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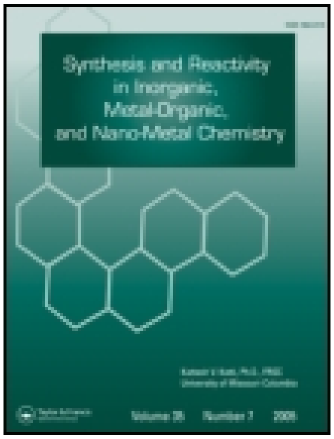

Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsrt20

Synthesis, Structure and Antimicrobial Study of N-Salicylidene-Phenylpropanolamine Bicopper(II) Complex

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Published online: 15 Feb 2007.

To cite this article: Tong-Tao Xu , Xing-You Xu , Jian Gao , Ming-Yan Wang , Lu-De Lu , Jia Ni & Guo-Xiang Xu (2006) Synthesis, Structure and Antimicrobial Study of N-Salicylidene-Phenylpropanolamine Bicopper(II) Complex, Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry, 36:9, 667-672

To link to this article: http://dx.doi.org/10.1080/15533170600962489

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Synthesis and Reactivity in Inorganic, Metal-Organic and Nano-Metal Chemistry, 36:667–672, 2006
Copyright © 2006 Taylor & Francis Group, LLC
ISSN: 0094-5714 print / 1532-2440 online
DOI: 10.1080/15533170600962489

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A new bicopper (II) complex [$Cu_2L_2Cl_2 \cdot H_2O$, H_2 L = C_6H_5-$CH(OH)CH(CH_3)N = CH(C_6H_5\text{-}2\text{-}OH)$], has been synthesized by Schiff base condensation of phenylpropanolamine with salicylaldehyde in the presence of Cu^{2+}. The crystal of the complex was characterized by X-ray diffraction, IR, ES-MS spectroscopy, molar conductivity and elemental analyses. Antimicrobial activity study found that the complex was active against *Candida albican*, *Bacillus pumilus* and *Bacillus coliforms*.

Keywords copper(II) complex, PPA, salicylaldehyde, crystal structure, toxicity

INTRODUCTION

Phenylpropanolamine (PPA) has been in use as an ingredient in many cold and cough remedies to relieve stuffy nose and congestion and in diet pills to control appetite[1–3] for many years. Podder reported its structure and Malone studied its chelating properties with copper(II)[4,5] Bhattacharyya studied its Schiff bases complexes with several metals, including nickel(II), palladium and platinum and described their formation and structure.[6] Recently, there are many of reports on PPA because it was linked to a significantly increased risk of stroke, especially in women ages 18 to 49.[7,8] However, information on the corresponding derivatives of the phenylpropanolamine Schiff base is still very scant. The structure of medicated active components is remolded, which is an effective way to prepare curative medicinal substances.[9] Therefore, it is important to develop new derivatives of PPA for potential biomedical applications. As part of our studies on the relationship between structure and antimicrobial activity of compounds with biologically active units, we have undertaken taken investigations on N-salicylidene-phenylpropanolamine Cu(II) complex, and the results are presented in this paper.

EXPERIMENTAL

Materials

All starting materials were of chemical purity. The solvents used in the physical measurements were of analytical purity (Nanjing Chemical Reagent Co. Ltd).

Received 27 May 2006; accepted 20 June 2006.

The project was supported by the National Science Foundation of Jiangsu Province (No. 02KJD150014) and the Key Laboratory of Marine Biotechnology of Jiangsu Province.

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Physical Measurements

Elemental analyses were determined with a Perkin-Elmer 240c instrument. Solution electrical conductivity was measured by a BSD-A numerical conductometer (Jiangsu, China) with solution concentration of $\sim 1.0 \times 10^{-3}\,\mathrm{mol \cdot dm^{-3}}$ in methanol at 297K. The cyclic voltammograms were obtained on a CHI660 electrochemical analyzer. IR spectrum was measured as KBr discs using a Nicolet 5DX FT-IR spectrophotometer. The ES mass spectral measurement of the complex was carried out on a LCQ System (Finngann MAT, USA) using methanol as mobile phase. The spray mass spectrum and capillary temperature were set at 4 KV and 200°C, respectively.

Synthesis of $Cu_2L_2Cl_2 \cdot H_2O$

To a stirred solution of salicylaldehyde (0.122 g, 1.0 mmol) and $Cu(ClO_4)_2 \cdot 6H_2O$ (0.372 g, 1.0 mmol) in 25 ml absolute methanol, a solution of phenylpropanolamine hydrochloride (0.187 g, 1.0 mmol) in 10 ml absolute methanol was added dropwise. Then, sodium hydroxide (0.040 g, 1.0 mmol) was added to the mixtures at 25°C. After stirring for 3 h at 45°C, the mixture was filtered and acetonitrile (5.0 ml) was added to the filtrate. The product $[Cu_2L_2Cl_2] \cdot H_2O$ was precipitated as green Schiff base complex in a yield of 59% (0.2140 g). M. P. 151.0°C (dec.). Anal. Calcd. for $C_{32}H_{34}Cl_2Cu_2N_2O_5$ (%): C, 52.10; H, 4.69; N, 3.86; Found: C, 52.15; H, 4.63; N, 3.81. IR (cm^{-1}): 2980s ν(NH); 1630 m ν(C=N); 2932s ν(OH);1545, 1446 m ν(aromatic ring). ES-MS: m/z (%):376.1(100), 349.1(39) and 633.1(38). Λ_M (CH_3OH, 297K):136 $\mathrm{S \cdot cm^2 \cdot mol^{-1}}$. The deep-green single crystals suitable for X-ray structure determination were obtained by slow evaporation of the resulting filtrates for about 2 days at ambient temperature.

Caution: Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of material should be prepared, and these should be handled with caution.

X-Ray Crystal Structure Determination

Crystal Data

$C_{32}H_{34}Cl_2Cu_2N_2O_5$, M = 724.59, green crystal, dimensions 0.20 mm × 0.20 mm × 0.15 mm, monoclinic, space group $P2_1/c$, $a = 10.224(2)$, $b = 13.675(3)$, $c = 24.632(5)$Å, $\beta = 96.197(4)°$; $V = 3423.8(12)$ Å^3, $F(000) = 1488$, $Z = 4$, $D_c = 1.406\ \mathrm{g/cm^3}$, $\mu = 1.438\ \mathrm{mm^{-1}}$, $\lambda = 0.71073$ Å; Largest diff. peak and hole, 0.467 and -0.260 e.A^{-3}.

Data Collection and Refinement of the Crystal Structure

A green block crystal of the title compound with dimensions of 0.20 mm × 0.20 mm × 0.15 mm was mounted on a glass fiber. X-ray diffraction intensity data were collected on a BRUKER SMART CCD diffractometer with the graphite monochromated $M_o - K_\alpha$ ($\lambda = 0.71073$ Å) radiation by using the $\omega - 2\theta$ scan technique ($1.66 \leq \theta \leq 25.00°$) at 293(2) K. A total of 17534 reflections were collected with 6025 unique reflections ($R_{int} = 0.0349$). The crystal structure was solved by direct methods and Fourier synthesis with the program SHELXS-97[10] and refined by full-matrix least-squares techniques on F^2 with the program SHELXS-97.[11] The non-hydrogen atoms were refined anisotropically and hydrogen atoms were added according to theoretical models. The final refinement converged at $R = 0.0512$ and $wR = 0.1249$ for 4350 observed reflections with $I > 2\sigma(I)$ $(W = 1/[\sigma^2 \quad (F_o^2) + (0.0741P)^2 + 1.4749P]$ where $P = (F_o^2 + 2\,Fc^2)/3)$, $S = 1.039$ and $(\Delta/\sigma)_{\max} = 1.675$. The largest peak and deepest hole on the final difference Fourier map are 0.467 and -0.260 e/Å^3, respectively.

Antimicrobial Activity Determination

As a preliminary screening for antimicrobial activity, agar diffusion method described in the previous paper[12] was used. $Cu_2L_2Cl_2 \cdot H_2O$ dissolved in DMF was tested against standard strains of *Candida albicans* CMCC (F) 98 001, *Bacillus coliforms* CMCC (B) 44 102 and *Bacillus pumilus* CMCC (B) 63 202. For the comparison, the antimicrobial activity of Cu $(ClO_4)_2 \cdot 6H_2O$ and PPA were also tested. Culture medium of antibiotic medium 1 was used for *Bacillus pumilus* and nutrient agar for *Candida albicans* and *Bacillus coliforms*. Culture medium was transferred to glass plates and froze at about 37°C. After test strains were spread on the solid culture medium surface, stainless steel tubes (7.8 × 6 × 10 mm) were placed vertically on the surface. 0.10 ml samples with certain concentration were injected to the steel tubes. They were allowed to incubate at 37°C for 24 h. The inhibition zone around the disc was calculated as zone diameter in millimeters. Blank tests showed that DMF in the preparation of the test solutions does not affect the test organisms. All tests were repeated three times and average data were taken as the final result.

RESULTS AND DISCUSSION

Crystal Structure of Complex

The selected bond distances and bond angles are summarized in Table 1. The molecular structure of the title compound and the packing diagram are shown in Figures 1 and 2, respectively. Crystal structure of the bicopper (II) complex consists of an isolated molecule unit of $Cu_2L_2Cl_2$ and H_2O molecule. In an isolated molecule unit, two hydrogen atoms of hydroxyl of salicylaldehyde were lost during the formation of coordinate bond for the charge balance. The asymmetrical system of hydrogen bonds breaks up the potential centrosymmetricity of both chelate molecules. In the molecule unit, two Cu (II) atoms are bridged by two chlorine atoms and locate in NO_2Cl_2 coordination environment with coordination number five and form two distorted square-pyramidal. The deformation parameters τ, computed on the basis of the two maximal valency angles of the Cu(1) and Cu(2) atom as $(\alpha_1\text{-}\alpha_2)/60$[13] are 13.75% and 18.05%, respectively, indicate that Cu(1) and Cu(2) polyhedron are all close to

TABLE 1
Selected bond lengths (Å) and bond angles (°)

Bond	Distance	Bond	Distance	Bond	Distance
Cl(1)-Cu(1)	2.2645(11)	Cl(1)-Cu(2)	2.7532(13)	Cl(2)-Cu(2)	2.2615(13)
Cl(2)-Cu(1)	2.7545(14)	Cu(1)-O(1)	1.376(4)	Cu(1)-N(1)	1.935(3)
Cu(1)-O(2)	2.028(3)	Cu(2)-O(3)	1.900(3)	Cu(2)-N(2)	1.935(4)
Cu(2)-O(4)	2.008(3)	C(1)-O(1)	1.321(5)	C(7)-N(1)	1.280(5)
Angle	**(°)**	**Angle**	**(°)**	**Angle**	**(°)**
Cu(2)-Cl(2)-Cu(1)	85.93(4)	O(1)-Cu(1)-N(1)	93.54(14)	O(1)-Cu(1)-O(2)	174.71(12)
N(1)-Cu(1)-O(2)	81.65(13)	O(1)-Cu(1)-Cl(1)	91.37(9)	N(1)-Cu(1)-Cl(1)	166.46(12)
O(2)-Cu(1)-Cl(1)	92.85(8)	O(1)-Cu(1)-Cl(2)	98.02(11)	N(1)-Cu(1)-Cl(2)	100.75(12)
O(2)-Cu(1)-Cl(2)	85.11(9)	Cl(1)-Cu(1)-Cl(2)	91.03(4)	O(3)-Cu(2)-N(2)	93.60(15)
O(3)-Cu(2)-O(4)	175.59(13)	N(2)-Cu(2)-O(4)	82.06(14)	O(3)-Cu(2)-Cl(2)	93.94(11)
N(2)-Cu(2)-Cl(2)	164.76(12)	O(4)-Cu(2)-Cl(2)	90.09(9)	O(3)-Cu(2)-Cl(1)	92.68(11)
N(2)-Cu(2)-Cl(1)	101.73(11)	O(4)-Cu(2)-Cl(1)	89.00(10)	Cl(2)-Cu(2)-Cl(1)	91.12(5)

square-pyramidal. All copper(II) centers are in a square-pyramidal environment, with four short bonds in the basal plane formed by two trans O atoms and one N atom of the tridentate ligand, and a bridge chloride ion. The fifth axial long bond is formed by a chloride ligand which lies in the basal plane of the neighbouring copper(II) ion. The molecular dimensions are as expected with the aromatic C-C bond distances between 1.360 to 1.448 Å, and aromatic C-C-C bond angles between 118.2 to 121.5°, almost within the normal range.[14,15] The bond length of C(7)−N(1) and C(23)−N(2) are 1.280Å and 1.275Å, belonging to the typical C=N Schiff base bond, and the bond length of C(8)−N(1) and C(24)−N(2) are 1.480 Å and 1.470 Å, belonging to the C−N single bond respectively. The individual Cu- Cl-Cu bridges formed by one short Cu-Cl and one long Cu-Cl bond have distinctly differentiated bond lengths. The short Cu-Cl bonds vary from 2.2615(13) Å to 2.2645 (11) Å and the long Cu-Cl bonds from 2.7532(13) Å to 2.7545(14) Å, which are accorded with the previously reported structure.[16] The Cu···Cu non-bonding distances is 3.438 Å.

The packing diagram as shown in Figure 2 provides evidence that the structure is comprised of unique hydrogen bonds. The O(2) of hydroxyl atom of PPA forms a strong intra-molecular hydrogen bond with O(3) of hydroxyl of

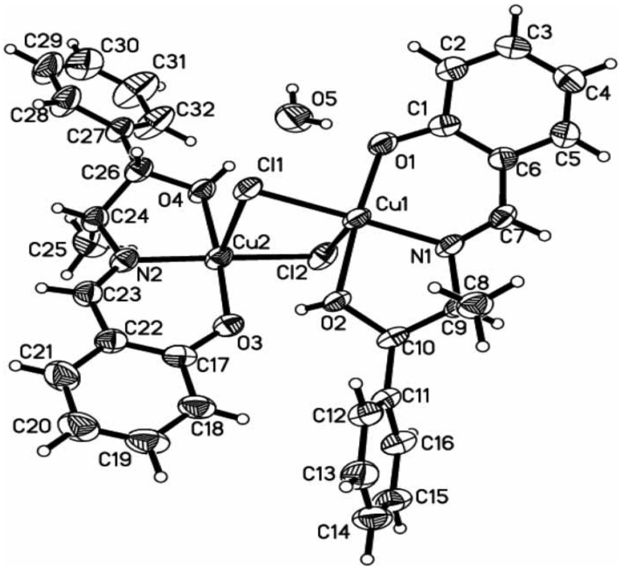

FIG. 1. The molecular structure of the title compound.

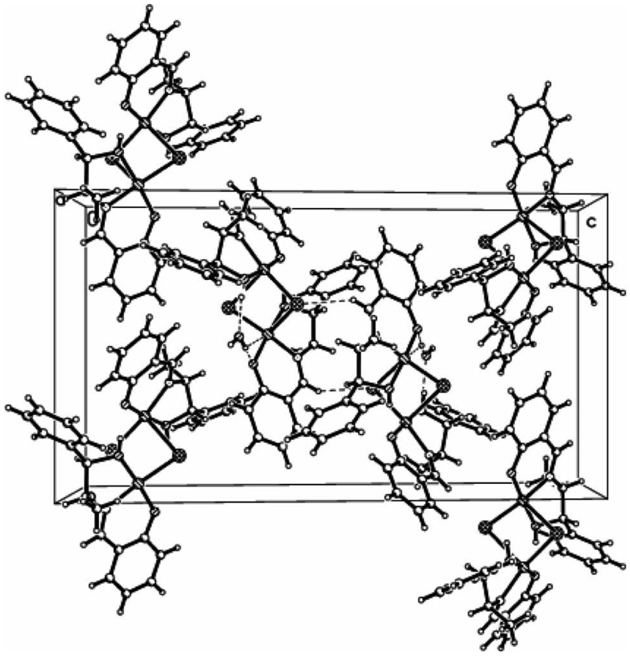

FIG. 2. The molecular packing diagram of the title compound.

TABLE 2
Hydrogen bond geometries (Å, deg.)

D–H···A	d_{D-H}	$d_{H\cdots A}$	$d_{D\cdots A}$	θ_{DHA}
O(2)–H(2A)···O(3)	0.850	1.774	2.623	178.09
O(4)–H(4A)···O(5)	0.850	1.813	2.660	173.80
O(5)–H(5B)···O(1)	0.850	1.988	2.812	163.22

salicylaldehyde, and the O(5) atom of the water molecule form two intermolecular hydrogen bonds with O(1) and O(4). The bond lengths and bond angles relevant to the hydrogen bond are given in Table 2. Intermolecular hydrogen bonds and intermolecular van der waals in the title complex produced a three-dimensional framework and stabilized the crystal structure.

Spectral Characteristics

The structure of title complex was further confirmed by spectral characteristics, as seen in Figure 3. Condensation of all primary amine groups and carbonyl groups is confirmed by the lack of N-H double stretching bands in the IR spectra in the region 3150–3450 cm^{-1} and also the characteristic presence of strong C═N stretching bands at 1630 cm^{-1} was noted.

The main peaks at *m/z* 376.1, 349.1 and 633.1 are observed in Figure 4, corresponding to the species of $[C_{16}H_{16}O_2NCu + CH_3CN + H_2O]^+$, $[C_{16}H_{16}O_2NCu + CH_3OH]^+$ and $[C_{16}H_{16}O_2NCu + C_{16}H_{16}O_2NCu\text{-}H^+]^+$, respectively.

Cyclic Voltammetric Study

The measurements were carried out in solution of phosphate buffer solution (PBS) and using a three-electrode cell in which the copper complex modified glassy carbon electrode (marked as MGC) was the working electrode, saturated calomel electrode (SCE) was the reference electrode and platinum wire

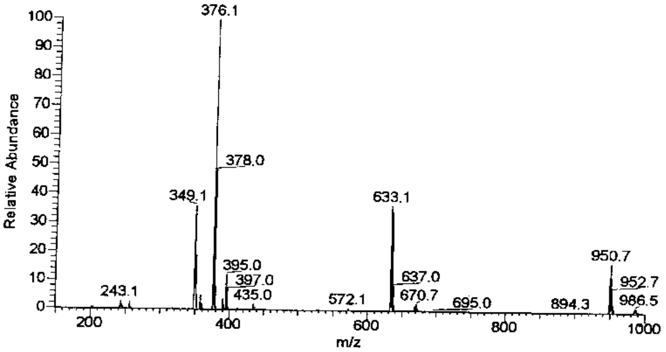

FIG. 4. The ES mass spectrum of the title compound.

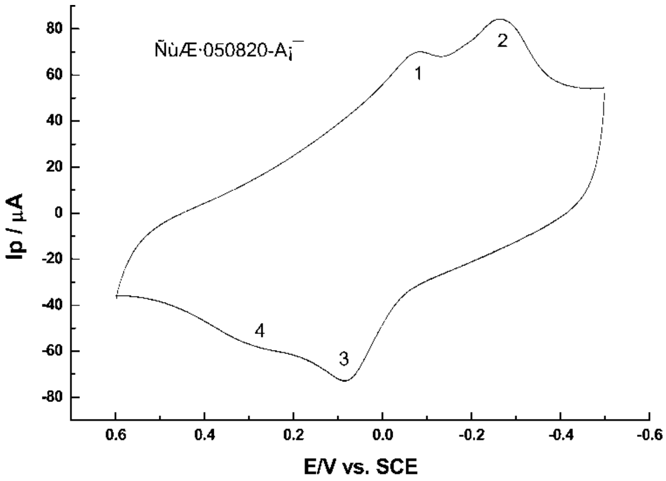

FIG. 5. Cyclic voltammogram of the title complex at scan rate of 1 mV s^{-1}.

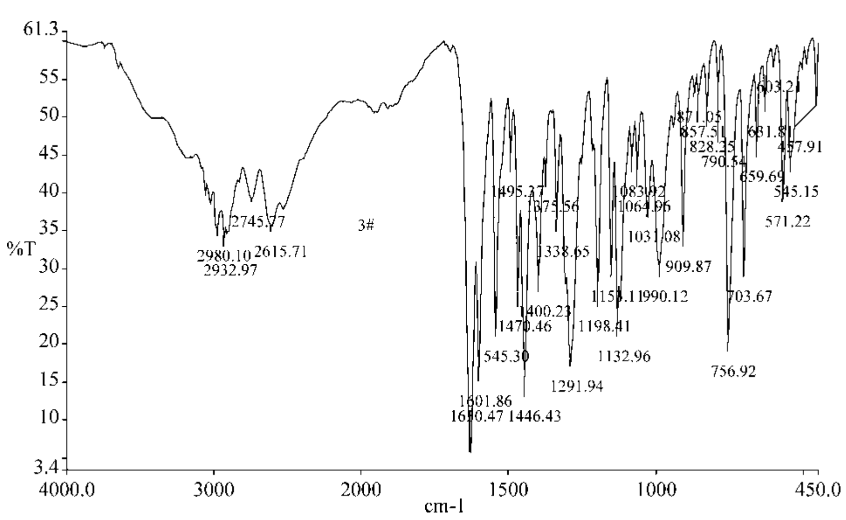

FIG. 3. The IR spectrum of the title compound.

TABLE 3
Cyclic voltammetric data of the title complex

Redox couple	E_{pa}(V)	E_{pc} (V)	ΔE (mV)	$E_{1/2}$ (V)	I_{pa}/I_{pc}	$\Delta E_{1/2}$ (V)
$Cu^{II}Cu^{II}/Cu^{I}Cu^{II}$	0.301	−0.084	385	0.109	0.69	0.198
$Cu^{I}Cu^{II}/Cu^{I}Cu^{I}$	0.085	−0.262	347	−0.089	2.55	

TABLE 4
The diameter of inhibition zone

		Diameter of inhibition zone (mm)		
Compound	Concentration (mg/ml)	*Candida albicans*	*Bacillus coliforms*	*Bacillus pumilus*
Title compound	8.0	22.5	15.3	20.0
	4.0	18.4	14.8	18.8
	2.0	17.2	13.0	16.4
	1.0	16.9	12.5	14.8
$Cu(ClO_4)_2$	8.0	19.3	15.0	14.0
	4.0	19.2	14.2	13.3
	2.0	16.8	13.4	12.8
	1.0	12.3	13.0	11.1
PPA	8.0	18.7	14.8	13.8
	4.0	17.6	13.3	12.5
	2.0	15.3	11.0	11.4
	1.0	12.0	10.6	9.3

was used as the counter electrode. The glassy carbon (GC) electrode was polished with fine emery paper and aluminum oxide powder on a chamois leather, respectively. The GC electrode was washed with 0.01 M H_2SO_4 solution and then sonicated in water for 20 s after polishing. The MGC electrode was constructed by depositing the dicopper complex on the GC electrode through cyclic voltammetric scan in the potential range of −0.5 to 0.6 V with scan rate of 100 mV s^{-1} for 600 in PBS solution with the title complex (1×10^{-4}mol · L^{-1}).) The cyclic voltammograms for the MGC in solution of PBS (pH 6.86) were recorded. In Figure 5, two reduction waves were obtained in the cathodic region corresponding to stepwise one-electron reductions through a $Cu^{I}Cu^{II}$ intermediate to give a binuclear Cu^{I} species. The two redox processes are assigned as follows: $Cu^{II}Cu^{II} \overset{e}{\rightleftharpoons} Cu^{II}Cu^{I} \overset{e}{\rightleftharpoons} Cu^{I}Cu^{II}$ The cyclic voltammetric data of the two redox couples are summarized in Table 3. In the redox couple $Cu^{II}Cu^{II}/Cu^{I}Cu^{II}$, the peak separation ΔE[17] and I_{pa}/I_{pc} value of 385 mV and 0.69, respectively, indicate a quasi-reversible electrode reaction. To another redox couple, ΔE was 347 mV, and I_{pa}/I_{pc} value was 2.55, so the electrode reaction was also a quasi-reversible process corresponding to the redox couple of $Cu^{II}Cu^{I}/Cu^{I}Cu^{I}$.

Antimicrobial Activity

From the data in Table 4, it is observed that the title complex, PPA and $Cu(ClO_4)_2 \cdot 6H_2O$ exhibited antibacterial activity against all test bacterial organisms. In the test range, these compounds were more active against the strains with increase in concentration. The highest antimicrobial activity among the group of these complexes was observed against *Candida albicans* and almost no difference in toxicity against *Bacillus coliforms* among the three complexes. The title complex showed higher activity against bacteria as compared to the metal salt $Cu(ClO_4)_2 \cdot 6H_2O$ and PPA. The reason may be attributed to the formation of the Schiff-base structure, which can increase the antimicrobial activity due to their active antibacterial and antitumor functions.[18,19]

SUPPLEMENTARY MATERIALS

Crystallographic data for the structures in this article have been deposited with the Cambridge Crystallographic Data Center as the supplementary publication nos. CCDC 600202 for the title complex. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK.

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