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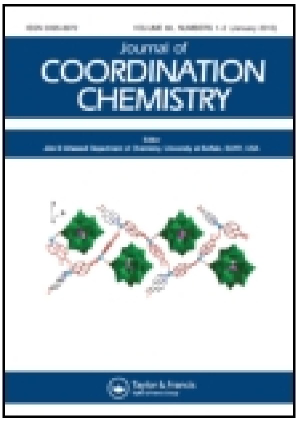

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Synthesis, spectral, and biological studies of transition metal chelates of N-[1-(3-aminopropyl)imidazole]salicylaldimine

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Synthesis, spectral, and biological studies of transition metal chelates of N-[1-(3-aminopropyl)imidazole]salicylaldimine

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Tridentate chelate complexes $M[LX \cdot 2H_2O]$, where M = Co(II), Ni(II), Cu(II), Zn(II), and Cd(II) have been synthesized from the Schiff base L = N-[1-(3-aminopropyl)imidazole]salicylaldimine and X = Cl. Microanalytical data, UV-Vis, magnetic susceptibility, IR, ^{1}H-NMR, mass, and EPR techniques were used to confirm the structures. Electronic absorption spectra and magnetic susceptibility measurements suggest square-planar geometry for copper complex and octahedral for other metal complexes. EPR spectra of copper(II) complex recorded at 300 K confirm the distorted square-planar geometry of the copper(II) complex. Biological activities of the ligand and metal complexes have been studied on *Staphylococcus aureus*, *Escherichia coli*, *Pseudomonas aeruginosa*, and *Candida albicans* by the well diffusion method. The activity data show the metal complexes to be more potent than the parent ligand against two bacterial species and one fungus. The electrochemical behavior of the copper complex was studied by cyclic voltammetry.

Keywords: Tridentate ligand; N-(3-Aminopropyl)imidazole; Metal complexes; Spectral studies; Biological activities

1. Introduction

Schiff bases have been used as ligands in coordination chemistry for their interesting and important properties, such as the ability to reversibly bind oxygen, catalytic activity in the hydrogenation of olefins, and proton transfer from the hydroxyl to the imine [1]. Complexes of Schiff bases showed promising applications in biological activity and biological modeling applications [2–5].

Salicylaldimines and their metal complexes possess important biological applications [6, 7]. Synthesis, characterization, and antimicrobial studies of transition metal complexes of 1-(3-aminopropyl)imidazole and imidazole derivative were reported [8–12]. Much research has been carried out on Schiff bases of salicylaldehyde and derivatives [13–16]. Tas *et al.* reported the synthesis and characterization of copper(II)

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complexes with bidentate salicylaldimines derived from 3,5-di-t-butyl-2-hydroxybenzaldehyde [17]. Taking into account the importance of salicylaldimines in various fields we attempted to synthesize and characterize transition metal complexes with NNO tridentate Schiff base N-[1-(3-aminopropyl)imidazole]salicylaldimine. The biological activities of the ligand and its complexes were examined.

2. Experimental

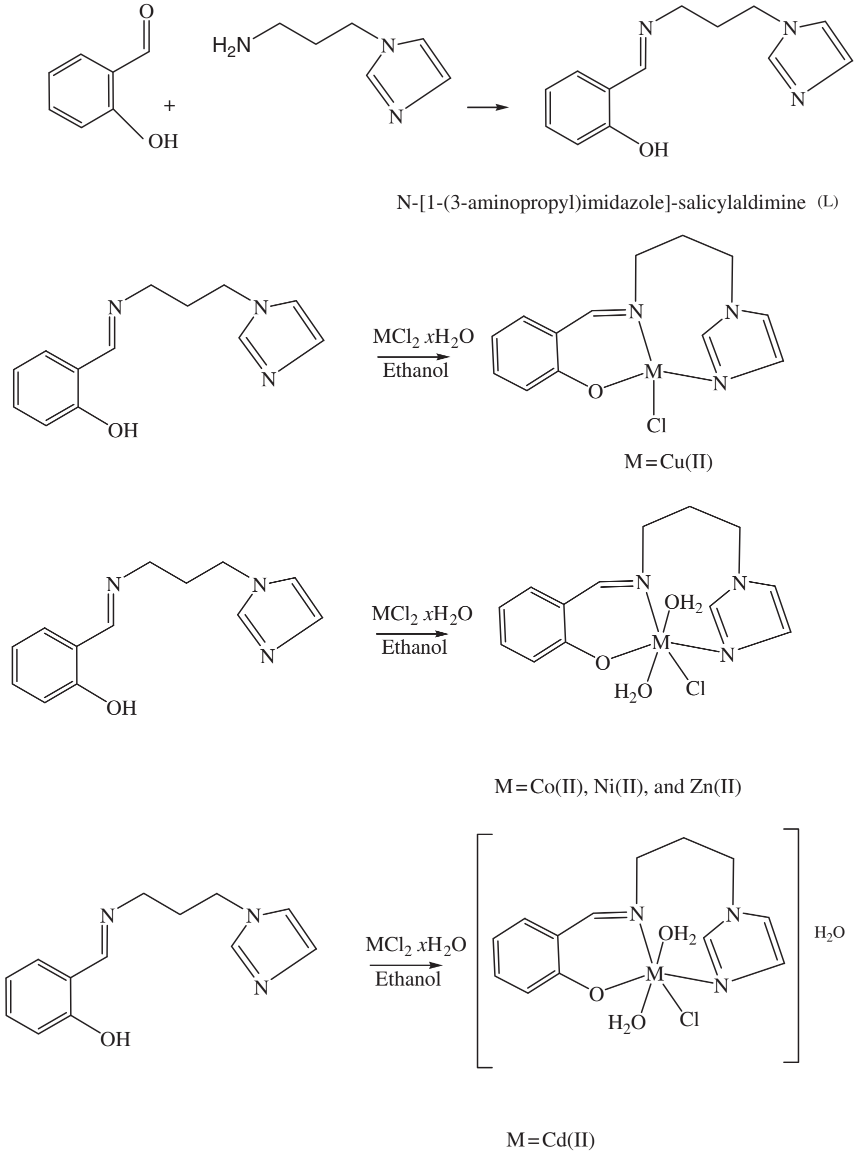
All chemicals were obtained from Aldrich Chemical & Co. and used without purification. The UV-Vis spectra of the ligand and metal complexes were recorded in DMF using a JASCO V-530 spectrophotometer. IR spectra in KBr discs were recorded on a JASCO FT-IR 460plus spectrophotometer at Thiagarajar College, Madurai. Cyclic voltammetry measurements were carried out at room temperature in DMSO (CH Instruments, USA, voltammograph) using a three-electrode cell containing a reference Ag/AgCl electrode, Pt wire auxiliary electrode, and glassy carbon working electrode with tetrabutylammonium perchlorate (TBAP) as supporting electrolyte. Elemental analyses were performed at SAIF, CDRI, Lucknow. ^{1}H-NMR spectra were recorded in $CDCl_3$ using a Bruker DRX-300, 300 MHz NMR spectrometer. EI mass spectra were recorded at IIT, Madras. EPR spectrum was recorded at SAIF, IIT, Bombay. Magnetic moments of the complexes were measured on a Magnetic Susceptibility Balance Mark 1 Sherwood UK at Thiagarajar College, Madurai. Effective magnetic moments were calculated using the formula $\mu_{\text{eff}} = 2.828\ (\chi_M T)^{1/2}$, where χ_M is the corrected molar susceptibility. Molar conductances of the complexes (10^{-3} mol L^{-1}) were measured in DMF at room temperature using a Systronic conductivity bridge.

2.1. *Synthesis of N-[1-(3-aminopropyl)imidazole]salicylaldimine (L)*

1.25 g (10 mmol) of 1-(3-aminopropyl)imidazole in 10 mL ethanol was added to 1.22 g (10 mmol) of salicylaldehyde in 20 mL of ethanol. The mixture was refluxed for 6 h and the ethanol was removed by distillation. The yellow liquid was reduced to one-half of the volume and refrigerated for 1 day giving yellow crystals, which were filtered and dried in vacuum over P_4O_{10}, m.p. = 78°C, IR in (KBr) $\nu_{\max}$ cm^{-1} 1631 (C=N), 1618 (C=N, imidazole ring). ^{1}H-NMR δ (300 MHz; $CDCl_3$), 8.32 (H, s, N=CH), 13.25 (H, s, OH), 2.23–2.15 (2H, m, CH_2–$\mathbf{CH_2}$–CH_2), 3.576–3.55 (2H, t, $\mathbf{CH_2}$–CH_2–CH_2), 4.09–4.05 (2H, t, CH_2–CH_2–$\mathbf{CH_2}$–N), 7.471–7.244 (7H, m, aromatic protons). The Schiff base has been characterized by ^{1}H-NMR spectroscopy. The spectrum shows proton signals for the proton attached to the imine group and the OH proton.

2.2. *Synthesis of complexes*

1.34 g (10 mmol) of $CuCl_2 \cdot 2H_2O$ in 10 mL of ethanol was added to 30 mL solution of 10 mmol (2.3 g) of L in ethanol. The mixture was stirred for 3 h and the green precipitate obtained was filtered and washed with water and then with ethanol and dried. The yield was 60%. Other complexes of $CoCl_2 \cdot 6H_2O$, $ZnCl_2$, $CdCl_2 \cdot 2.5H_2O$ were prepared by the same procedure, taking 10 mmol of the ligand and 10 mmol of the metal salt in ethanol (scheme 1). For the preparation of nickel(II) complex 10 mmol of L was added



Scheme 1. Synthesis of ligand and metal(II) complexes.

to 10 mmol of $NiCl_2 \cdot 6H_2O$ in 15 mL of hot ethanol and refluxed with stirring at 50–60°C for 2 h. The precipitated green nickel complex was filtered and washed with water and then with ethanol and dried.

3. Results and discussion

The tridentate ligand N-[1-(3-aminopropyl) imidazole]salicylaldimine forms stable complexes with Co(II), Ni(II), Cu(II), Zn(II), and Cd(II). The complexes have been characterized by IR, UV-Vis, ^{1}H-NMR, and EPR spectra, magnetic susceptibility measurements, and conductance. The analytical data of the ligand and the complexes together with their physical properties are given in table 1. Elemental analyses of the complexes were in agreement with calculated data for 1 : 1 (M : L) ratio. Based on the elemental analyses and mass spectra, [MLCl] was suggested for the copper(II) complex and [$MLCl \cdot 2H_2O$] for other complexes. Arish and Sivasankaran Nair [18] reported coordination by N_2O ligand with L-histidine which is a 4-substituted imidazole nucleus. Gao *et al.* [19] reported 2 : 1 complexes with N_2O_4 metal centers. Sang and Lin [20] reported complexes of chloride-bridged centrosymmetric Cu(II) complexes. Budagumpi *et al.* [21] synthesized complexes of M_2L composition. This study describes the coordination of N_2O of N-(1)substituted imidazole salicylaldimine with metal ions, and the complexes were found to be mononuclear. The purity of the Schiff-base complexes was tested by TLC and elemental analysis.

3.1. *Electronic spectra and magnetic moment*

The electronic spectra of the complexes were recorded in DMF (table 2). Electronic spectra of the ligand in ethanol showed bands at 30,769 and 35,335 cm^{-1} attributed to benzene π–π^* transition. The band at 39,215 cm^{-1} is assigned to imino π–π^* or n–π^* transition [22]. Absorption at 14,903 cm^{-1} for copper(II) complex is tentatively assigned to $^2B_{1g} \rightarrow {}^2A_{1g}$ for square-planar geometry [23]. Co(II) complexes exhibit three absorption maxima at 11,160, 15,873, and 16,806 cm^{-1} attributed to $^4A_{2g} \rightarrow {}^4T_{2g}$, $^4A_{2g} \rightarrow {}^4T_{1g}(F)$, and $^4A_{2g} \rightarrow {}^4T_{1g}(P)$, respectively, characteristic of octahedral geometry [24]. The Ni(II) complex shows absorptions at 15,627 and 24,154 cm^{-1}, tentatively assigned as $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ and $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$, suggesting an octahedral structure [25]. Octahedral geometry has been proposed for zinc and cadmium complexes [19, 26].

Magnetic moment data (table 2) show paramagnetic behavior of Cu(II), Co(II), and Ni(II) complexes. The value of 2.06 BM for copper complex falls within the range normally observed for square-planar Cu(II) complexes [23]. The magnetic moment measurement for cobalt(II) complex of 4.68 BM is indicative of octahedral geometry [27]. The Ni(II) complex reported herein has a room temperature magnetic moment value of 3.01 BM in the normal range observed for octahedral Ni(II) complexes (μ_{eff} = 2.9–3.3 BM) [27]. As expected, the Zn(II) and Cd(II) complexes are diamagnetic having a d^{10} system.

3.2. *IR spectra*

Spectral data for N-[1-(3-aminopropyl)imidazole]salicylaldimine and the complexes are presented in table 3. A strong band of the free ligand at 1631 cm^{-1}, which is attributed to the C=N stretch shifted to *ca* 1618–1641 cm^{-1} in spectra of all complexes, indicates coordination of the azomethine nitrogen to copper [28, 29]. The C=N (ring) stretching frequency in the Schiff base at 1618 cm^{-1} shifts to 1618–1634 cm^{-1} in the complexes, showing coordination of imidazole nitrogen [12]. The absence of O–H stretching frequency in the complexes indicates the coordination of deprotonated hydroxyl [17]. The broad band at 3419–3456 cm^{-1} is due to O–H stretching in coordinated water [30].

Table 1. Physical characterization, analytical, molar conductance data, Λ_M of the ligand, and its metal(II) complexes.

				Experimental (Calcd %)				
No.	Compound	Color	m.p. (°C)	Formula weight (FW) ($g\,mol^{-1}$)	C	H	N	Λ_M ($\Omega^{-1}\,cm^2\,mol^{-1}$)
1.	Ligand (L) $C_{13}H_{15}N_3O$	Yellow	78	229	68.12 (68.55)	6.55 (6.71)	19.04 (18.98)	–
2.	[CuLCl]	Pale green	155	327	47.00 (47.70)	4.00 (4.28)	11.90 (12.84)	12
3.	$[CoLCl \cdot 2H_2O]$	Violet	175	358.39	43.19 (43.52)	4.88 (5.02)	11.20 (11.71)	10
4.	$[NiLCl \cdot 2H_2O]$	Green	210	358.15	43.12 (43.57)	4.89 (5.02)	11.31 (11.72)	10
5.	$[ZnLCl \cdot 2H_2O]$	Yellow	180	364.82	42.24 (42.76)	4.22 (4.93)	11.04 (11.51)	12
6.	$[CdLCl \cdot 2H_2O]H_2O$	Yellow	195	429.85	37.00 (36.36)	3.95 (4.66)	10.00 (9.79)	14

Table 2. Electronic spectral data of ligand and metal(II) complexes.

Compound	λ_{max} (cm^{-1})	Transition	Geometry	μ_{eff} (BM)
Ligand (L)	30,769	INCT	–	–
	35,335	INCT		
	39,215	INCT		
[CuLCl]	14,556	$^2B_{1g} \rightarrow {}^2A_{1g}$	Distorted square planar	2.06
[CoLCl · 2H$_2$O]	11,160	$^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$	Distorted octahedral	4.68
	15,873	$^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$		
	16,806	$^4T_{1g}(F) \rightarrow {}^4T_{2g}(P)$		
[NiLCl · 2H$_2$O]	15,267	$^3A_{2g} \rightarrow {}^3T_{1g}(F)$	Distorted octahedral	3.04
	24,154	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$		

Table 3. IR spectral data of the ligand and metal(II) complexes (cm^{-1}).

Compound	ν(O–H)	ν(C=N)	ν(C=N) ring	ν(C–O)
Ligand	3383	1631	1618	1275
Cu complex	–	1618	1609	1226
Co complex	3419	1618	1605	1232
Ni complex	3446	1626	1597	1228
Zn complex	3420	1617	1600	1240
Cd complex	3456	1641	1634	1234

3.3. ^{1}H-NMR spectra

The ^{1}H-NMR spectrum of L recorded in $CDCl_3$ (Supplementary material) is assigned as follows: azomethine proton as singlet (s, 8.32 δ), hydroxyl group proton as singlet (s, 13.25 δ), aromatic protons as multiplet at 7.471–7.244 δ, CH_2–CH_2–CH_2 at (2H, m, 2.23–2.15 δ) and 2H, t, CH_2–CH_2–CH_2 (3.576–3.55 δ), 2H, t, CH_2–CH_2–CH_2–N (4.09–4.05 δ). The ^{1}H-NMR spectra of zinc(II) and cadmium(II) complexes have the azomethine proton signal shifted downfield (8.45 δ for Zn(II) and 8.47 δ for Cd(II)) compared to the free ligand, suggesting coordination of azomethine nitrogen. The absence of OH proton signal in the zinc(II) and cadmium(II) complexes indicates deprotonation of the ligand and coordination to the metal.

3.4. Mass spectra

The mass spectra of L, Zn(II), and Cd(II) complexes were recorded (Supplementary material). The molecular ion peak for L was observed at 229 m/z, whereas molecular ion peaks of Zn(II) and Cd(II) complexes were observed, respectively, at 364 and 429 m/z, confirming [ZnLCl · 2H$_2$O], [CdLCl · 2H$_2$O]H$_2$O. The presence of lattice water in the Cd(II) complex was confirmed by loss of mass (4.19%) while heating the complex in the temperature range 80–105°C [31]. Moreover, complexation of Zn(II) and Cd(II) were confirmed by good observed and calculated isotopic distributions [32].

3.5. EPR spectra

A powder ESR spectrum of copper(II) complex was recorded at room temperature using 2,2-diphenyl-1-picrylhydrazyl (DPPH) as reference. The spectrum exhibits anisotropic signals with $g_{||} = 2.254$ and $g_{\perp} = 2.210$, characteristic for axial symmetry [33]. Since $g_{||}$ and $g_{\perp}$ are close to 2 and $g_{||} > g_{\perp}$ suggesting a tetragonal distortion around Cu(II) corresponding to elongation along the four fold *z*-axis [34]. The trend $g_{||} > g_{\perp} > g_e$ (2.0023) shows the unpaired electron localized in the $d_{x^2-y^2}$ orbital characteristic of distorted square-planar geometry in Cu(II) complexes [18]. In addition, exchange coupling interaction between two Cu(II) ions is explained by Hathaway expression $G = (g_{||} - 2)/(g_{\perp} - 2)$. When the value $G < 4.0$, a considerable exchange coupling is present in the solid complex ($G = 1.2476$) [35]. Kivelson and Neiman showed that for an ionic environment, $g_{||}$ is normally 2.3 or larger, but for a covalent environment, $g_{||}$ is less than 2.3. The $g_{||}$ value for the Cu(II) complex is 2.254, consequently the environment is covalent.

3.6. *Electrochemical studies*

3.6.1. Cyclic voltammetry. The redox behavior of Cu(II) complexes has been investigated by cyclic voltammetry using glassy carbon electrode as the working electrode, platinum wire as counter electrode, and Ag/AgCl electrode as the reference and TBAP as supporting electrolyte (Supplementary material). The free ligand does not show oxidation or reduction. The cathodic current values of copper complex were independent of the scan rate. The repeated scan as well as different scan rates shows that dissociation does not take place in these complexes. The cyclic voltammogram of copper complex shows a well-defined redox process corresponding to the Cu(II)/Cu(I) couple at $E_{pa} = 0.13\,V$ and the associated cathodic peak at $E_{pc} = 0.38\,V$. This couple is found to be quasireversible with one-electron oxidation/reduction reaction, which is attributed to Cu(II)/Cu(I) [17].

3.7. *Molar conductance*

Values of molar conductance of the complexes are given in table 1. The low values in DMF indicate that the complexes are nonelectrolytes [36].

3.8. *Biological activities*

The well diffusion method was employed for screening antibacterial and antifungal activities [37]. The bacteria used are *Pseudomonas aeruginosa*, *Escherichia coli* (Gram-negative), and *Staphylococcus aureus* (Gram-positive). The fungus used is *Candida albicans*. Stock solution (0.001 mol) was prepared by dissolving the compounds in DMSO and the solutions were serially diluted to find the minimum inhibitory concentration (MIC) values ($\mu g\,mL^{-1}$). Antimicrobial activity studies were performed in triplicate and the average was taken as the final reading. Error limits are also indicated in the respective table. The MIC values of the compounds are summarized in table 4. A comparative study of the MIC values for ligands and their complexes indicates that the complexes exhibit higher antimicrobial activity than the ligand. Such an increased activity of the complexes can be explained on the basis of Overtone's concept [38] and Tweedy's chelation theory [39]. Zinc(II) and cadmium(II) complexes were found to be more potent than the other complexes.

Table 4. MIC of the synthesized compounds against growth of bacteria and fungus ($\mu g\,mL^{-1}$).

Compound	*S. aureus*	*E. coli*	*P. aeruginosa*	*C. albicans*
Ligand	85	110	80	76
[CuLCl]	74	98	70	58
$[CoLCl \cdot (2H_2O)]$	78	94	71	55
$[NiLCl \cdot (2H_2O)]$	73	100	75	54
$[ZnLCl \cdot (2H_2O)]$	52	75	48	38
$[CdLCl \cdot 2H_2O]H_2O$	55	73	42	35
Amikacin	20	30	15	–
Ketokonazole	–	–	–	20

Each value observed is within the error limits of ±2.

4. Conclusion

Complexes of N-[1-(3-aminopropyl)imidazole]salicylaldimine with Cu(II), Co(II), Ni(II), Zn(II), and Cd(II) were synthesized and characterized by various physical–chemical methods. The complexes are different from earlier work with Schiff base of L-histidine (4-substituted imidazole) and cuminaldehyde. The Schiff base is a tridentate chelating ligand coordinating through azomethine nitrogen, imidazole nitrogen, and oxygen. The proposed geometry for copper(II) is distorted square planar and distorted octahedral for other metal ions. Biological activities of the ligand and their metal complexes show that the activity of the metal complexes is higher than the ligand.

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