

Investigations on some tridentate Schiff base metal complexes

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Abstract : The Schiff base complex species formed in cobalt(II), nickel(II), copper(II) and zinc(II)-vanillidene- β -alanine systems were synthesized and characterized. The analytical data show the composition of the metal complex to be MLX, where L is the Schiff base ligand and X is a water molecule. The results demonstrate the tridentate binding of the Schiff base ligand and cobalt(II) and nickel(II) complexes have tetrahedral geometries, while the copper(II) complex has square planar geometry. The ligand and the complexes were moderately active against gram-positive, gram-negative bacteria and fungi species.

Keywords : Schiff base, vanillin, β -alanine, electronic spectra, biological studies.

In continuation of our earlier work on the chemistry of Schiff base complexes^{1,2}, we report here the synthesis, characterization and antimicrobial activities of Schiff base metal complexes derived from vanillin and β -alanine with bivalent cobalt, nickel, copper and zinc ions.

Results and discussion

The analytical data of ligand and its complexes are given in Table 1. The complexes are stable, soluble in ethanol, methanol, dimethylformamide and dimethylsulfoxide. The analytical data show that the metal to ligand ratio is 1 : 1 in all the systems, with the general formulae [MLX], where M = cobalt(II), nickel(II), copper(II) and zinc(II), L = Schiff base ligand and X = water molecule.

Table 1. Analytical data of the ligand and its complexes

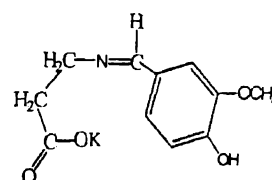
Ligand/ complex	Molecular formulae and color	Found (Calcd.) (%)			
		C	H	N	M
KH[L]	C ₁₁ H ₁₃ NO ₄ K Light yellow	50.56 (50.37)	4.63 (4.99)	5.36 (5.34)	14.96 (14.90)
[CoLX]	C ₁₁ H ₁₄ NO ₃ Co Light violet	44.59 (44.16)	4.31 (4.72)	4.32 (4.68)	19.32 (19.70)
[NiLX]	C ₁₁ H ₁₄ NO ₃ Ni Pale green	44.35 (44.20)	4.40 (4.72)	4.70 (4.69)	19.70 (19.63)
[CuLX]	C ₁₁ H ₁₄ NO ₃ Cu Bluish green	43.27 (43.49)	4.32 (4.65)	4.53 (4.61)	20.79 (20.92)
[ZnLX]	C ₁₁ H ₁₄ NO ₃ Zn Colorless	43.57 (43.23)	4.39 (4.62)	4.41 (4.58)	21.56 (21.39)

Conductivity measurements :

The molar conductance values of complexes measured in DMF at the concentration of 10⁻³ M solutions are found to be 21.77, 22.07, 21.52 and 23.56 Ω^{-1} cm² mol⁻¹ respectively for the cobalt(II), nickel(II), copper(II) and zinc(II) complexes. The low conductance values indicate the non-electrolytic nature of the metal complexes³.

IR spectra :

The intense band at 1651 cm⁻¹ for the Schiff base ligand can be assigned to the ν (C-N) azomethine stretching. On complexation, this band was found to shift to lower frequency



in the 1636–1645 cm⁻¹ range indicating the coordination of the azomethine nitrogen atom to the central metal ion⁴. The asymmetric carboxyl stretching ν_{as} (COO) is shifted to higher frequency in the 1575–1581 cm⁻¹ range and the symmetric carboxyl stretching ν_{s} (COO) is shifted to lower frequency in the 1341–1356 cm⁻¹ range, indicating the linkage between the metal ion and carboxylato oxygen atom. The ν (C-O) phenolic band shifts in the complexes to higher frequency in the 1232–1235 cm⁻¹ range indicating the coordination of the phenolic oxygen atom with the metal ion⁴. The spectra of the complexes show a broad band in the 3319–3351 cm⁻¹, which can be attributed to the stretching vibration of the O-H group⁴. This indicates that a water molecule occupies in the fourth

position. In the complexes, weak bands in the 525–541 and 429–457 cm^{-1} range may be attributed to $\nu(\text{M}-\text{N})$ and $\nu(\text{M}-\text{O})$ stretching⁴. From the IR results it may be concluded that the Schiff base ligand is tridentate and coordinates the central metal ion through the phenolic oxygen, azomethine nitrogen and carboxylato oxygen atoms.

Electronic spectra :

The Schiff base ligand shows a broad band at 321 nm, which is assigned to $\pi-\pi^*$ transition of the $\text{C}=\text{N}$ chromophore. On complexation this band was shifted to lower wavelength region, suggesting the coordination of azomethine nitrogen with the metal ion⁵. Cobalt(II) complex shows only one absorption band in the visible region at 625 nm, which is due to ${}^4\text{A}_2(\text{F}) \rightarrow {}^4\text{T}_1(\text{F})$ transition⁵. This indicates tetrahedral geometry for the cobalt(II) complex. The electronic spectrum of the nickel(II) complex shows an intense absorption band at 552 nm, which is due to the ${}^3\text{T}_1(\text{F}) \rightarrow {}^3\text{T}_1(\text{P})$ transition. This indicates tetrahedral geometry for the nickel(II) complex. The copper(II) ion with d^9 configuration in a complex can be either distorted octahedral or tetrahedral or square planar. For square planar copper(II) complexes, the expected transitions are ${}^2\text{B}_{1g} \rightarrow {}^2\text{A}_{1g}$ and ${}^2\text{B}_{1g} \rightarrow {}^2\text{E}_g$ with the respective absorption at 510 and 640 nm⁵. In general, due to Jahn-Teller distortions, square planar copper(II) complexes give a broad absorption band between 600 and 700 nm and the peak at 510 nm merges with the broad band. The λ_{max} value of 602 nm for the present copper(II) complex indicates square planar geometry.

Table 2. Antimicrobial activity of the ligand and its complexes

Complex	<i>Pseudomonas aeruginosa</i>	<i>Bacillus cirroflagellosus</i>	<i>Penicillium notatum</i>	<i>Aspergillus niger</i>
KH[L]	+	+	+	+
[CoLX]	+	+	-	-
[NiLX]	+	+	-	-
[CuLX]	+	+	-	+
[ZnLX]	-	+	+	-

*(-) No inhibition zone = inactive; 1–5 mm (+) = less active.

Magnetic measurements :

The magnetic behaviour of the cobalt(II), nickel(II) and copper(II) complexes were measured using vibrating sample magnetometer, in which magnetisation (M) is plotted against applied field (H). A hysteresis loop was obtained at room

temperature for copper(II) and nickel(II) complexes. This indicates ferromagnetic behaviour⁶. But for the copper(II) complex a straight line was obtained instead of hysteresis loop indicating paramagnetic behaviour^{6,7}.

Antimicrobial activity :

The results of antibacterial and antifungal activities are given in Table 2. In the present study the Schiff base ligand was found to be moderately active against the gram-positive, gram-negative bacteria and fungi species. Antibacterial results show that the ligand and the complexes are moderately active against *Pseudomonas aeruginosa* and *Bacillus cirroflagellosus* bacteria species. Antifungal studies show that copper(II) and zinc(II) complexes are active against *Aspergillus niger* and *Penicillium notatum* respectively^{8,9}, while the other complexes are inactive against both the bacteria and fungi species.

Experimental

All the chemicals used were of A.R. grade. β -Alanine was obtained from Fluka, vanillin was obtained from Sisco and metal(II) salts were purchased from Merck. All other experimental details were described elsewhere^{2,9}.

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