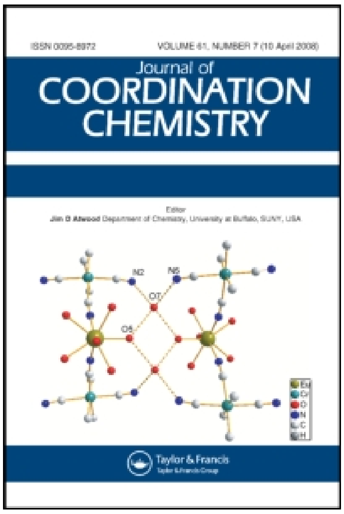

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Synthesis, characterization and antimicrobial activity of transition metal complexes with the Schiff base derived from imidazole-2-carboxaldehyde and glycylglycine

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Synthesis, characterization and antimicrobial activity of transition metal complexes with the Schiff base derived from imidazole-2-carboxaldehyde and glycylglycine

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The Co(II), Ni(II) and Cu(II) complexes of the Schiff base derived from imidazole-2-carboxaldehyde and glycylglycine were synthesized and characterized by elemental analysis, PMR, molar conductance, IR, electronic, magnetic measurements, ESR, redox properties, thermal studies, XRD and SEM. Conductance measurements indicate that the complexes are 1 : 1 electrolytes. IR data show that the ligand is tetradentate with imidazole nitrogen, azomethine nitrogen, amide nitrogen and carboxylato oxygen donor groups. Electronic spectral measurements indicate tetrahedral geometry for Co(II) and Ni(II) complexes and square-planar geometry for Cu(II). Magnetic measurements show weak ferromagnetic behavior for Co(II) and Ni(II) complexes, and paramagnetic for Cu(II) complex. The X-band ESR spectral data indicate a covalent link between metal and ligand. The complexes were found to be stabilized in unusual oxidation states of metal during electrolysis. Thermal analysis of the complexes indicate that decomposition takes place in three steps. XRD shows that Ni(II) and Cu(II) complexes have the respective crystallite size of 42 and 34 nm, while the Co(II) complex is amorphous. The surface morphology of the complexes was studied by SEM. The antimicrobial activities of the ligand and its complexes indicate that the metal complexes possess high antibacterial and antifungal activities towards the bacterial species *S. aureus*, *E. coli*, *K. pneumaniae*, *P. vulgaris* and *P. aeruginosa* and the fungal species *A. niger*, *R. stolonifer*, *A. flavus*, *R. bataicola* and *C. albicans*.

Keywords: Schiff base; Conductance; IR; Electronic; Redox properties; Thermal analysis; XRD; SEM; Antibacterial activity

1. Introduction

Investigations on the complexing ability of metal ions with model ligands assist in the understanding of the function of physiological systems. Among complexing ligands, Schiff bases have special interest due to their industrial, antifungal and biological applications [1–9]. Imidazole and its derivatives play an important role because of their therapeutic properties and interesting spectral, magnetic and structural aspects [10]. Coordination of peptides in metal complexes has attracted many reserachers for a better understanding of metal ion-enzyme-substrate complexes. However, little attention has

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been paid to systems in which the Schiff bases are derived from imidazoles and peptides. In this article, the synthesis and characterization of Co(II), Ni(II) and Cu(II) complexes of a Schiff base derived from imidazole-2-carboxaldehyde and glycylglycine are reported. The antibacterial and antifungal activity of the Schiff base and its complexes were also studied.

2. Experimental

2.1. *Materials*

Glycylglycine was purchased from Fluka and used without further purification. Imidazole-2-carboxaldehyde was obtained from Lancaster and Co(II), Ni(II) and Cu(II) nitrates were obtained from Merck. All other reagents and solvents were purchased from commercial sources and were of analytical grade.

2.2. *Synthesis of Schiff base ligand*

Glycylglycine (0.66 g, 5 mmol) was dissolved in 40 cm^3 of methanol containing KOH (0.28 g, 5 mmol). A solution of imidazole-2-carboxaldehyde (0.48 g, 5 mmol) in 20 cm^3 of absolute methanol was added dropwise with stirring and refluxed at 50°C for 2 h. The volume of the yellow solution was reduced *in vacuo* using a rotary evaporator. Anhydrous ether was added to deposit a yellowish precipitate, which was then recrystallized from EtOH.

2.3. *Synthesis of the Schiff base metal(II) complexes*

Glycylglycine (0.66 g, 5 mmol) was dissolved in 40 cm^3 of methanol containing KOH (0.28 g, 5 mmol). A solution of imidazole-2-carboxaldehyde (0.48 g, 5 mmol) in 20 cm^3 of absolute methanol was added dropwise with stirring and refluxed at 50°C for 2 h. To the yellowish solution, a solution of Co(II), Ni(II) or Cu(II) nitrates (5 mmol) was dissolved in 10 cm^3 of methanol. The above mixture was magnetically stirred for 2 h. The solid product obtained was filtered off, washed several times with cold EtOH and then ether, and then dried *in vacuo* over anhydrous $CaCl_2$. The above products were then recrystallized from EtOH.

The purities of the solid Schiff base and its metal complexes were tested by literature procedure [11].

2.4. *Physical measurements*

Elemental analyses were obtained using a Perkin-Elmer elemental analyzer. The metal contents in the complexes were determined by standard EDTA titration [11]. The 400 MHz PMR of the ligand was recorded using TMS as internal standard. Molar conductances of the complexes were measured in DMSO (10^{-3} M) solutions using a coronation digital conductivity meter. IR spectra were recorded in KBr discs on a JASCO FT/IR-410 spectrometer in the 4000–400 cm^{-1} region. Electronic spectra were recorded on a Perkin–Elmer Lambda-25 UV–Vis spectrometer. Room temperature magnetic measurements were performed on an EG & G PARC vibrating sample magnetometer with a maximum applied field of 7 kOe. Solid state X-band ESR spectrum of Cu(II) complex was recorded on a Varian E112 X-band spectrometer. Redox properties were carried out on a Bio Analytical System CV-50W electrochemical analyzer. Thermal studies were carried out on a Perkin-Elmer 7 Series thermal analyzer, with a heating rate of $10^\circ C\,min^{-1}$ under N_2. XRD was recorded on a Rigaku Dmax X-ray diffractometer with Cu-Kα radiation ($\lambda = 1.5404\,\text{Å}$). SEM images were recorded in a Hitachi SEM analyzer.

2.5. *Antimicrobial activities*

Antibacterial and antifungal activities of the ligand and its complexes were tested *in vitro* against the bacteria *Staphylococcus aureus*, *Escherichia coli*, *Klebsiella pneumaniae*, *Proteus vulgaris* and *Pseudomonas aeruginosa* and the fungi *Aspergillus niger*, *Rhizopus stolonifer*, *Aspergillus flavus*, *Rhizoctonia bataicola* and *Candida albicans* by Kirby Bauer Disc diffusion method [12]. *Amikacin*, *Ofloxacin* and *Ciprofloxacin* were used as standards for antibacterial activiy and *Nystatin* was used as the standard for antifungal activity. The test organisms were grown on nutrient agar medium in petri plates. The compounds were prepared in DMSO and soaked in filter paper disc of 5 mm diameter and 1 mm thickness. The discs were placed on the previously seeded plates and incubated at 37°C and the diameter of inhibition zone [13, 14] around each disc was measured after 24 h for antibacterial and 72 h for antifungal activities.

3. Results and discussion

The ligand and its complexes were stable in air. The metal complexes are insoluble in common organic solvents, but soluble in DMF and DMSO. Analytical data (table 1) are in good agreement with calculated values, as expected for the assigned formula, $[ML](NO_3)(H_2O)$, where M = Co(II), Ni(II) and Cu(II); L = Schiff base. The PMR spectrum of the ligand shows azomethine proton at 8.3 δ, amide proton at 9.2 δ and NH proton of imidazole ring at 11.7 δ. The experimental molar conductance values of 54, 62 and 66 $\Omega^{-1}\,cm^2\,mol^{-1}$, respectively, for the Co(II), Ni(II) and Cu(II) complexes indicate that all the complexes behave as 1 : 1 electrolytes [15].

Table 1. Physical and analytical data of the ligand and its complexes.

Compound	Empirical formula	Color	Found (Calcd) (%) C	H	N	M
K(HL)	$KC_8H_9N_4O_3$	Yellow	38.70 (38.32)	3.65 (3.49)	22.57 (22.51)	–
$[CoL](NO_3)(H_2O)$	$CoC_8H_{11}N_5O_7$	Pink	27.60 (27.45)	3.18 (3.01)	20.12 (20.11)	16.93 (16.74)
$[NiL](NO_3)(H_2O)$	$NiC_8H_{11}N_5O_7$	Pale green	27.62 (27.43)	3.19 (3.90)	20.13 (20.56)	16.87 (16.54)
$[CuL](NO_3)(H_2O)$	$CuC_8H_{11}N_5O_7$	Light blue	27.24 (27.89)	3.14 (3.89)	19.85 (19.34)	18.01 (18.43)

3.1. *IR spectra*

The important IR absorption bands are given in table 2. The Schiff base shows ν(C=N) azomethine band at $1631\,\text{cm}^{-1}$, which shifts to lower values in all the systems on complexation (table 2), showing that the azomethine nitrogen is coordinated to the metal [16]. In the Schiff base, imidazole nitrogen appeared at $1612\,\text{cm}^{-1}$ and shifted to lower frequency in the complexes (table 2), indicating that the imidazole nitrogen is involved in coordination. In the spectrum of Schiff base, the peptide band appeared at $1538\,\text{cm}^{-1}$, shifting to lower frequency on complexation (table 2), indicating linkage between metal ion and the peptide nitrogen [16]. The asymmetric carboxyl stretching $\nu_{\text{asym}}(\text{COO}^-)$ is shifted to higher frequency and the symmetric carboxyl stretching $\nu_{\text{sym}}(\text{COO}^-)$ is shifted to lower frequency, indicating linkage between the metal ion and carboxylato oxygen [17, 18]. The asymmetric and symmetric stretching vibration of the carboxylato group in the complexes show separation ($\Delta\nu$) greater than $200\,\text{cm}^{-1}$, indicating monodentate binding in the complexes [19, 20]. The IR spectra of the complexes show the bands at $1364–1378\,\text{cm}^{-1}$, ascribed to the presence of free NO_3^- [21]. Furthermore, the observed broad bands at $3400–3443\,\text{cm}^{-1}$ in the complexes may be attributed to O–H stretching of lattice water molecules as supported from thermal analysis [16, 21]. The appearance of two bands at 520–567 and $434–463\,\text{cm}^{-1}$ correspond to ν(M–O) and ν(M–N) stretching vibrations [22], respectively. These bands are not observed in the spectrum of the ligand. Thus the IR spectrum indicates that the Schiff-base ligand (figure 1) in all the complexes under investigation is tetradentate, binding through imidazole nitrogen, azomethine nitrogen, amide nitrogen and carboxylato oxygen.

Table 2. Infrared spectral data (cm^{-1}) of the ligand and its complexes.

Compound	ν(C=N) (imidazole)	ν(C=N) (azomethine)	$\nu(\text{CON}^-)$	$\nu_{\text{asym}}(\text{COO}^-)$	$\nu_{\text{sym}}(\text{COO}^-)$	ν(M–O)	ν(M–N)
K(HL)	1612	1631	1538	1591	1382	–	–
$[\text{CoL}](\text{NO}_3)(\text{H}_2\text{O})$	1602	1626	1529	1587	1384	520	434
$[\text{NiL}](\text{NO}_3)(\text{H}_2\text{O})$	1609	1621	1528	1585	1383	556	450
$[\text{CuL}](\text{NO}_3)(\text{H}_2\text{O})$	1607	1617	1521	1589	1379	567	463

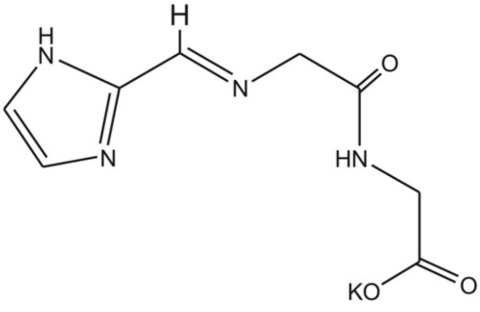

Figure 1. Proposed structure of the Schiff base.

3.2. *Electronic spectra*

The UV–Vis spectrum of the Schiff base shows an absorption band at 320 nm assigned to the π–π^* transition of the azomethine chromophore. On complexation, this band shifts to lower wavelength, suggesting coordination of azomethine nitrogen with the metal [23]. The Co(II) complex shows a band at 545 nm, due to $^4A_2(\mathrm{F}) \rightarrow {}^4T_1(\mathrm{F})$ transition of tetrahedral geometry. The Ni(II) complex shows absorption band at 581 nm, attributed to $^3T_1(\mathrm{F}) \rightarrow {}^3T_1(\mathrm{P})$, corresponding also to tetrahedral geometry. In general, due to Jahn-Teller distortion, square planar Cu(II) complexes give a broad absorption between 600 and 700 nm [24]. The value of 640 nm observed for the present Cu(II) complex demonstrates its square-planar geometry.

3.3. *Magnetic measurements*

The plot of magnetization (M) *versus* applied field (H) for the Co(II) and Ni(II) complexes (Supplementary Material) show the hysteresis loop at room temperature and gives a saturation magnetization of 0.20 emu g^{-1}. Also, they show coercivities of 316 and 287 Oe, respectively. The low saturation magnetization and the presence of coercivities for the samples indicate that these complexes are weakly ferromagnetic [25]. The Cu(II) complex did not show a hysteresis loop at room temperature, indicating that the Cu(II) complex is paramagnetic [25, 26].

3.4. *ESR spectrum*

The X-band ESR spectrum of the Cu(II) complex in the solid state at room temperature (Supplementary Material) shows an intense broad band with $g = 2.12$. The value of g and the shape of ESR signals suggest square-planar coordination for the Cu(II) complex [27]. According to Fidone and Stevens [28], the positive contribution in the g value over the free electron value of 2.0023 indicates an increase in the covalent nature of the bonding between the metal and the ligand.

3.5. *Redox properties*

Cyclic voltammograms of the metal complexes were recorded in DMSO solution, with 0.1 mol dm^{-3} TBAP as supporting electrolyte, and the results are summarized in table 3. The cyclic voltammogram of cobalt complex shows a redox process corresponding to

Table 3. Cyclic voltammetric data of the Co(II), Ni(II) and Cu(II) Schiff-base complexes.

Compound	Couple	Epc (V)	Epa (V)	ipc (µA)	ipa (µA)
$[\mathrm{CoL}](\mathrm{NO_3})(\mathrm{H_2O})$	Co(II)/Co(I)	−0.702	−0.591	23.38	30.34
	Co(II)/Co(III)	–	+0.205	–	10.16
	Reduction of ligand	−0.942	–	31.27	–
$[\mathrm{NiL}](\mathrm{NO_3})(\mathrm{H_2O})$	Ni(II)/Ni(I)	−0.602	−0.93	87.44	18.58
$[\mathrm{CuL}](\mathrm{NO_3})(\mathrm{H_2O})$	Cu(II)/Cu(I)	−0.694	−0.600	24.97	12.45
	Cu(II)/Cu(III)	–	+0.420	12.0	–
	Cu(I)/Cu(0)	−0.902	–	38.40	–

Table 4. Thermoanalytical results of the Co(II), Ni(II) and Cu(II) Schiff-base complexes.

Compound	Temp. range (°C)	Mass loss found (Calcd) (%)	DSC Peak (°C)	ΔH (Jg^{-1})	Assignment
$[CoL](NO_3)(H_2O)$	50–110	6.2 (5.17)	118	326.87	H_2O
	110–287	72.89 (73.30)	240	2.47	NO_3^- and ligand
	287–397	22.68 (21.52)	375	−0.85	CoO
$[NiL](NO_3)(H_2O)$	50–120	5.5 (5.18)	131	160.86	H_2O
	120–250	73.1 (73.35)	291	5.78	NO_3^- and ligand
	250–370	22 (21.46)	384	−147.67	NiO
$[CuL](NO_3)(H_2O)$	50–128	5.5 (5.10)	121	121.59	H_2O
	128–197	72.1 (72.34)	195	3.77	NO_3^- and ligand
	197–380	22.3 (22.55)	377	−189.73	CuO

Co(II)/Co(I) couple. It is quasi-reversible with $\Delta E_p = 111\,mV$; the ratio of anodic and cathodic peak currents (ipc/ipa = 1) correspond to a simple one-electron transfer process. There are also two irreversible peaks corresponding to the Co(II)/Co(III) oxidative response at 0.283 V and reduction of ligand at −0.942 V. The nickel complex shows a quasi-reversible nature in the negative region, characteristic of the Ni(II)/Ni(I) couple. The copper complex (Supplementary Material) shows one redox couple for Cu(II)/Cu(I). This redox couple is quasi-reversible, characterized by a peak-to-peak separation value at $\Delta E_p = 94\,mV$. This couple occurs with oxidative response at −0.694 V and the reductive response at −0.600 V. The other two responses are irreversible, corresponding to formation of Cu(I)/Cu(0) and Cu(II)/Cu(III) −0.902 and +0.420 V peaks, respectively. These observations suggest the ligand can stabilize unusual oxidation states of the metal ions (0), (+1) and (+3) during electrolysis, probably due to the presence of the imidazole group in the Schiff-base ligand [6, 29].

3.6. *Thermal studies*

Thermal decompositions of the metal complexes were performed using TGA and DSC analysis. The assignment of the different decomposition steps are given in table 4. The Cu(II) complex (Supplementary Material) undergo decomposition in three different steps. The first from 50–128°C corresponds to dehydration and release of loosely bound lattice water with a weight loss of 5.10% [24, 30]. The DSC curve of the complex shows an endothermic peak at 121°C, which may be due to evaporation of lattice water. Partial decomposition starts with the second step, which follows immediately after the first step in the range 128–197°C. This includes the partial separation of ligand and NO_3^- from the complex and also shows weight loss of 72.34%. The DSC curve of the complex shows a broad endothermic peak with an onset temperature at 195°C, due to evaporation of Schiff base. Above 195°C, the decomposition was observed likely due to NO_3^- from the complex. During the final decomposition above 340°C, metal oxide is formed. An endothermic peak was obtained in the DSC curve in the temperature range 340–400°C, due to final decomposition of the metal complex into metal oxide [30, 31]. Similar TGA and DSC results were obtained for Co(II) and Ni(II) complexes.

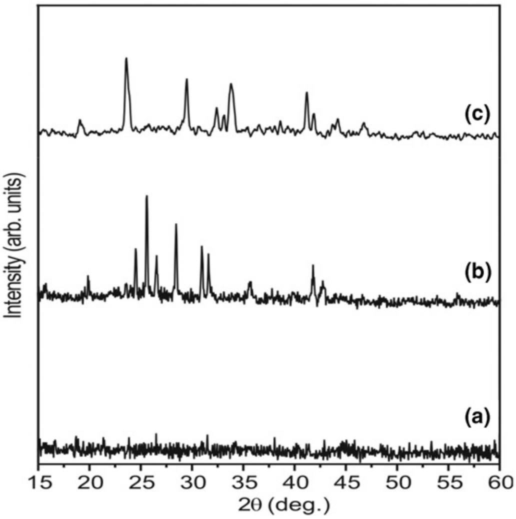

Figure 2. XRD patterns of (a) Co(II), (b) Ni(II) and (c) Cu(II) Schiff-base complexes.

3.7. *XRD*

The powder XRD pattern of Co(II) complex [figure 2(a)] does not show any well-defined peak, indicating that the sample is in a disordered phase [32]. However, Ni(II) and Cu(II) complexes have sharp peaks [figures 2(b) and (c)], indicating crystalline phase. The value of (2θ), interplanar spacing d(Å) and the relative intensities (I/I^0) of the Ni(II) and Cu(II) complexes are given in Supplementary Material. The d-values calculated for Ni(II) and Cu(II) complexes in the present study compare favorably with the literature values [24, 33]. The crystallite size of the complexes d_{XRD} were calculated using Scherre's formula [32, 34]. The Ni(II) and Cu(II) complexes have an average crystallite size of 42 and 34 nm, respectively, suggesting that the complexes are in nanocrystalline phase.

3.8. *SEM*

The SEM micrographs of the Co(II), Ni(II) and Cu(II) complexes (Supplementary Material) show that the Co(II) and Cu(II) complexes have platelet-like structure, while Ni(II) complex exhibits cauliflower-like structure. The surface morphology of the complexes show that the particles are agglomerated. The smaller average crystallite size found from XRD also shows that the particles are agglomerated.

3.9. *Antimicrobial activity*

The results of the antibacterial and antifungal activities are given in tables 5 and 6. Against all organisms, the ligand is moderately active, and the complexes are more active than the ligand. The Cu(II) complex is highly active against the bacterial and fungal species compared with known standards. The mechanism of toxicity of

Table 5. Antibacterial activities of the ligand and its complexes.

Compound	Gram positive			Gram negative	
	Staphylococcus aureus	*Klebsiella pneumaniae*	*Proteus vulgaris*	*Escherichia coli*	*Pseudomonas aeruginosa*
K(HL)	++	++	++	++	+
$[CoL](NO_3)(H_2O)$	++	+++	+++	+++	+++
$[NiL](NO_3)(H_2O)$	+++	++	+	++	++
$[CuL](NO_3)(H_2O)$	+++	+++	+++	+++	+++
Amikacin[a]	++	++	++	+++	++
Ofloxacin[a]	++	++	++	++	+
Ciprofloxacin[a]	++	++	++	+++	++

Inhibition values = 0.1–0.5 cm beyond control = + (less active); inhibition values = 0.6–1.0 cm beyond control = ++ (moderately active); inhibition values = 1.1–1.5 cm beyond control = +++ (highly active).

[a] Standards.

Table 6. Antifungal activities of the ligand and its complexes.

Compound	*Candida albicans*	*Rhizopus stolonifer*	*Aspergillus niger*	*Aspergillus flavus*	*Rhizoctonia bataicola*
K(HL)	+	+	+	+	+
$[CoL](NO_3)(H_2O)$	++	+++	++	+++	+++
$[NiL](NO_3)(H_2O)$	++	++	++	++	++
$[CuL](NO_3)(H_2O)$	+++	+++	+++	++	++
Nystatin[a]	+++	+++	+++	+++	+++

Inhibition values = 0.1–0.5 cm beyond control = + (less active); inhibition values = 0.6–1.0 cm beyond control = ++ (moderately active); inhibition values = 1.1–1.5 cm beyond control = +++ (highly active).

[a] Standards.

the complexes with the ligand may be ascribed to the increase of lipophilic nature of the complexes arising from chelation. Chelation reduces the polarity of the metal atom mainly because of partial sharing of its positive charge with the donor groups and possible π electron delocalization within the chelate ring. Also, the chelation increases the lipophilic nature of the central metal, which subsequently favors permeation through the lipid layer of cell membrane [12]. The mode of action of the complexes can involve formation of hydrogen bonds, as well as the presence of two imine groups important in elucidating the mechanism of transformation reactions in biological systems [35]. The activity increases with increase in concentration of complexes. It is suggested that the complexes having antimicrobial activity may act either by killing the microbe or by inhibiting multiplication of the microbe by blocking their active sites [36]. The activity order of the synthesized complexes is as follows: Cu > Co > Ni > L.

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