial activity of the complex was investigated using agar well diffusion method [13]. The activities of the free Schiff base ligand and standard drug Imipenem were also studied against the *Staphylococcus aureus* and *Bacillus subtilis* (as Gram-positive bacteria) and *Pseudomonas aerugi-*

Table 2. Selected bond lengths (Å) and angles (deg) for the complex*

Bond	d, Å	Bond	d, Å
Cu(1)–N(1)	1.954(6)	Cu(1)–O(1)	1.963(5)
Cu(1)–Cl(1)	2.543(3)	Cu(2)–N(2)	1.963(6)
Cu(2)–O(3)	1.975(5)	Cu(2)–Cl(2)	2.528(3)
Cu(2)–Cu(3)	2.9160(15)	Cu(3)–O(1)	1.942(4)
Cu(3)–O(3)	1.943(4)		
Angle	**ω, deg**	**Angle**	**ω, deg**
N(1)Cu(1)N(1*A*)	96.9(4)	N(1)Cu(1)O(1*A*)	160.9(2)
N(1)Cu(1)O(1)	91.3(2)	O(1)Cu(1)O(1*A*)	76.1(3)
O(1)Cu(1)Cl(1)	85.35(15)	N(1)Cu(1)Cl(1)	108.21(19)
N(2)Cu(2)N(2*A*)	96.4(4)	N(2)Cu(2)O(3*A*)	160.7(2)
N(2)Cu(2)O(3)	91.5(2)	N(2)Cu(2)Cl(2)	107.05(18)
O(3)Cu(2)O(3*A*)	76.0(3)	O(1)Cu(3)O(1*A*)	77.1(3)
O(1)Cu(3)O(3*A*)	178.6(2)	O(1)Cu(3)O(3)	102.7(2)
O(3)Cu(3)O(3*A*)	77.4(3)		

* Symmetry operation for *A*: x, $1/2 - y$, z.

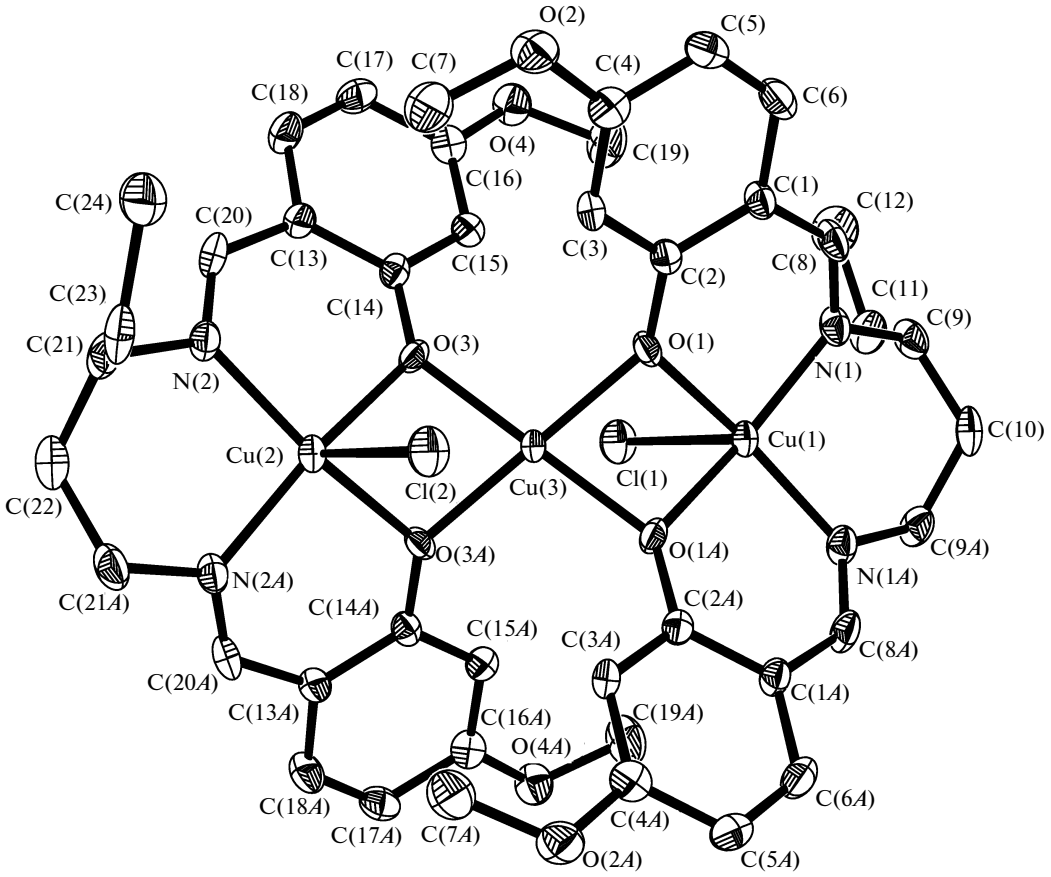


Fig. 1. Molecular structure of the complex. Hydrogen atoms have been omitted for clarity. Symmetry operation for *A*: x, $1/2 - y$, z.

nosa, *Escherichia coli* and *Salmonella typhi* (as Gram-negative bacteria). Strains were obtained from Dalian Medical University. The solution of 2 mg/mL of each compound (free Schiff base ligand and Imipenem) in DMSO was prepared for testing against bacteria. Centrifuged pellets of bacteria from a 24 h old culture containing approximately 10^4–10^6 CFU (colony forming unit) per ml were spread on the surface of Muller Hinton Agar plates. Wells were created in medium with the help of a sterile metallic bores and nutrients agar media (agar 20 g + beef extract 3 g + peptones 5 g) in 1000 mL of distilled water (pH 7.0), autoclaved and cooled down to 45°C. Then it was seeded with 10 mL of prepared inocula to have 10^6 CFU/mL. Petri plates were prepared by pouring 75 mL of seeded nutrient agar. The activities were determined by measuring the diameters of the inhibition zones (in mm). The growth inhibition was calculated according to reference [13].

RESULTS AND DISCUSSION

The Schiff base ligand was prepared by a 1 : 2 condensation of propane-1,3-diamine with 4-methoxysalicylaldehyde in methanol. Reaction of the ligand with copper chloride in methanol gave the copper complex.

The crystal structure analysis of the complex reveals that it is a phenolate oxygen-bridged trinuclear copper(II) compound, which has a crystallographic mirror plane symmetry (Fig. 1). The mirror plane passes through the atoms Cu(1), Cu(2), Cu3), Cl(1), Cl(2), C(10), and C(22). The intramolecular Cu(1)···Cu(3) and Cu(2)···Cu(3) distances are 2.900(1) and 2.916(1) Å, respectively. The terminal Cu(1) and Cu(2) atoms are in square pyramidal coordination with two phenolate O and two imine N atoms of the Schiff base ligand located at the basal plane and with one C(l) atom occupying the apical position. The square pyramidal coordinations are distorted, as evidenced from the bond angles among the apical and basal donor atoms, ranging from 85.3(2)° to 108.2(2)° for Cu(1), and from 87.2(2)° to 107.0(2)° for Cu(2). Atoms Cu(1) and Cu(2) displaced out of the least-squares planes defined by the basal donor atoms in the direction of the C(l) atoms by 0.271(2) and 0.279(2) Å, respectively. The Cu(3) atom is coordinated by four phenolate O atoms from two Schiff base ligands, forming a square planar coordination. The square planar is also distorted, as evidenced from the perpendicular

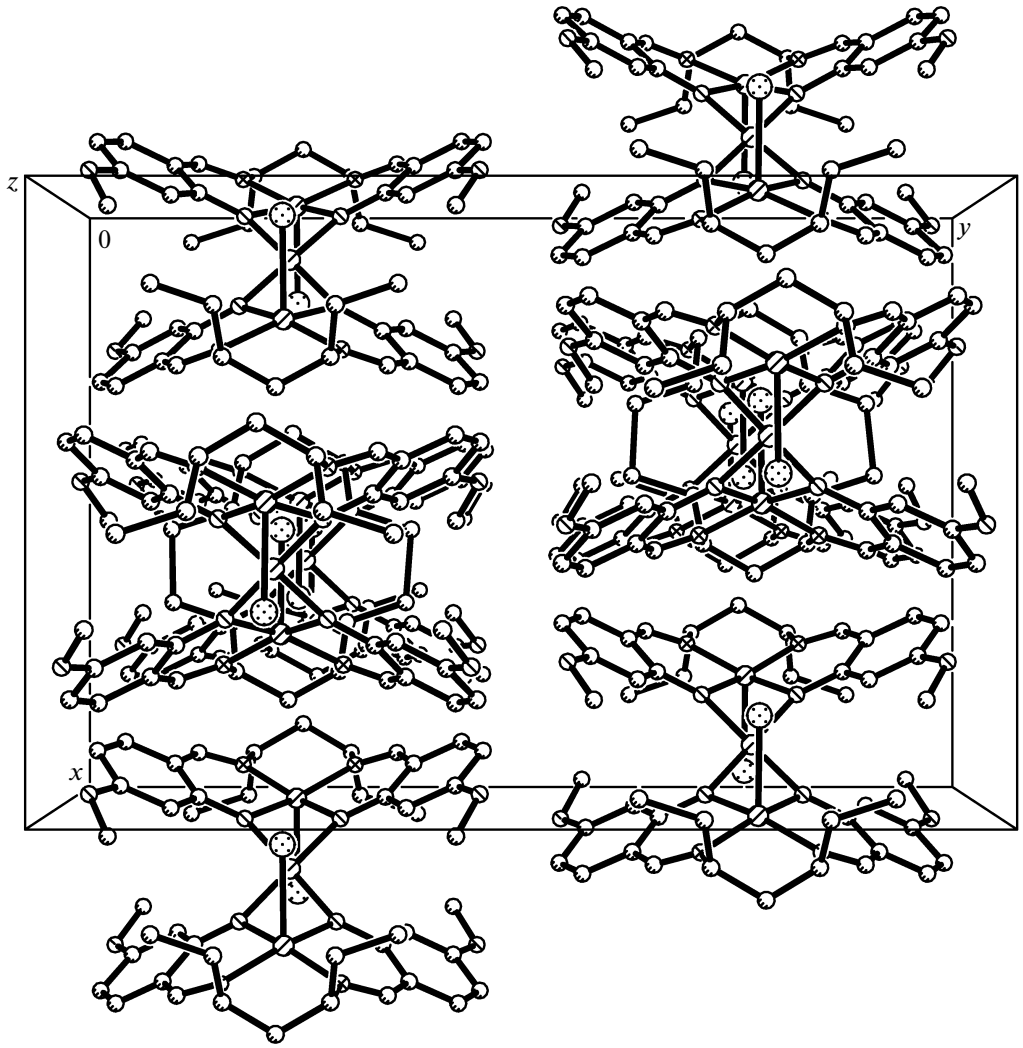


Fig. 2. The molecular packing structure of the complex, viewed along the *z* axis.

bond angles, ranging from 77.1(3)° to 102.7(2)°. The distortion of the square pyramidal and square planar coordinations are mainly caused by the strain force created by the roof-shaped four-membered chelate rings Cu(1)–O(1)–Cu(3)–O(1*A*) and Cu(2)–O(3)–Cu(3)–O(3*A*). The coordinate bond lengths are typical and within the values observed in other similar copper(II) complexes with Schiff bases [14–16].

In the CuL units of the complex, the dihedral angles between the two benzene rings of the Schiff base ligands are 59.8(3)° and 57.4(3)°. The chelate rings formed by the atoms Cu(1), N(1), C(9), C(10), C(9*A*), N(1*A*) (Ring 1) and Cu(2), N(2), C(21), C(22), C(21*A*), N(2*A*) (Ring 2) have chair conformations. In Ring 1, the diagonally positioned atoms, Cu(1) and C(10), are shifted from the least-squares plane defined by the atoms N(1), C(9), C(9*A*), and N(1*A*) by 0.617(2) and 0.673(3) Å, respectively. In Ring 2, the distances of the two diagonally positioned atoms, Cu(2) and C(22), from the least-squares plane defined by the atoms N(2), C(21), C(21*A*), and N(2*A*) are 0.623(2) and 0.695(5) Å, respectively.

In the crystal structure of the complex, molecules are stacked along the *z* axis via weak π···π interactions, as shown in Fig. 2.

The weak absorption centered at 3421 cm^{-1} is assigned to the ν(O–H) of the Schiff base ligand, which is absent in the complex, indicating the coordination through the deprotonated form of the Schiff base ligand. The strong absorption band at 1639 cm^{-1} for the Schiff base is assigned to the azomethine groups, ν(C=N), which shifts to lower wave number (1610 cm^{-1}) in the complex, indicating the coordination of the nitrogen atoms of the azomethine groups to the Cu atoms. The weak bands in the region 400–600 cm^{-1} for the complex can be assigned to the ν(Cu–O) and ν(Cu–N).

The copper complex, the free Schiff base, and the standard drug Imipenem were screened separately for

Table 3. Bactericidal screening data of the tested materials (inhibition zone in mm)

Microorganism	The copper complex	H_2L	Imipenem
Staphylococcus aureus	+++	++	++++
Bacillus subtilis	+++	+	++++
Pseudomonas aeruginoca	++		++++
Escherichia coli	+		++++
Salmonella typhi	+		++++

++++ = excellent activity (>90% inhibition), +++ = significant activity (70–90% inhibition), ++ = moderate activity (40–70% inhibition), + = weak activity (<40% inhibition).

their antibacterial activities against the bacteria *Staphylococcus aureus*, *Bacillus subtilis*, *Pseudomonas aeruginoca*, *Escherichia coli*, and *Salmonella typhi*. The diffusion agar technique was used to evaluate the antibacterial activities of the compounds [17]. The results are summarized in Table 3. From the results, it is obvious that the copper complex is more active towards Gram-positive strains than Gram-negative strains. This may be caused by the difference in the structures of the cell walls. The walls of Gram-negative cells are more complex than those of Gram-positive cells. The copper complex showed significant activity against *Staphylococcus aureus* and *Bacillus subtilis* and moderate activities against *Pesudomonas aeruginoca*, but weak or moderate activities against *Escherichia coli* and *Salmonella typhi*. The free Schiff base H_2L has moderate activity against *Staphylococcus aureus*, and weak activity against *Bacillus subtilis*, but no activity against *Pseudomonas aeruginoca*, *Escherichia coli* and *Salmonella typhi*. In general, the copper complex showed stronger antibacterial activities than the free Schiff base ligand.

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