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Synthesis, Crystal Structures, and Antibacterial Activities of Schiff Base Zinc(II) Complexes $[Zn(L^1)_2]$ and $[Zn(L^2)_2]$[1]

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Abstract—The reaction of cyclopentylamine with 2-hydroxy-1-naphthaldehyde and 5-nitrosalicylaldehyde, respectively, in methanol affords two new Schiff bases, 1-(cyclopentyliminomethyl)naphthalen-2-ol (HL^1) and 4-nitro-2-(cyclopentyliminomethyl)phenol (HL^2). Two new zinc(II) complexes, $[Zn(L^1)_2]$ (**I**) and $[Zn(L^2)_2]$ (**II**), derived from the Schiff bases, have been prepared and characterized by single-crystal X-ray diffraction, FT-IR, and elemental analysis. Complex **I** crystallizes in the monoclinic space group $P2_1/c$ with $a = 17.834(4)$, $b = 14.738(3)$, $c = 9.868(2)$ Å, $\beta = 91.20(3)°$, $V = 2593.1(9)$ Å^3, $Z = 4$. Complex **II** crystallizes in the triclinic space group $P\bar{1}$ with $a = 10.206(1)$, $b = 10.502(1)$, $c = 12.554(1)$ Å, $\alpha = 66.771(2)°$, $\beta = 78.133(2)°$, $\gamma = 76.292(2)°$, $V = 1191.8(1)$ Å^3, $Z = 2$. The Zn atom in each complex is coordinated by two N and two O atoms from two Schiff base ligands, forming a tetrahedral geometry. The Schiff bases and the complexes were assayed for antibacterial activities.

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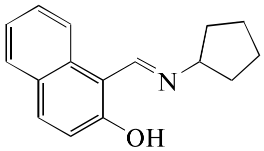
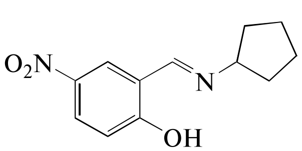
INTRODUCTION

Schiff bases in general have been reported to possess antimicrobial [1, 2] and antitumour activities [3, 4]. Metal complexes with Schiff base ligands have played an important role in the development of coordination chemistry due to their preparative accessibility, structural variety, and biological properties [5–7]. Zinc is an essential element for all forms of life and is present at the active site of various enzymes [8, 9]. The diversity in the functions of zinc is attributed to its versatile coordination chemistry. In this work, two new Schiff bases, 1-(cyclopentyliminomethyl)naphthalen-2-ol (HL^1) and 4-nitro-2-(cyclopentyliminomethyl)phenol (HL^2), were prepared and two new zinc complexes, $[Zn(L^1)_2]$ (**I**) and $[Zn(L^2)_2]$ (**II**), derived from the Schiff bases have been prepared and characterized by single-crystal X-ray diffraction, FT-IR, and elemental analysis. Their antibacterial activities against *Bacillus subtilis*, *Staphylococcus aureus*, *Escherichia coli*, and *Pseudomonas fluorescens* were evaluated.



(HL^1)



(HL^2)

EXPERIMENTAL

Materials and measurements. 2-Hydroxy-1-naphthaldehyde, 5-nitrosalicylaldehyde, and cyclopentylamine were purchased from Sigma. All other chemicals were commercial products and used without further purification. C, H, and N elemental analyses were performed on a Vario EL-III analyzer. Infrared spectra were recorded as KBr pellets on a Nicolet Avatar 360 spectrophotometer in the range 4000–400 cm^{-1}. Molar conductivity was determined in methanol at room temperature on a DDS-11A conductometer.

$(Zn(ClO_4)_2$ is potentially explosive. Although no problem has been encountered during the synthesis of the complexes, it should be handled with proper care.

Synthesis of HL^1. 2-Hydroxy-1-naphthaldehyde (1.72 g, 0.01 mol) dissolved in methanol (30 mL) was added to cyclopentylamine (0.85 g, 0.01 mol) in methanol (30 mL). The reaction mixture was heated to 50°C for 1 h and then cooled to room temperature followed by concentrating the resulting mixture to a yellow solid product. The yield was 2.33 g (97%).

For $C_{16}H_{17}NO$

anal. calcd., %:	C, 80.3;	H, 7.2;	N, 5.8.
Found, %:	C, 80.1;	H, 7.3;	N, 5.9.

Synthesis of HL^2 was carried out according to a similar procedure as that for HL^1 with 5-nitrosalicyla-

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[1] The article is published in the original.

ldehyde instead of 2-hydroxy-1-naphthaldehyde. The yield was 2.29 g (98%).

For $C_{12}H_{14}N_2O_3$

anal. calcd., %:	C, 61.5;	H, 6.0;	N, 12.0.
Found, %:	C, 61.3;	H, 6.1;	N, 11.9.

Synthesis of I. $Zn(ClO_4)_2 \cdot 6H_2O$ (0.19 g, 0.5 mmol) in methanol (20 mL) was added dropwise to HL^1 (0.24 g, 1 mmol) in methanol (20 mL), and the resultant colorless reaction mixture was stirred at room temperature for 1 h to give a clear solution. Colorless single crystals were obtained by slow evaporation of the solution in air. The yield was 0.17 g (63%).

For $_{32}H_{32}N_2O_2Zn$

anal. calcd., %:	C, 70.9;	H, 6.0;	N, 5.2.
Found, %:	C, 71.2;	H, 5.8;	N, 5.1.

Synthesis of II. The colorless single crystals of complex **II** were synthesized according to a similar procedure as that for **I** with HL^2 instead of HL^1. The yield was 0.20 g (77%).

For $_{24}H_{26}N_4O_6Zn$

anal. calcd., %:	C, 54.2;	H, 4.9;	N, 10.5.
Found, %:	C, 54.5;	H, 4.9;	N, 10.3.

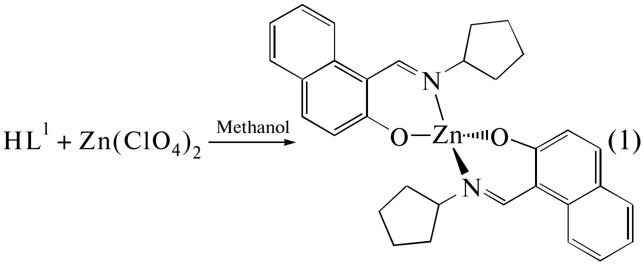
X-ray structure determination. Crystal structure determination of the two complexes were carried out on a Bruker APEX II CCD area diffractometer equipped with graphite-monochromatized MoK_α (λ = 0.71073 Å) radiation. The structures were solved by direct methods and refined on F^2 by full-matrix least-squares methods using SHELX-97 [10]. All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included at geometrically calculated positions and refined using a riding model. The crystal data, experimental details, refinement results, and details of structure determinations are shown in Table 1.

Selected bond lengths and bond angles are listed in Table 2.

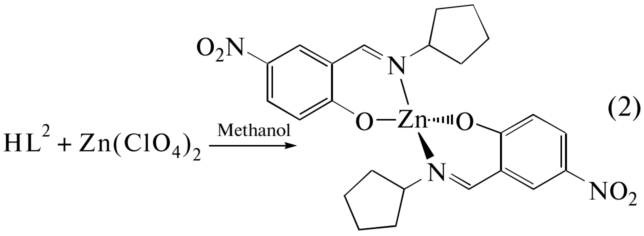
Supplementary material for structures **I** and **II** has been deposited with the Cambridge Crystallographic Data Centre (nos. 812144 for **I** and 812145 for **II**; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

The Schiff bases HL^1 and HL^2 were prepared in excellent yields (over 95%) in absolute methanol. The compounds are yellow solids and stable in air at room temperature. The elemental analyses are in good agreement with the chemical formulas proposed for the compounds. The two zinc(II) complexes were prepared by the reaction of the Schiff bases with zinc perchlorate in methanol in acordance to reactions (1) and (2):



(1)



(2)

Both the Schiff bases and the zinc complexes are stable in air at room temperature, and soluble in common polar organic solvents, such as DMSO, DMF, methanol, ethanol, and acetonitrile. The molar conductance values of the complexes measured in methanol at concentrations of 10^{-3} M at 298 K are in the range 15–21 Ω^{-1} cm^2 mol^{-1}, indicating that they are nonelectrolytes.

The IR spectra of the Schiff bases showed weak bands due to the phenolic groups in the region 3180–3215 cm^{-1} due to the vibrations. The bands of the phenolic group are absent in the IR spectra of the zinc complexes, indicating the deprotonation of the phenolic groups. The intense bands at 1280 cm^{-1} assigned to phenolic C–O linkage shifting toward a higher wave number of 1302–1310 cm^{-1} confirmed the involvement of the deprotonated phenolic groups in bond formation with the zinc atoms. The strong bands in the Schiff bases around 1645 cm^{-1} region underwent a negative shift of about 20 cm^{-3} in the complexes, confirming the coordination of the azomethine N atoms to the zinc atoms. The weak absorption bands at about 450 and 418 cm^{-1} are assigned to the Zn–N and Zn–O bonds, respectively.

The crystal structures of **I** and **II** with the atomic numbering scheme are presented in Figs. 1 and 2, respectively. Both compounds are structurally similar mononuclear zinc(II) complexes. The Zn atom in each complex is four-coordinated by two imino N atoms and two phenolic O atoms from two Schiff base ligands, forming a tetrahedral geometry. The bond lengths of Zn–O and Zn–N in both complexes are comparable to each other and also comparable to those in similar Schiff base zinc(II) complexes [11–13]. The angles subtended at the Zn atoms are in the range 93.9(2)°–122.2(2)° for **I** and 96.8(1)°–120.0(1)° for **II**, indicating that tetrahedral coordinations are distorted. The cyclopentyl rings in the complexes

Table 1. Crystallographic data and structure refinement for the complexes **I** and **II**

Parameter	Value	
	I	**II**
Formula weight	541.97	531.86
Temperature, K	298(2)	298(2)
Scan mode	Multi-scan	Multi-scan
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$
Unit cell dimensions:		
a, Å	17.834(4)	10.206(1)
b, Å	14.738(3)	10.502(1)
c, Å	9.868(2)	12.554(1)
α, deg	90	66.771(2)
β, deg	91.20(3)	78.133(2)
γ, deg	90	76.292(2)
V, Å^3	2593.1(9)	1191.84(8)
Z	4	2
ρ_{calcd}, g cm^{-3}	1.388	1.482
μ, mm^{-1}	0.980	1.078
F(000)	1136	552
Crystal size, mm^3	0.17 × 0.15 × 0.15	0.32 × 0.30 × 0.30
θ Range for data collection, deg	1.79–25.50	1.78–27.00
Indices h, k, l	$-21 \le h \le 19$, $-16 \le k \le 17$, $-11 \le l \le 11$	$-12 \le h \le 12$, $-13 \le k \le 13$, $-10 \le l \le 16$
Reflections collected	12206	7367
Observed reflections ($I > 2\sigma(I)$)	2952	4070
Max and min transmission	0.8511 and 0.8669	0.7241 and 0.7380
Data/restraints/parameters	4515/12/334	5089/0/316
Goodness-of-fit on F^2	1.027	1.024
Final R_1, wR_2 indices ($I > 2\sigma(I)$)	0.0848, 0.2070	0.0408, 0.1013
R_1, wR_2 indices (all data)	0.1233, 0.2370	0.0543, 0.1095
$\Delta\rho_{max}/\Delta\rho_{min}$, e Å^{-3}	0.41/–0.54	0.46/–0.37

Table 2. Selected bond lengths and bond angles for the complex **I** and **II**

Bond	*d*, Å	Bond	*d*, Å
I			
Zn(1)–O(1)	1.912(4)	Zn(1)–O(2)	1.897(5)
Zn(1)–N(1)	1.968(5)	Zn(1)–N(2)	1.996(5)
II			
Zn(1)–O(1)	1.910(2)	Zn(1)–O(2)	1.911(2)
Zn(1)–N(1)	2.015(2)	Zn(1)–N(2)	2.011(2)
Angle	ω, deg	Angle	ω, deg
I			
O(1)Zn(1)O(2)	120.0(1)	O(1)Zn(1)N(2)	113.3(1)
O(2)Zn(1)N(2)	96.9(1)	O(1)Zn(1)N(1)	96.8(1)
O(2)Zn(1)N(1)	112.3(1)	N(2)Zn(1)N(1)	119.0(1)
II			
O(2)Zn(1)O(1)	121.6(2)	O(2)Zn(1)N(1)	111.9(2)
O(1)Zn(1)N(1)	93.9(2)	O(2)Zn(1)N(2)	95.5(2)
O(1)Zn(1)N(2)	113.8(2)	N(1)Zn(1)N(2)	122.2(2)

adopt enveloped conformation with the C(12) and C(28) atoms in **I** and are displaced by 0.390(8) and 0.453(8) Å, respectively, from the least-squares planes defined by the remaining four C atoms. The C(8) and C(20) atoms in **II** are displaced by 0.424(3) and 0.556(3) Å, respectively, from the least-squares planes defined by the remaining four C atoms.

Table 3. Antibacterial activity of the tested material (MIC, μg mL^{-1})

Compound	*Bacillus subtilis*	*Staphylococcus aureus*	*Escherichia coli*	*Pseudomonas fluorescens*
HL^1	25	25	50	75
HL^2	12.5	25	25	>100
I	6.25	12.5	12.5	25
II	1.56	3.13	6.25	50
Penicillin	0.78	3.13	>100	>100

All the synthesized compounds were screened for antibacterial activity against *Bacillus subtilis*, *Staphylococcus aureus*, *Escherichia coli*, and *Pseudomonas fluorescens* by the MTT (3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide) method. The minimum inhibitory concentrations (MICs) of the compounds against these bacteria are presented in Table 3. Penicillin was used as a reference. The results revealed that most of the synthesized compounds exhibited significant antibacterial activity. The Schiff bases HL^1 and HL^2 showed stronger antibacterial activity against *Escherichia coli* and *Pseudomonas fluorescens* but weaker antibacterial activity against *Bacillus subtilis* and *Staphylococcus aureus* than Penicillin. The zinc complexes showed relatively stronger activities against all the bacteria than the Schiff base ligands. It is notable that complex **II** has the low MIC values against *Bacillus subtilis* and *Staphylococcus aureus*, which deserves further study.

Thus, two new Schiff bases derived from cyclopentylamine with 2-hydroxy-1-naphthaldehyde and 5-nitrosalicylaldehyde, respectively, have been synthe-

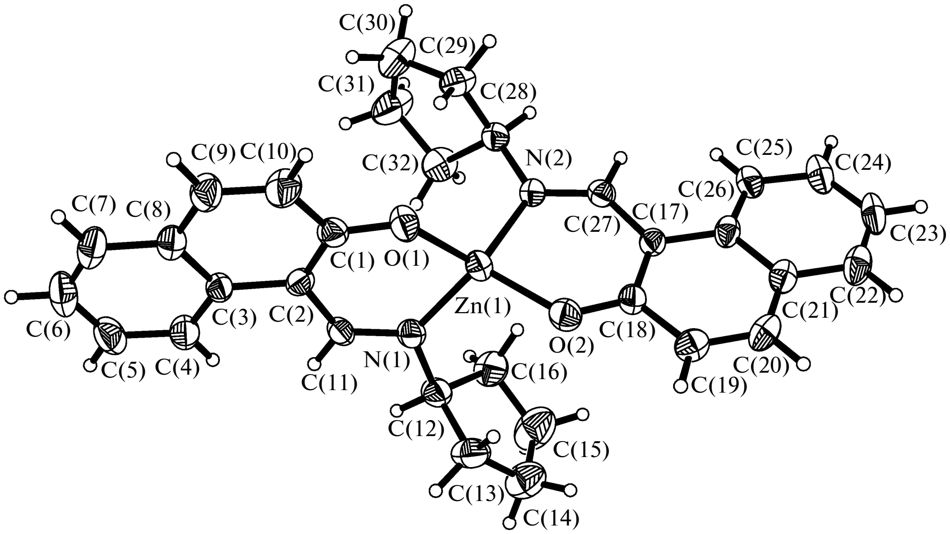


Fig. 1. ORTEP plots (30% probability level) for **I**.

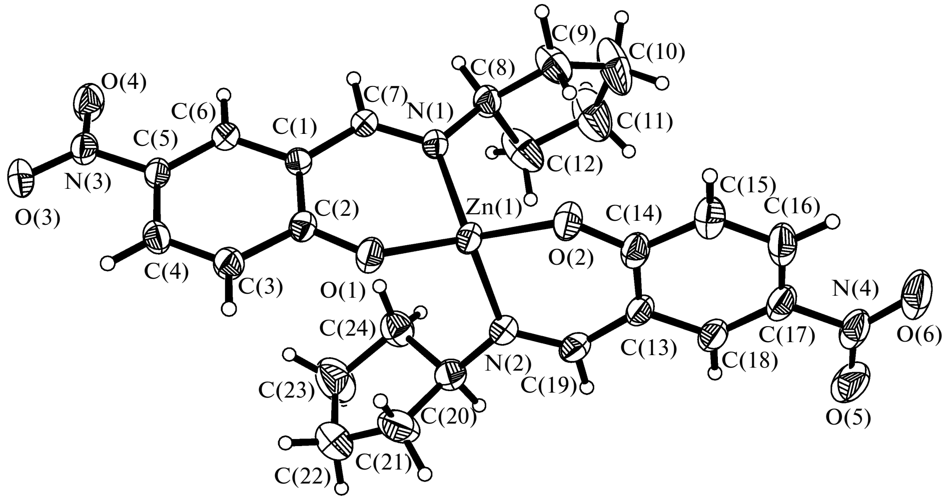


Fig. 2. ORTEP plots (30% probability level) for **II**.

sized. Reaction of the Schiff bases with zinc acetate led to the formation of two new mononuclear complexes. The Schiff bases and the zinc complexes were assayed for antibacterial activities by MTT method. The complex **II** has the low MIC values against *Bacillus subtilis* and *Staphylococcus aureus*, which deserves further study.

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