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Synthesis and characterization of Co(II), Ni(II), Cu(II) and Zn(II) complexes of tridentate Schiff base derived from vanillin and DL-α-aminobutyric acid

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Abstract

Co(II), Ni(II), Cu(II) and Zn(II) complexes of the Schiff base derived from vanillin and DL-α-aminobutyric acid were synthesized and characterized by elemental analysis, IR, electronic spectra, conductance measurements, magnetic measurements, powder XRD and biological activity. The analytical data show the composition of the metal complex to be [ML(H_2O)], where L is the Schiff base ligand. The conductance data indicate that all the complexes are non-electrolytes. IR results demonstrate the tridentate binding of the Schiff base ligand involving azomethine nitrogen, phenolic oxygen and carboxylato oxygen atoms. The IR data also indicate the coordination of a water molecule with the metal ion in the complex. The electronic spectral measurements show that Co(II) and Ni(II) complexes have tetrahedral geometry, while Cu(II) complex has square planar geometry. The powder XRD studies indicate that Co(II) and Cu(II) complexes are amorphous, whereas Ni(II) and Zn(II) complexes are crystalline in nature. Magnetic measurements show that Co(II), Ni(II) and Cu(II) complexes have paramagnetic behaviour. Antibacterial results indicated that the metal complexes are more active than the ligand.

Keywords: Schiff base metal complex; Vanillidene-DL-α-aminobutyrate; IR; Electronic spectra; Magnetic measurements; Powder XRD; Antimicrobial activity

1. Introduction

Schiff bases have gained importance because of physiological and pharmacological activities associated with them. A large number of Schiff base compounds are often used as ligands in coordination chemistry by considering their metal binding ability. Schiff base metal complexes have ability to reversibly bind oxygen in epoxidation reactions [1], biological activity [2,3], catalytic activity in hydrogenation of olefins [4,5] and photochromic properties [6]. Vanillin is most prominent as the principal flavor and aroma compound in vanilla. Synthetic vanillin is used as a flavoring agent in foods, beverages, and pharmaceuticals [7]. However, only few transition metal complexes of vanillin were reported [8–10]. Recently we have studied some tridentate Schiff base metal complexes [11–13]. In this paper, we report the synthesis, characterization and biological activity of some novel tridentate Schiff base K(HL) metal complexes derived from vanillin and DL-α-aminobutyric acid.

2. Experimental

2.1. Materials

DL-α-Aminobutyric acid (Fluka), vanillin (Sisco Research Lab) and metal(II) nitrates were purchased from Merck. All the chemicals used were of Analar grade. Solvents were purified and dried before use according to the standard method [14].

2.2. Analytical and physical measurements

Carbon, hydrogen and nitrogen were obtained using a Perkin-Elmer elemental analyzer. The metal contents were determined by complexometric titrations with EDTA [15]. The IR spectra were recorded in KBr pellets on a JASCO FT/IR-410 spectrometer in the range 400–4000 cm^{-1}. Electronic spectra were recorded on a Perkin-Elmer Lambda-25 UV–vis spectrometer using MeOH as solvent. Conductivity measurements were

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Table 1
Analytical and physical data of the Schiff base ligand and its complexes

Compound	Empirical formula, colour	Found (calculated) (%)				Molar conductance (S cm^2 mol^{-1})	μ_{eff} (μ_B)
		C	H	N	M		
K(HL)	$C_{12}H_{14}NO_4K$, yellow	52.35 (52.79)	5.12 (4.63)	5.09 (5.02)	–	–	–
[CoL(H$_2$O)]	$C_{12}H_{15}NO_5Co$, brown	46.17 (46.31)	4.84 (4.39)	4.49 (4.90)	18.88 (18.09)	19.81	3.97
[NiL(H$_2$O)]	$C_{12}H_{15}NO_5Ni$, pale green	46.20 (46.35)	4.85 (4.40)	4.49 (4.09)	18.81 (18.20)	10.72	2.83
[CuL(H$_2$O)]	$C_{12}H_{15}NO_5Cu$, bluish green	45.50 (45.64)	4.77 (4.93)	4.42 (4.39)	20.06 (21.26)	13.32	1.85
[ZnL(H$_2$O)]	$C_{12}H_{15}NO_5Zn$, colourless	45.23 (45.18)	4.74 (4.98)	4.40 (4.85)	20.52 (20.90)	11.57	Dia.

made on freshly prepared 10^{-3} M solutions in DMF at room temperature with a coronation digital conductivity meter. XRD were recorded on a Rigaku D/max X-ray diffractometer with Cu Kα radiation. The magnetic measurements were carried out at room temperature using EG & G PARC vibrating sample magnetometer and magnetic moment calculations were done using the method described elsewhere [16].

2.3. Preparation of the potassium salt of the Schiff base ligand

To a solution of DL-α-aminobutyric acid (0.089 g, 1 mmol) in MeOH (15 cm^3) containing KOH (0.056 g, 1 mmol), vanillin (0.152 g, 1 mmol) in MeOH (10 cm^3) was added. The above solution was magnetically stirred for 1 h. The volume of yellow solution was reduced *in vacuo* using rotary evaporator. Anhydrous ether was added to deposit the yellowish precipitate and it was recrystallized from EtOH (yield = 67%).

2.4. Preparation of metal complexes

Metal(II) nitrates (1 mmol) was dissolved in MeOH (10 cm^3) and the solution was filtered and added dropwise into a (15 cm^3) methanolic solution of K(HL) ligand (1 mmol). The above mixture was magnetically stirred for 2 h. The coloured complex obtained was filtered off, washed with MeOH and Et$_2$O dried *in vacuo* (yield = 55–61%).

2.5. Antimicrobial activity

The ligand and its complexes were tested against the bacterial species *Staphylococcus aureus*, *Escherichia coli*, *Klebsiella pneumaniae*, *Proteus vulgaris* and *Pseudomonas aeruginosa*, also the antifungal activity against *Candida albicans*. These studies were carried out using *Amikacin* as standard antibacterial agent and *Terbinafin* as standard antifungal agent by Kirby Bauer disc diffusion method [17]. The test solutions were prepared in DMSO. Diffusion method [18,19] was used to evaluate the antimicrobial activities of the tested compounds as follows: 0.5 ml spore suspension (10^6 to 10^7 spore ml^{-1}) of each of the investigated organisms was added to a sterile agar medium just before solidification, then poured into sterile Petri dishes (9 cm in diameter) and left to solidify. Using sterile cork borer (6 mm in diameter), wells were made in each dish, then 0.1 ml of the tested compounds dissolved in DMSO were poured into three wells and the dishes were incubated at 37 °C for 48 h (for bacteria) and 30 °C for 72 h (for fungi), where clear or inhibition zones were detected around each well.

3. Results and discussion

The analytical and physical data of the Schiff base ligand and its complexes are given in Table 1. The complexes are soluble in DMF and DMSO and are insoluble in some common organic solvents. The analytical data show that the metal to ligand ratio is 1:1 in all the complexes. The composition of the complexes is [ML(H$_2$O)], where (M = Co(II), Ni(II), Cu(II) and Zn(II) and LH$_2$ = vanillidene-DL-α-aminobutyrate. The low molar conductance values (Table 1) of 10^{-3} M solutions in DMF showed them to be non-electrolytes [20].

3.1. Infrared spectra

The IR spectral data are given in Table 2. The IR spectrum of the Schiff base ligand and a representative system of Cu(II) complex are shown in Fig. 1. In the Schiff base ligand, the strong band observed at 1644 cm^{-1} can be assigned to the ν(C=N) azomethine stretching vibration. On complexation, this band was shifted to lower frequency in the 1617–1638 cm^{-1} range indicating the coordination of the azomethine nitrogen atom to the central metal ion [21]. The asymmetric car-

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

Compound	ν(C=N)	ν(O—H)	ν_{asym}(COO$^-$)	ν_{sym}(COO$^-$)	ν(M—N)	ν(M—O)
K(HL)	1644	3453	1584	1343	–	–
[CoL(H$_2$O)]	1630	3405	1582	1332	537	456
[NiL(H$_2$O)]	1635	3442	1571	1335	574	457
[CuL(H$_2$O)]	1617	3439	1570	1383	584	420
[ZnL(H$_2$O)]	1638	3419	1583	1385	580	437

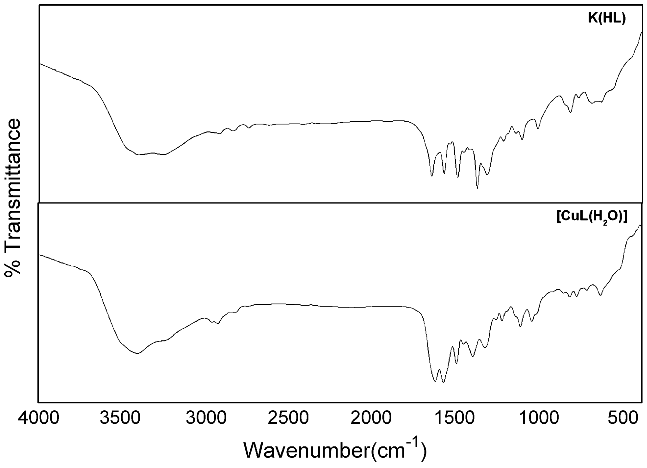
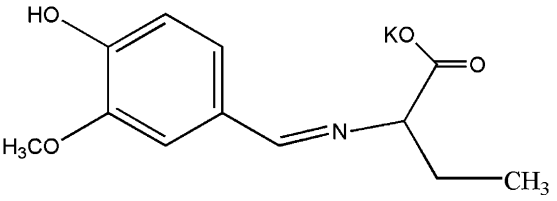


Fig. 1. IR spectra of K(HL) and [CuL(H_2O)] complex.

boxyl stretching $\nu_{asym}(COO^-)$ is shifted to higher frequency in the 1570–1583 cm^{-1} range and the symmetric carboxyl stretching $\nu_{sym}(COO^-)$ is shifted to lower frequency in the 1332–1385 cm^{-1} range, indicating the linkage between the metal ion and carboxylato oxygen atom [21–23]. The difference between $\nu_{asym}(COO^-)$ and $\nu_{sym}(COO^-)$ for the Co(II), Ni(II), Cu(II) and Zn(II) complexes in the present study are, respectively 250, 236, 187 and 198 cm^{-1}. This value compares favorably with that of 191–225 cm^{-1}, characteristic for the monodentate coordination of the carboxylato group [24–26]. Thus, in all the complexes, the carboxylato group is monodenatate. The ν(C–O) phenolic band in the complexes was shifted to lower frequency in the 1224–1231 cm^{-1} range indicating the coordination of the phenolic oxygen atom with the metal ion [21]. The spectra of the complexes show broad bands in the 3405–3442 cm^{-1} range, which can be attributed to the stretching vibration of the O–H group [21]. This indicates that a water molecule occupies in the fourth position. In the complexes, weak bands in the 537–580 and 420–457 cm^{-1} range, can be attributed to ν(M–N) and ν(M–O), respectively [27–29]. From the IR results, it may be concluded that the Schiff base ligand is tridentate (Scheme 1) and coordinates with the metal ion through the phenolic oxygen, azomethine nitrogen and carboxylato oxygen atoms.

3.2. Electronic spectra

The electronic spectrum of the Schiff base ligand (Fig. 2) shows a broad band at 317 nm, which is assigned to π–π* transition of the C=N chromophore. On complexation, this band was shifted to lower wavelength region, suggesting the coordination of azomethine nitrogen with the metal ion. Co(II) complex shows only one absorption band in the visible region at 551 nm, which is due to $^4A_2\,(F) \rightarrow {}^4T_1(F)$ transition [30]. This indicates tetrahedral geometry for the complex. The electronic spectrum of the Ni(II) complex shows an intense absorption band at 610 nm, which is due to the $^3T_1(F) \rightarrow {}^3T_1(P)$ transition, indicating tetrahedral geometry. For square planar Cu(II) complexes, the expected transitions are $^2B_{1g} \rightarrow {}^2A_1g$ and $^2B_{1g} \rightarrow {}^2Eg$ with the respective absorption bands [30]. In general, due to Jahn–Teller distortion, square planar Cu(II) complexes give a broad absorption band between 600 and 700 nm and the peak at 510 nm merges with the broad band. The electronic spectrum of Cu(II) complex (Fig. 2) exhibit a broad band centered at 683 nm indicating square planar geometry.



Scheme 1. Structure of Schiff base ligand, K(HL).

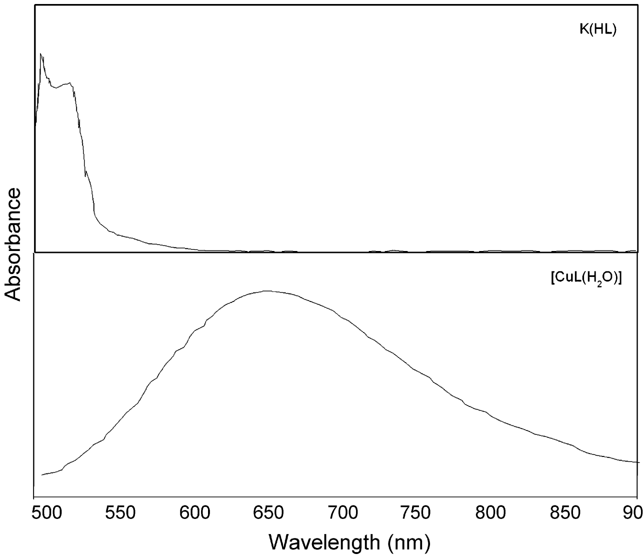


Fig. 2. Electronic spectra of K(HL) and [CuL(H_2O)] complex.

3.3. Magnetic properties

As a representative system, the magnetic behaviour of the Cu(II) complex is shown in Fig. 3, in which magnetization (M) is plotted against applied field (H). The linear fit of M *vs.* H values for all the systems under investigation indicate paramagnetic behaviour of the complexes [16,31]. The magnetic moments of the complexes determined at room temperature are given in Table 1. The magnetic moment of Co(II) complex is $3.97\mu_B$, which compares favorably with that of $4.1–4.8\mu_B$ expected for the Co(II) complexes with three unpaired electrons [32–34]. Thus, in agreement with the electronic spectral studies, Co(II) complex has tetrahedral geometry. The Ni(II) complex has a magnetic moment value of $2.83\mu_B$, which is close to that of $3.0–3.5\mu_B$ for the more distorted tetrahedral complexes [34–36]. The magnetic moment of Cu(II) complex is $1.85\mu_B$ indicating the presence of one unpaired electron [37–41]. The electronic spectral results clearly indicated square planar geometry for the Cu(II) system, which should contain one unpaired electron, where μ_{eff} value would be in the range $1.8–2.1\mu_B$.

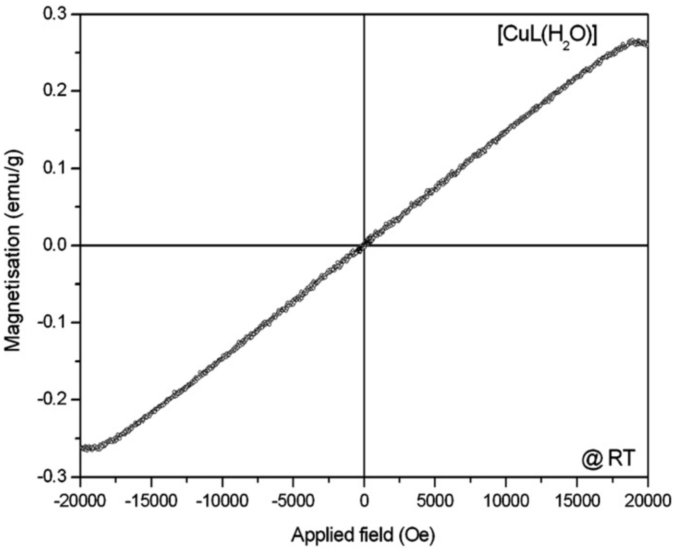


Fig. 3. Magnetization *vs*. field plot of [CuL(H_2O)] complex.

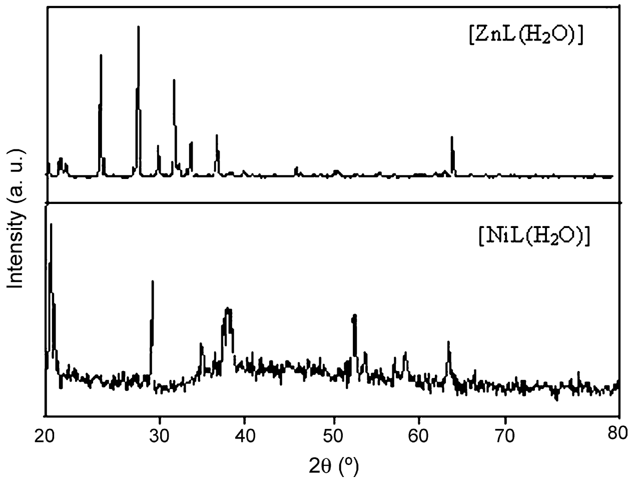


Fig. 4. XRD diffraction pattern of [NiL(H_2O)] and [ZnL(H_2O)] complexes.

3.4. Powder XRD

X-ray diffraction patterns of the complexes were recorded at $2\theta = 20–80°$ range and Ni(II) and Zn(II) complexes are shown in Fig. 4. The Co(II) and Cu(II) complexes did not show any peaks, indicating their amorphous nature, but the Ni(II) and Zn(II) complexes show sharp peaks. This shows that the above complexes are crystalline in nature [42]. The line broadening of the crystalline diffraction peak in the Zn(II) complex shows higher crystallinity than that of Ni(II) complex.

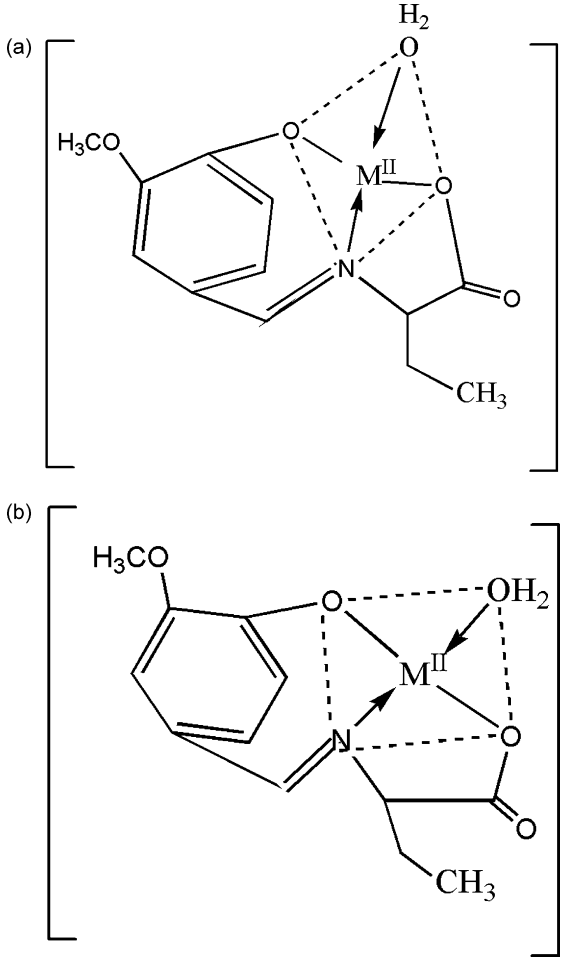


Fig. 5. (a). Proposed molecular structure of tetrahedral [ML(H_2O)] complexes, where M = Co(II), Ni(II) and Zn(II). (b). Proposed molecular structure of square planar [CuL(H_2O)] complex.

3.5. Antimicrobial activity

The antibacterial and antifungal activities of the ligand and its complexes are given in Table 3. The activity increases with

Table 3
Antibacterial and antifungal activities of the Schiff base ligand and its complexes

Compound	*S. aureus*	*E. coli*	*K. pneumaniae*	*P. vulgaris*	*P. aeruginosa*	*C. albicans*
K(HL)	0	0	+	+	+	+
[CoL(H_2O)]	0	0	0	0	++	0
[NiL(H_2O)]	0	0	0	0	0	+
[CuL(H_2O)]	+++	+	+++	+++	++	+
[ZnL(H_2O)]	0	0	0	0	0	0
Terbinafin[a]	−	−	−	−	−	++
Amikacin[a]	++	++	++	++	++	−

The test was done using the diffusion agar technique. Well diameter = 0.6 cm beyond control (+) (less active); inhibition values = 0.6–1.0 cm beyond control (++) (moderate active); inhibition values = 1.1–1.5 cm beyond control (+++) (highly active); not active (0).

[a] Standards.

increase in concentration of test solution containing the complexes [17]. The antibacterial results (Table 3) showed that the metal complexes are more active than their Schiff base ligand. Among the four complex, the Cu(II) complexes was found to be more active towards both gram positive and gram negative bacteria. The results of fungicidal screening (Table 3) showed that the Ni(II) and Cu(II) complexes are moderate in active than the Schiff base ligand, when compared to other complexes.

4. Conclusion

Co(II), Ni(II), Cu(II) and Zn(II) form complexes of composition [ML(H_2O)], where L is the Schiff base ligand, vanillidene-DL-α-aminobutyrate. The results clearly demonstrate that L is tridentate, Co(II), Ni(II) and Zn(II) complexes have tetrahedral geometry, while the Cu(II) complex has square planar geometry (Fig. 5(a) and (b)). The antimicrobial activities show that Cu(II) complex is more active than the other metal complexes.

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