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Synthesis, Crystal Structures, and Antibacterial Activities of Schiff Base Nickel(II) and Cadmium(II) Complexes with Tridentate Schiff Bases[1]

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Abstract—Reaction of tridentate Schiff bases with nickel and cadmium salts in methanol afforded two new mononuclear complexes, $[Ni(L^1)_2]$ (**I**) and $[Cd(L^2)_2]$ (**II**), where L^1 and L^2 are the anions of 2-bromo-4-chloro-6-[(3-dimethylaminopropylimino)methyl]phenol (HL^1) and 2-bromo-4-chloro-6-[(3-morpholin-4-ylpropylimino)methyl]phenol (HL^2), respectively. The complexes were characterized by single-crystal X-ray diffraction (CIF files CCDC nos. 1428653 (**I**) and 1428654 for (**II**)), FT-IR, and elemental analysis. Complex **I** crystallizes in the monoclinic space group $P2_1/c$, with $a = 8.8216(8)$, $b = 14.0424(8)$, $c = 11.8687(12)$ Å, $\beta = 111.238(2)°$, $V = 1370.4(2)$ Å^3, $Z = 2$. Complex **II** crystallizes in the monoclinic space group $P2_1/n$, with $a = 9.6774(4)$, $b = 15.8970(6)$, $c = 20.3144(7)$ Å, $\beta = 90.408(2)°$, $V = 3125.1(2)$ Å^3, $Z = 4$. The metal atoms in the complexes are coordinated by two tridentate Schiff base ligands, forming octahedral coordination. The free Schiff bases and the complexes were assayed for antibacterial activities. Both complexes are more active against the bacteria than the free Schiff bases. Complex **II** has the MIC value of 0.39 μg mL^{-1} against *Bacillus subtilis*.

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INTRODUCTION

The chemistry and the biological potential of Schiff base ligands and their metal complexes have been investigated extensively. Schiff bases are reported to possess various biological activities, such as antibacterial [1, 2] and antitumour activities [3, 4]. Metal complexes with Schiff bases as ligands have played important role in the development of coordination chemistry due to their preparative accessibility, structural variety, and biological properties [5–7]. Interest is still high as few have found their way into application as therapeutic drugs, health, skin care products and in paint dye manufacturing [8]. Nickel and cadmium complexes with Schiff bases have interesting biological properties [9–12]. We report herein the synthesis and characterization of two new mononuclear complexes, $[Ni(L^1)_2]$ (**I**) and $[Cd(L^2)_2]$ (**II**), where L^1 and L^2 are the anions of 2-bromo-4-chloro-6-[(3-dimethylaminopropylimino)methyl]phenol (HL^1) and 2-bromo-4-chloro-6-[(3-morpholin-4-ylpropylimino)methyl]phenol (HL^2), respectively (Scheme 1). Their antibacterial activities against *Bacillus subtilis*, *Staphylococcus aureus*, *Escherichia coli*, and *Pseudomonas fluorescens* were evaluated.

EXPERIMENTAL

Materials and measurements. 3-Bromo-5-chlorosalicylaldehyde, N,N-dimethylpropane-1,3-diamine, and 3-morpholin-4-ylpropylamine were purchased from Sigma-Aldrich. All other chemicals were commercial products and used without further purification. Nickel perchlorate and cadmium perchlorate were prepared from perchloric acid with nickel carbonate and cadmium carbonate, respectively, in distilled water. C, H, and N elemental analysis was performed on a Vario EL-III analyzer. Infrared spectra were recorded as KBr pellet 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.

Synthesis of HL^1. 3-Bromo-5-chlorosalicylaldehyde (2.35 g, 0.01 mol) dissolved in methanol (30 mL) was added to N,N-dimethylpropane-1,3-diamine (0.10 g, 0.01 mol) in methanol (30 mL). The reaction mixture was heated under reflux for 1 h and then cooled to room temperature followed by concentrating the resulting mixture to give a yellow gummy product with quantitative yield.

For $C_{12}H_{16}N_2OClBr$

anal. calcd., %:	C, 45.09;	H, 5.05;	N, 8.76.
Found, %:	C, 44.83;	H, 5.12;	N, 8.85.

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[1] The article is published in the original.

(HL^1) (HL^2)

Scheme 1.

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

Parameter	Value	
	I	**II**
Formula weight	695.95	833.71
Temperature, K	298(2)	298(2)
Wavelength, Å	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$
Unit cell dimensions:		
a, Å	8.8216(8)	9.6774(4)
b, Å	14.0424(8)	15.8970(6)
c, Å	11.8687(12)	20.3144(7)
β, deg	111.238(2)	90.408(2)
V, Å^3	1370.4(2)	3125.1(2)
Z	2	4
ρ_{calcd}, g cm^{-3}	1.687	1.772
μ, mm^{-1}	3.848	3.467
F(000)	700	1656
Crystal size, mm	0.20 × 0.20 × 0.18	0.18 × 0.17 × 0.15
θ Range for data collection, deg	2.87–25.49	3.17–25.50
Limiting indices hkl	$-10 \leqslant h \leqslant 8$, $-13 \leqslant k \leqslant 17$, $-12 \leqslant l \leqslant 14$	$-9 \leqslant h \leqslant 11$, $-19 \leqslant k \leqslant 16$, $-24 \leqslant l \leqslant 24$
Reflections collected	4543	15570
Observed reflections ($I > 2\sigma(I)$)	1822	4390
Max and min transmission	0.5133 and 0.5443	0.5742 and 0.6243
Data/restraints/ parameters	2328/0/162	5812/0/370
Goodness-of-fit on F^2	1.050	1.040
Final R_1, wR_2 indices ($I > 2\sigma(I)$)	0.0364, 0.0812	0.0345, 0.0687
R_1, wR_2 indices (all data)	0.0557, 0.0912	0.0560, 0.0782
Largest diff. peak/hole, e Å^{-3}	0.427/–0.505	0.464/–0.433

Synthesis of HL^2. The yellow gummy product of HL^2 was synthesized according to a similar procedure as that for HL^1 with 3-morpholin-4-ylpropylamine (0.14 g, 0.01 mol) instead of N,N-dimethylpropane-1,3-diamine.

For $C_{14}H_{18}N_2OCl_2Br$

anal. calcd., %: C, 46.49; H, 5.02; N, 7.75.
Found, %: C, 46.31; H, 5.12; N, 7.86.

Synthesis of complex I. Nickel perchlorate (0.37 g, 1 mmol) in methanol (20 mL) was added to HL^1 (0.32 g, 1 mmol) in methanol (20 mL), and the resultant green reaction mixture was stirred at room temperature for 1 h to give a clear solution. Green single crystals were obtained by slow evaporation of the solution in air. The yield was 0.17 g (51%).

For $C_{24}H_{30}N_4O_2Cl_2Br_2Ni$

anal. calcd., %: C, 41.42; H, 4.34; N, 8.05.
Found, %: C, 41.53; H, 4.17; N, 8.16.

Synthesis of complex II. The colorless single crystals of complex **II** were prepared according to a similar procedure as that for **I** with HL^2 (0.36 g, 1 mmol) instead of HL^1 and with cadmium perchlorate (0.42 g, 1 mmol) instead of nickel perchlorate. The yield was 0.27 g (65%).

For $C_{28}H_{34}N_4O_4Cl_2Br_2Cd$

anal. calcd., %: C, 40.34; H, 4.11; N, 6.72.
Found, %: C, 40.20; H, 4.18; N, 6.87.

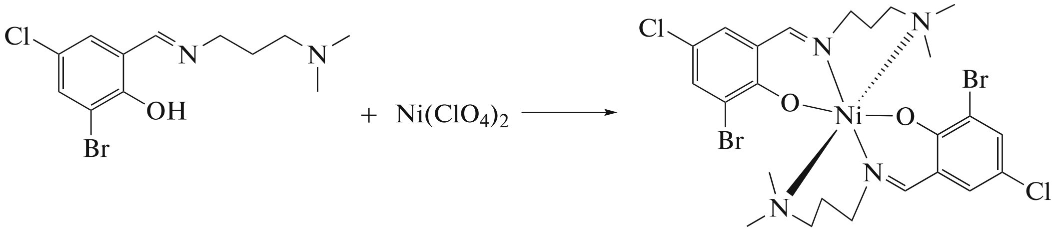
X-ray crystallography. Crystal structure determination of the complexes were carried out on a Bruker APEX II CCD area diffractometer equipped with graphite-monochromatized MoK_α (λ = 0.71073 Å) radiation. Structures of both complexes were solved by direct methods and refined on F^2 by full-matrix least-squares methods using SHELX-97 [13]. 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 listed in Table 1. Selected bond lengths and bond angles are listed in Table 2.

Supplementary material for structures has been deposited with the Cambridge Crystallographic Data

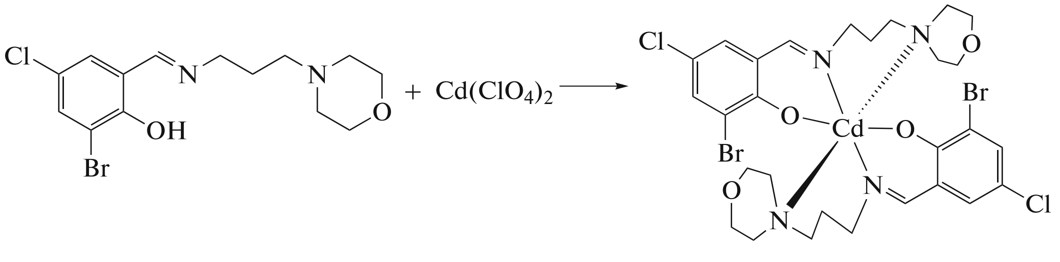
Centre (nos. 1428653 (**I**) and 1428654 for (**II**); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

The Schiff bases HL^1 and HL^2 were prepared in quantitative yields in methanol. The compounds are yellow gummy product. The elemental analyses are in good agreement with the chemical formulae proposed for the compounds. Complexes **I** and **II** were prepared by the reaction of the Schiff bases with nickel perchlorate and cadmium perchlorate, respectively, in methanol according to the following synthetic procedure:



(I)



(II)

Both the Schiff bases and the metal 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} mol L^{-1} at 298 K are 32 and 26 Ω^{-1} cm^2 mol^{-1}, indicating the non-electrolytic nature [14].

The IR spectra of the free Schiff bases showed weak bands due to the phenolic groups in the region 3350–3500 cm^{-1}, which are assigned to the ν(OH) vibrations. The bands of the phenolic group are absent in the IR spectra of the nickel and cadmium complexes, indicating the deprotonation of the phenolic groups. The intense bands at about 1280 cm^{-1} assigned to phenolic C–O linkage shifting towards to higher wave numbers of 1307 cm^{-1} for **I** and 1311 cm^{-1} for **II**, confirming the involvement of the deprotonated phenolic groups in bond formation with the metal atoms [15]. The strong bands in the Schiff bases at 1636 cm^{-1} for both HL^1 and HL^2 underwent a negative shift of about 10–15 cm^{-1} in the complexes, confirming the coordination of the azomethine N atoms to the metal atoms [16]. The weak absorption bands in the 400–600 cm^{-1} region are assigned to the vibrations of M–N and M–O coordinate bonds.

The structures of the nickel and cadmium complexes are similar (Fig. 1). From the crystallographic point of view, complex **I** has a center of inversion, while complex **II** not has such a center. In complex **I**, the Ni atom is coordinated by two phenolate O, two imine N and two amine N atoms from two Schiff base ligands, forming octahedral coordination. In complex **II**, the Cd atom is coordinated by two phenolate O, two imine N and two morpholine N atoms from two Schiff base ligands, also forming octahedral coordination. The Ni–N and Ni–O bonds in complex **I** are shorter than the Cd–N and Cd–O bonds in **II**. All of the coordinate bond values are within normal values as compared with other similar nickel and cadmium complexes with Schiff bases [17–20]. The *cis* and *trans* angles subtended at the Ni atom in complex **I** are in the ranges 80.99(12)–99.01(12)° and 180°, respectively. The *cis* and *trans* angles subtended at the Cd atom in complex **II** are in the ranges 78.21(10)°–104.69(10)° and 173.51(9)°–177.26(10)°, respectively. Thus, the

Table 2. Selected bond lengths (Å) and bond angles (deg) for complexes **I** and **II**

Bond	d, Å	Bond	d, Å
	I		
Ni(1)–O(1)	2.025(2)	Ni(1)–N(1)	2.049(3)
Ni(1)–N(2)	2.283(3)		
	II		
Cd(1)–O(1)	2.230(2)	Cd(1)–O(3)	2.219(2)
Cd(1)–N(1)	2.240(3)	Cd(1)–N(2)	2.609(3)
Cd(1)–N(3)	2.270(3)	Cd(1)–N(4)	2.606(3)
Angle	**ω, deg**	**Angle**	**ω, deg**
	I		
O(1)Ni(1)N(1)	87.75(11)	N(1)Ni(1)N(2)	80.99(12)
O(1)Ni(1)N(2)	92.58(11)		
	II		
O(3)Cd(1)O(1)	173.51(9)	O(3)Cd(1)N(1)	104.69(10)
O(1)Cd(1)N(1)	81.31(9)	O(3)Cd(1)N(3)	80.78(10)
O(1)Cd(1)N(3)	93.30(9)	N(1)Cd(1)N(3)	174.38(10)
O(3)Cd(1)N(4)	95.27(9)	O(1)Cd(1)N(4)	86.06(9)
N(1)Cd(1)N(4)	99.62(11)	N(3)Cd(1)N(4)	78.34(10)
O(3)Cd(1)N(2)	83.73(9)	O(1)Cd(1)N(2)	95.22(9)
N(1)Cd(1)N(2)	78.21(10)	N(3)Cd(1)N(2)	103.97(10)
N(4)Cd(1)N(2)	177.26(10)		

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

Compound	*Bacillus subtilis*	*Staphylococcus aureus*	*Escherichia coli*	*Pseudomonas fluorescens*
HL^1	3.13	6.25	25	>100
HL^2	3.13	12.5	12.5	>100
I	1.56	6.25	12.5	25
II	0.39	6.25	3.13	3.13
Penicillin	0.78	3.13	>100	>100

octahedral coordination in both complexes are distorted.

The free Schiff bases and two complexes 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 the bacteria are presented in Table 3. Penicillin was used as a reference. The results revealed that the free Schiff bases HL^1 and HL^2 showed medium activity against *Bacillus subtilis*, *Staphylococcus aureus*, and weak activity against *Escherichia coli*, but no activity against *Pseudomonas fluorescens*. It is clear that the activities of two complexes are much effective than the free Schiff bases. Complex **I** has strong activity against *Bacillus subtilis*, medium activity against *Staphylococcus aureus* and *Escherichia coli*, and weak activity against *Pseudomonas fluorescens*. Complex **II** has strong activity against *Bacillus subtilis*, *Escherichia coli*, and *Pseudomonas fluorescens*, and medium activity against *Staph-*

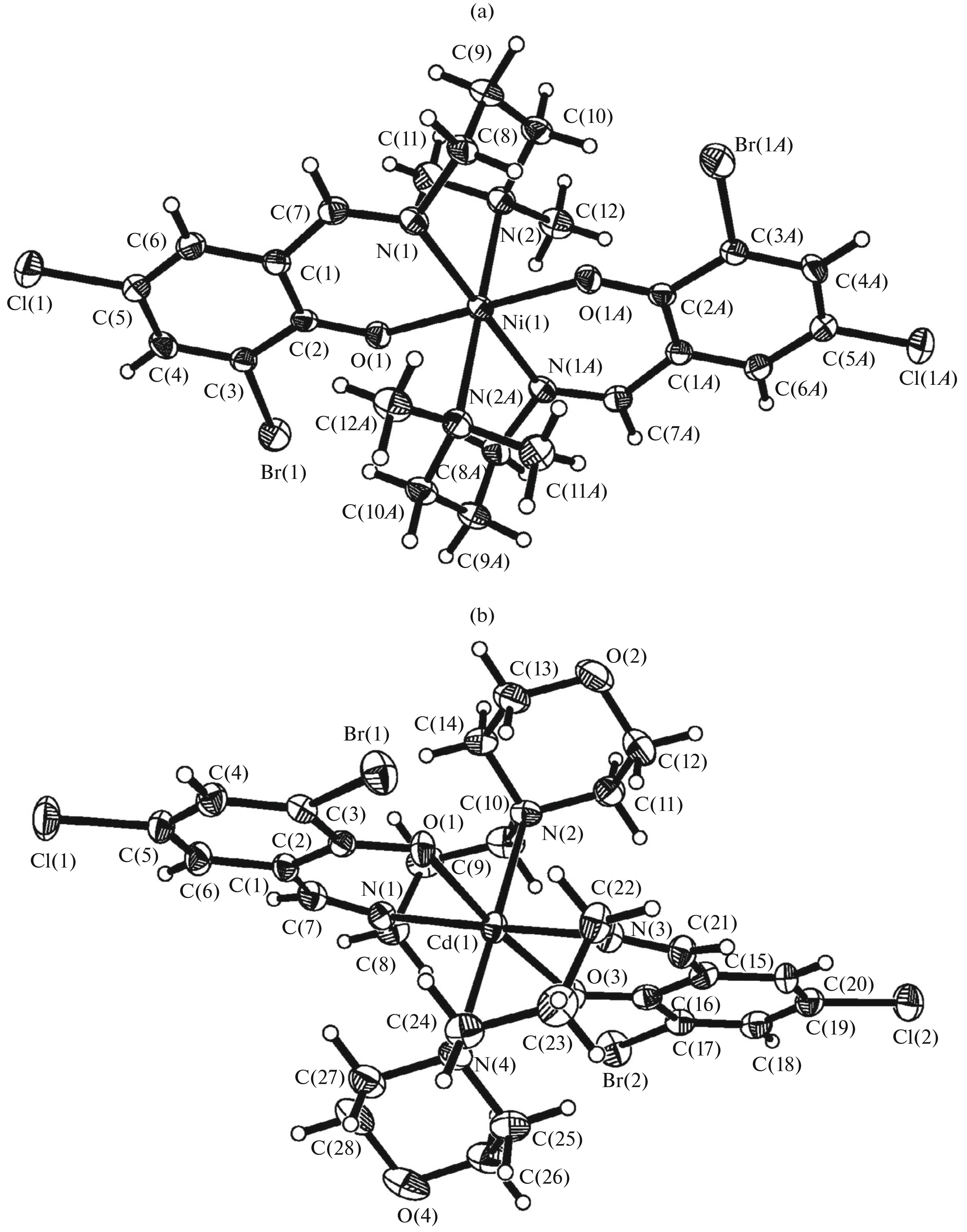


Fig. 1. ORTEP plots (30% probability level) and numbering scheme for **I** (a) and **II** (b). Symmetry operations for generating atoms for **I**: (*A*) $2 - x, 1 - y, 1 - z$.

ylococcus aureus. It should be noted that complex **II** has the MIC value of 0.39 μg mL^{-1} against *Bacillus subtilis*, which is much lower than the reference drug.

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