

Coordination of Cobalt(II), Nickel(II) and Copper(II) with Schiff bases derived from Pyridine-2-Carboxaldehyde and Amino acids

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Abstract: New complexes of Co(II), Ni(II) and Cu(II) with Schiff bases obtained by condensation of pyridine-2-carboxaldehyde and L-Histidine, L-Valine have been synthesized and characterized by various physico-chemical techniques. The complexes have been found to possess 1:2(M:L) stoichiometry. The electronic spectral data and magnetic moment measurement suggest octahedral geometry of the complexes. TGA studies showed absence of water molecules in all complexes.

Key words: amino acids, metal(II) ions, pyridine-2-carboxaldehyde, Schiff bases, spectra.

1. INTRODUCTION

Schiff bases are the condensation product of an amino compound with an active carbonyl compound. Schiff bases are considered as very important class of organic ligands which have wide application in many biological aspects[1]. In azomethine derivatives, the C=N linkage is essential for biological activity, several azomethines were reported to possess remarkable antibacterial, antifungal, anticancer and diuretic activities[2,3]. Schiff bases and their complexes were recently found to have significant antitumor and biological activity[4]. amino acid-based Schiff bases are very effective metal chelators and their metal complexes are models for a number of important biological systems[5]. During the last decade, the coordination chemistry of Schiff bases derived from 2-pyridine carboxaldehyde has received much attention[6]. The Schiff base complexes of pyridine-2-carboxaldehyde and its derivatives have been reported as high superoxide dismutase activities[7] and some of them have been found to be good herbicides used for the protection of plants[8].

A literature survey revealed that the Schiff base complexes formed by pyridine-2-carboxaldehyde in solution state have been studied. The present study deals with the structural aspects of some Ni(II), Co(II) and Cu(II) complexes with Schiff base derived from pyridine-2-carboxaldehyde and amino acids.

2.0 EXPERIMENTAL

2.1 Preparation of Schiff bases

Condensation between aldehydes and amino acids is realized in different reaction conditions and in different solvents. The presence of dehydrating agents normally favours the formation of Schiff bases. The water produced in the reaction can also be removed by using some solvents. Ethanol at room temperature or in refluxing condition is also a valuable solvent for the preparation of Schiff bases [9]. The Schiff bases were prepared by stirring ethanolic solution of amino acids with ethanolic solution of pyridine-2- carboxaldehyde in 1:1 molar ratio and mixtures were refluxed for 2 hr. followed by cooling to room temperature. The crystals were filtered and washed with ethanol.

2.2 Preparation of metal complexes

Ligands were dissolved in absolute ethanol and ethanolic solutions of metal salts were mixed dropwise in 1:1 ratio. The mixture was refluxed for 2 hr. and left to cool to room temperature. The products formed were filtered, washed with ethanol & ether. The samples were dried in vacuum desiccators over anhydrous calcium chloride.

2.3 Material and methodology

The metal chlorides used were of analytical grade. The pyridine-2-carboxaldehyde and amino acids were procured from Aldrich and were used as received. The stoichiometric analysis(C, H, N) were performed using Elementar vario E1 III (Germany) model. Metal contents were estimated on an AA-640-13 Shimadzu flame atomic absorption spectrophotometer in solutions prepared by decomposing the complex in hot concentrated HNO₃. I.R. spectra were recorded on Perkin-Elmer FT-IR spectrophotometer spectrum 2000 in KBr and polyethylene pellets. The molar conductances at 10³ molar dilutions were measured by Elico-conductometer Bridge. The magnetic susceptibility measurement were carried out at room temperature in powder form on vibrating sample magnetometer PAR155 with 5000G-field strength, using Co[Hg(SCN)₄] as the calibrant (magnetic susceptibility $\approx 1.64 \times 10^{-5} \text{ cm}^3 \text{ g}^{-1}$) determined by Gouy balance using copper sulphate as standard material. Electronic spectra were recorded on Beckman DU-64 spectrophotometer with quartz cells of 1 cm path length.

3.0 RESULT AND DISCUSSION

The metal complexes were solid and non-hygroscopic. The empirical composition of the complexes has been confirmed on the basis of analytical data (Table-1). The molar conductance values at room temperature and 10⁻³ M dilution in DMSO showed that all complexes are non-electrolytic in nature.

The vibrational spectral data of the ligands exhibit the characteristic C=N bands in 1630-1646 cm⁻¹ region, while the complexes C=N band were observed in 1628-1638 cm⁻¹ region. The C=N stretching frequency is generally shifted to a lower frequency, indicating a decrease in the C=N bond due to the coordinate bond of the metal with the imine nitrogen lone pair[10,11]. As for as the coordination of the carboxylate ion is concerned the information is drawn from the position of asymmetric and symmetric COO⁻ frequencies occurring in the range of 1590-1515 and 1390-1330 cm⁻¹ respectively in the spectrum of the complexes[12]. This is clear indication of the involvement of the carboxylate ion in the coordination.

The presence of very sharp band in the range 610-530 cm⁻¹ indicated the formation of M-N bond involving N atom of pyridine ring [13]. In this way ligands are behaving in tridentate manner coordinating through carboxylate ion, N atom of pyridine ring and N atom of azomethine group.

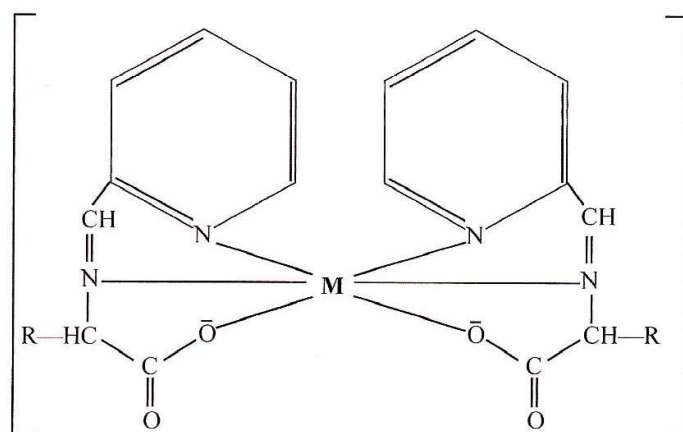
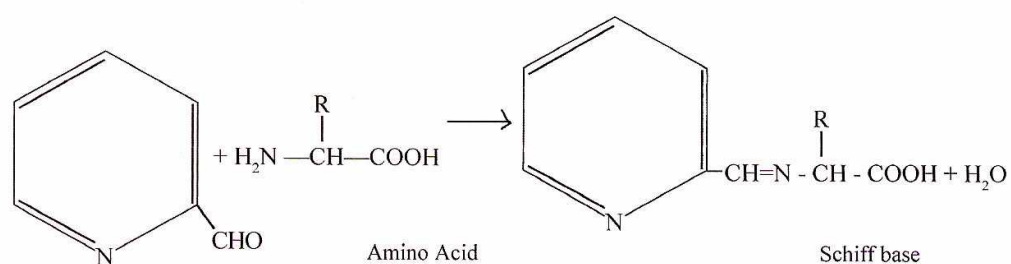
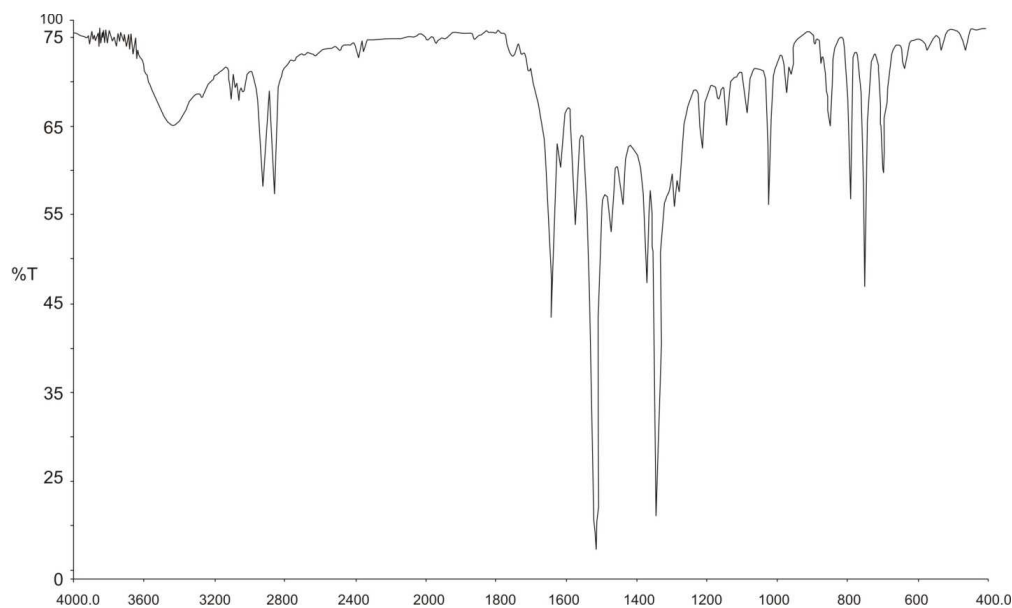
The electronic spectra of the Ni(II) complexes give bands in the range of 13880-13999 cm⁻¹, 16000-16500 cm⁻¹ and 22152-22700 cm⁻¹. The bands are assigned to the transition ${}^3A_{2g} \rightarrow {}^3T_{2g}$, ${}^3A_{2g} \rightarrow {}^3T_{1g}$ and ${}^3A_{2g} \rightarrow {}^3T_{1g}$ (P) respectively, suggesting that the Ni(II) complexes are six coordinated and probably octahedral geometry[13,14]. The spectral data shows bands in the range 25400-25500 cm⁻¹ which may be attributed to ligands to metal charge transfer. The complexes have magnetic moment in the range of 2.90-3.20 B.M. which

corresponding the magnetic moment of two unpaired electrons[14]. This also supports of octahedral geometry of the nickel complexes. The Co(II) complexes give bands in the range of 13000-13562, 16450-16700 and 21273-22500 cm^{-1} . These bands are assigned to the transitions ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$, ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ and ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(P)$ respectively, suggesting that there are octahedral geometry around Co(II) ions[13,14,15]. The spectra show also a band in the range 268990-27560 cm^{-1} which may be attributed to ligands to metal charge transfer. The magnetic susceptibility measurement, found to be range 4.30-5.20 B.M. which is normal range of octahedral Co(II) complexes indicating octahedral geometry[13].

The electronic spectra of the Cu(II) complexes give band in the range of 16200-16500 cm^{-1} . The 2E_g and ${}^2T_{2g}$ states of the octahedral Cu(II) ion d^9 split under the influence of the tetragonal distortion and the distortion can therefore be such as to facilitate the three transitions ${}^2B_{1g} \rightarrow {}^2B_{2g}$, ${}^2B_{1g} \rightarrow {}^2E_g$ and ${}^2B_{1g} \rightarrow {}^2A_{1g}$ which remain unresolved in the spectra (13,14,15). The magnetic moment of complexes was found to be in the range 1.70-1.90 B.M. which is normal range of octahedral Cu (II) complexes [16].

Table1:

S. No	Name & Empirical Formula of the Complexes	Colour	M.P. (in $^{\circ}\text{C}$)	Elemental Analyses				Magnetic moment in B.M.
				% of C	% of H	% of N	% of M	
1	Pyridine-2-carboxaldehyde-L-Histidine Ni(II) ($\text{C}_{11}\text{H}_{13}\text{N}_2\text{O}_2$) ₂ Ni(II)	Green	170	53.073 (52.872)	4.955 (4.038)	21.000 (20.560)	11.273 (10.778)	2.90
2	Pyridine-2-carboxaldehyde-L-ValineNi(II) ($\text{C}_{11}\text{H}_{13}\text{N}_2\text{O}_2$) ₂ Ni(II)	Yellow	200	57.432 (56.324)	5.985 (4.547)	12.050 (11.947)	12.985 (12.525)	3.20
3	Pyridine-2-carboxaldehyde-L-HistidineCo(II) ($\text{C}_{12}\text{H}_{11}\text{N}_4\text{O}_2$) ₂ Co(II)	Light Yellow	225	53.775 (52.850)	4.525 (4.037)	21.713 (20.553)	11.450 (10.814)	4.80
4	Pyridine-2-carboxaldehyde-L-ValineCo(II) ($\text{C}_{11}\text{H}_{13}\text{N}_2\text{O}_2$) ₂ Co(II)	Pale Yellow	195	57.271 (56.298)	5.950 (5.544)	12.426 (11.942)	13.070 (12.566)	5.20
5	Pyridine-2-Carboxaldehyde-L-HistidineCu(II) ($\text{C}_{12}\text{H}_{11}\text{N}_4\text{O}_2$) ₂ Cu(II)	Light Blue	205	53.650 (52.406)	4.505 (4.003)	21.890 (20.380)	12.700 (11.560)	1.70
6	Pyridine-2-carboxaldehyde-L-ValineCu(II) ($\text{C}_{11}\text{H}_{13}\text{N}_2\text{O}_2$) ₂ Cu(II)	Dark Brown	175	56.213 (55.749)	5.950 (5.490)	12.273 (11.825)	14.580 (13.419)	1.76



Schiff base complex $M = \text{Co(II)}, \text{Ni(II)}, \text{Cu(II)}$
 R - Remaining part of amino acid

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