

Co(II), Ni(II), Cu(II) And Cr(III) Complexes Of Heterocyclic Schiff Base Ligand: Synthesis, Spectroscopic And Thermal Study

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Abstract: In the present study the Schiff base ligand was synthesized by condensing 1-(3-chloro-6-hydroxy-2-methyl)ethanone with chlorobenzaldehyde. From this ligand new transition metal complexes of Co(II), Ni(II), Cu(II) and Cr(III) with a Schiff base ligand 3-(3-chloro-6-hydroxy-2-methylphenyl)-5-(4-chlorophenyl)-4,5-dihydro-1H-pyrazol-1-yl(pyridin-4-yl)methanone were synthesized and characterized on the basis of elemental, ^1H NMR, IR, Mass, Electronic Spectra and molar conductance data. The thermal data has been investigated to observed degradation pattern and kinetic parameters Entropy Change (ΔS), Free Energy Change (ΔF) and Frequency Factor (Z) were calculated using Freeman-Carol and Sharp-Wentworth method.

Keywords: Pyrazoline, Metal complexes, IR, Electronic Spectra, Freeman-Carol.

1. Introduction

In the recent years there has been considerable interest in the chemistry of transition metal complexes of Schiff base because Metal complexes of Schiff base play an important role in the development of coordination chemistry. These Schiff bases generally are a sulphur and nitrogen analogue of aldehyde and ketone having a good ability to form metal complexes. Many such Schiff bases ligands have been synthesized by condensing primary and secondary amines with carbonyl compound [1-4]. These compounds have wide application in food industry, dye industry, analytical chemistry, agrochemical, catalysis and biological activities [5-6]. A large number of reports are available on the chemistry and the biological activities of transition metal complexes containing O, N and O, S donor atom. From the survey of literature it appears that a heterocyclic Schiff base has been extensively used as a biological active complexing agent [7]. By considering the above fact in mind newly ligand by condensing chalcone with isoniazide and its metal complexes Co(II), Ni(II), Cu(II) and Cr(III) has been synthesized and characterized by IR, ^1H NMR, Mass, molar conductance and thermal analysis.

2. Experimental:

2.1. Material Reagents and Method:

All chemicals and solvent used were of analytical grade and of the highest purity available. They include isoniazide, p-chloro benzaldehyde, $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$, $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$, $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$, $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, methanol, ethanol etc. IR spectra measurement was recorded using Perkin Elmer-Spectrum RX-IFTIR model in nujol in the region 4000-400 cm^{-1} . ^1H -NMR data of ligand was recorded by using Bruker FT NMR spectrometer (400 MHz) using DMSO- d_6 as solvent and TMS as internal standard. The FAB-Mass spectra of ligand and complexes were recorded with Thermo

Scientific TSQ 8000 Gas Chromatograph-Mass Spectrometer. The thermal analysis was performed with a Perkin Elmer (TGS-2 model) thermal analyzer at a heating rate of $10^\circ\text{C min}^{-1}$ in the temperature range 40-800 $^\circ\text{C}$.

2.2. Synthesis of Organic Compounds:

2.2.1. Synthesis of chalcone-

A ketone 1-(3-chloro-6-hydroxy-2-methylphenyl)ethanone (0.01 mol) and chlorobenzaldehyde (0.01 mol) was dissolved in a hot ethanol. To this add NaOH (40%) solution dropwise and stirred. The reaction mixture was heated for 5-10 min and by keeping overnight to this mixture adds dil. HCl, the residue obtained was filtered off and recrystallized [8].

2.2.2. Synthesis of Schiff base ligand-

The chalcone 1-(3-chloro-6-hydroxy-2-methylphenyl)-3-(4-chlorophenyl)prop-2-en-1-one (0.01 mol) and isoniazide (0.01 mol) was dissolved in ethanolic solution. This mixture was refluxed for about 2 hours and the progress of reaction in determined by TLC in solvent medium 9:1 chloroform methanol system. The reaction mixture was added into the ice cold water and the residue obtained dried and further recrystallized by using diethyl ether [9-10].

Yield: 72 %; M.P. 169 $^\circ\text{C}$; Colour: Brown.

Anal. Calc./Obs for $\text{C}_{22}\text{H}_{17}\text{Cl}_2\text{N}_3\text{O}_2$: C, 61.98/61.90; H, 4.02/3.98; N, 9.86/9.87; Cl, 16.63/16.60 %.

IR (KBr, cm^{-1}): 3365, $\nu(\text{OH})$; 1612, $\nu(\text{C}=\text{N})$, 1640, $\nu(\text{C}=\text{O})$, 1415, $\nu(\text{C}-\text{O})$.

^1H -NMR (DMSO- d_6 , δ (ppm): 11.38 (s, 1H, OH); 7.49-8.00 (m, 10H, Ar-proton); 2.22 (s, 3H, CH_3); 3.91 (dd, 1H, pyrazoline proton); 4.19 (dd, 1H, pyrazoline proton); 4.61 (dd, 1H, pyrazoline proton).

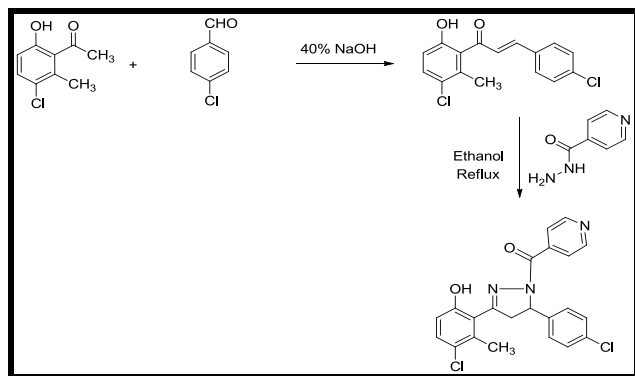


Fig 1: Reaction Scheme

2.3 Synthesis of metal complexes-

All the metal complexes were prepared by adding hot ethanolic solution of metal salt (II) (III) (0.01 mol) to a hot ethanolic solution of ligand. The reaction mixture was refluxed for 8-10 hours, residue obtained filtered and left for drying. Crystallization of the complexes was done with methanol.

2.3.1 [Co(L)OAc].2H₂O

Colour- Green solid, M.P. > 300⁰C;

Anal. Calc. /Obs for C₂₂H₁₇Cl₂N₃O₂: M, 10.17/**10.21**; C, 49.76/**49.70**; H, 4.00/**3.98**; N, 7.25/**7.32**; Cl, 12.24/**12.20**%.

Molar Conductivity $\Lambda(\Omega^{-1}\text{cm}^2\text{mol}^{-1})$: 7.92

IR (KBr, cm⁻¹): 1590, $\nu(\text{C}=\text{N})$; 1625, $\nu(\text{C}=\text{O})$; 1429, $\nu(\text{C}-\text{O})$; 491, $\nu(\text{M}-\text{O})$; 449, $\nu(\text{M}-\text{N})$.

2.3.2 [Ni(L)OAc].H₂O

Colour-Red solid, M.P. > 300⁰C;

Anal. Calc. /Obs for C₂₂H₁₇Cl₂N₃O₂: M, 10.46/**10.52**; C, 51.38/**51.37**; H, 3.77/**3.81**; N, 7.49/**7.60**; Cl, 12.64/**12.60**%.

Molar Conductivity $\Lambda(\Omega^{-1}\text{cm}^2\text{mol}^{-1})$: 7.14

IR (KBr, cm⁻¹): 1585, $\nu(\text{C}=\text{N})$, 1631, $\nu(\text{C}=\text{O})$, 1427, $\nu(\text{C}-\text{O})$; 489, $\nu(\text{M}-\text{O})$; 453, $\nu(\text{M}-\text{N})$.

2.3.3 [Cu(L)OAc].H₂O

Colour-Green, M.P. > 300⁰C;

Anal. Calc. /Obs for C₂₂H₁₇Cl₂N₃O₂: M, 11.23/**11.22**; C, 50.94/**51.02**; H, 3.74/**3.70**; N, 7.43/**7.40**; Cl, 12.53/**12.57**%.

Molar Conductivity $\Lambda(\Omega^{-1}\text{cm}^2\text{mol}^{-1})$: 8.24

IR (KBr, cm⁻¹): 1593, $\nu(\text{C}=\text{N})$, 1622, $\nu(\text{C}=\text{O})$, 1433, $\nu(\text{C}-\text{O})$; 479, $\nu(\text{M}-\text{O})$; 452, $\nu(\text{M}-\text{N})$.

2.3.4 [Cr(L)Cl₂(H₂O)].2H₂O

Colour-Brown, M.P. > 300⁰C;

Anal. Calc./Obs. for C₂₂H₁₇Cl₂N₃O₂: M, 8.63/**8.65**; C, 43.88/**43.90**; H, 3.68/**3.64**; N, 6.98/**6.91**; Cl, 23.55/**23.50**%.

Molar Conductivity $\Lambda(\Omega^{-1}\text{cm}^2\text{mol}^{-1})$: 9.10

IR (KBr, cm⁻¹): 1597, $\nu(\text{C}=\text{N})$, 1619, $\nu(\text{C}=\text{O})$, 1431, $\nu(\text{C}-\text{O})$; 487, $\nu(\text{M}-\text{O})$; 455, $\nu(\text{M}-\text{N})$.

3. Result and Discussion

The complexes are insoluble in organic solvent like methanol, ethanol, acetone etc. but are soluble in coordinating solvent like DMF, DMSO. The analytical data are in good agreement with the proposed structure of schiff base ligand as well as

metal complexes. The lower values of molar conductivity indicate that all complexes are act as non-electrolyte.

3.1 Infrared Spectra

FTIR Spectra gives valuable information regarding the nature of binding mode and the functional group attached to metal ion. Hence to identify the binding mode of ligand with metal complexes IR spectrum of ligand has been compared with metal complexes (in range between 400-4000 cm⁻¹). The spectrum of ligand shows broad peak in the region 3365 cm⁻¹ which may be due to $\nu(\text{O}-\text{H})$ and the broadening of the peak is due to intermolecular H-bonding between OH and azomethine group. While in all metal complexes this peak totally disappeared confirms the participation of phenolic oxygen in coordination mode. In addition, the IR spectrum of the ligand revealed a sharp peak at 1415 cm⁻¹ belonging to phenolic C-O stretching which is slightly shifted to higher frequency range 1427-1433 cm⁻¹ after complexation in all metal complexes. The azomethine C=N stretching frequency of free ligand was appeared at 1612 cm⁻¹ while in complexes it was shifted to lower frequency in range 1585-1597 cm⁻¹ due to the coordination of nitrogen atom to metallic ion. This lowering of wave number is due to decrease in electron density of the azomethine group. Two additional peaks which were absent in ligand present in the IR spectra of complexes in the range 487-491 & 449-455 cm⁻¹ belonging to (M-O) & (M-N) stretching [11-12].

3.2 Mass Spectra

The mass spectra of Cu (II), Ni (II), Co (II), VO (IV), Fe (III) and Cr (III) complexes with Schiff base ligand have been recorded. The data obtained are in good agreement with the proposed molecular formula for ligand and all metal complexes. The mass spectrum of LH shows well-defined peak at m/z 425 (M⁺), while for the complexes it appeared at m/z= 575 [Co(L)OAc].2H₂O, m/z=559 [Ni(L)H₂O], m/z=552 [Cu(L)H₂O], m/z= 602 [Cr(L)Cl(H₂O)₂].

3.3 Electronic Spectra

The electronic spectrum of Co(II) complex shows band in the region 26455 cm⁻¹ and 19646 cm⁻¹ ascribe to INCT and ¹A_{1g} → ¹B_{1g} transition. The values are matched to the square planar geometry for Co(II) complex. The magnetic moment values i.e. 3.84 also suggest the square planar geometry for Co(II) complex. In the electronic spectrum of Ni(II) complex three band are appeared at 19047 cm⁻¹, 16949 cm⁻¹ and 14084 cm⁻¹ for the transition ¹A_{1g}-¹A_{2g}, ¹A_{1g}-¹B_{2g} and ¹A_{1g}-¹E_g respectively. Data matched to the square planar geometry for Ni(II) complex which was supported by diamagnetic magnetic measurement. The electronic spectrum of Cu(II) complex shows transition bands at 33003 cm⁻¹ and at 18450 cm⁻¹ ascribe to charge transfer and ²B_{1g}-²A_{1g} transition. This transition indicates square planar geometry for Cu(II) complex. Octahedral geometry suggested for Cr(III) complex due to appearance of bands at 19801 cm⁻¹ and at 24271 cm⁻¹ for the ⁴A_{2g}(F)-⁴T_{1g}(F) and ⁴T_{2g}(F)-⁴T_{1g}(F) transition [13-15].

Table 1 Electronic absorption spectral and magnetic moment data of complexes.

Compound	Maximum Absorption Wavelength (cm ⁻¹)	Band Assignment	Magnetic Moment μ(B.M.)	Geometry
[Co(L)OAc].2H ₂ O	26455 19646	INCT ¹ A _{1g} → ¹ B _{1g}	3.84	Square Planar
[Ni(L)OAc].H ₂ O	19047 16949	¹ A _{1g} - ¹ A _{2g} ¹ A _{1g} - ¹ B _{2g}	0	Square Planar
[Cu(L)OAc].H ₂ O	14084 33003	¹ A _{1g} - ¹ E _g Charge Transfer	1.70	Square Planar
[Cr(L)Cl ₂ (H ₂ O)].H ₂ O	18450 19801 24271	² B _{1g} - ² A _{1g} ⁴ A _{2g} (F)- ⁴ T _{1g} (F) ⁴ T _{2g} (F)- ⁴ T _{1g} (F)	3.52	Octahedral

Table 2 : Thermal decomposition data of ligand and its complexes

Complexes	Half Decom. Temp (°C)	Ea(kJ/mole)		Z (S ⁻¹)	ΔS ^o (J/mole/K)	ΔF (kJ/mol)	(n)
		FC	SW				
[Co(L)OAc].2H ₂ O	480	19.77	19.70	152.14	-147.85	66.05	0.98
[Ni(L)OAc].H ₂ O	370	20.96	20.42	180.20	-147.37	67.04	0.96
[Cu(L)OAc].H ₂ O	410	20.25	20.29	210.10	-115.17	38.07	0.91
[Cr(L)Cl ₂ (H ₂ O)].2H ₂ O	470	15.50	15.53	140.00	-103.41	33.92	0.99

3.4 Thermal Analysis

Thermal analysis of metal complexes is an important method as it provides useful information about thermal stability of complexes as well as coordination ability of water whether it is inside the coordination sphere or outside. So thermal data have been analyzed by for all metal complexes. The half decomposition temperature, activation energy, frequency factor, apparent entropy of activation and free energy change of complexes were calculated by employing Freeman Carroll and Sharp Wentworth method [16-17]. The TGA thermal curves of complexes were obtained in nitrogen environment with heating rate 10^o C min⁻¹ are given in fig. 2 while the kinetic parameters are assigned in Table. All the complexes are stable upto 40^o C and further decomposes in three stages. In Co(II) complexes weight loss Obs./Calc: 6.28/6.21 upto 120^oC observed for the removal of two lattice water molecule. There is no weight loss further upto 220^oC indicates the absence of coordinate water molecule. The further loss above 360^oC observed for decomposition of coordinate part of ligand. It has been

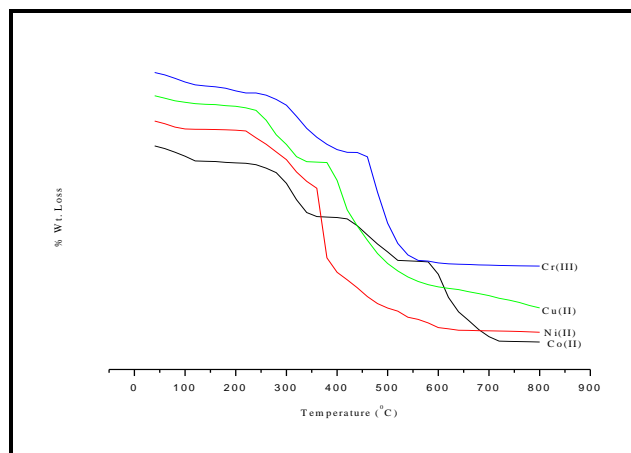


Fig 2 Thermal graph of Co(II), Ni(II), Cu(II) and Cr(III) complexes

observed that complexes are not decomposed completely and finally converted into their respective metal oxides. In Ni(II) and Cu(II) complexes decomposition of one lattice water molecule respectively observed at 120^oC with a mass loss of Obs./Calc:3.56/3.20 & 3.27/3.18. Further decomposition above 220^oC indicates the loss of coordinate part of ligand. For Cr(III) complex weight loss at 120^oC Obs./Calc:5.75/5.95 and at 220^oC Obs./Calc:3.24/2.99 shows the removal of two lattice and one coordinate water molecule. Further loss above 420^oC observed for the decomposition of coordinate part of ligand and finally formation of metal oxides occurs.

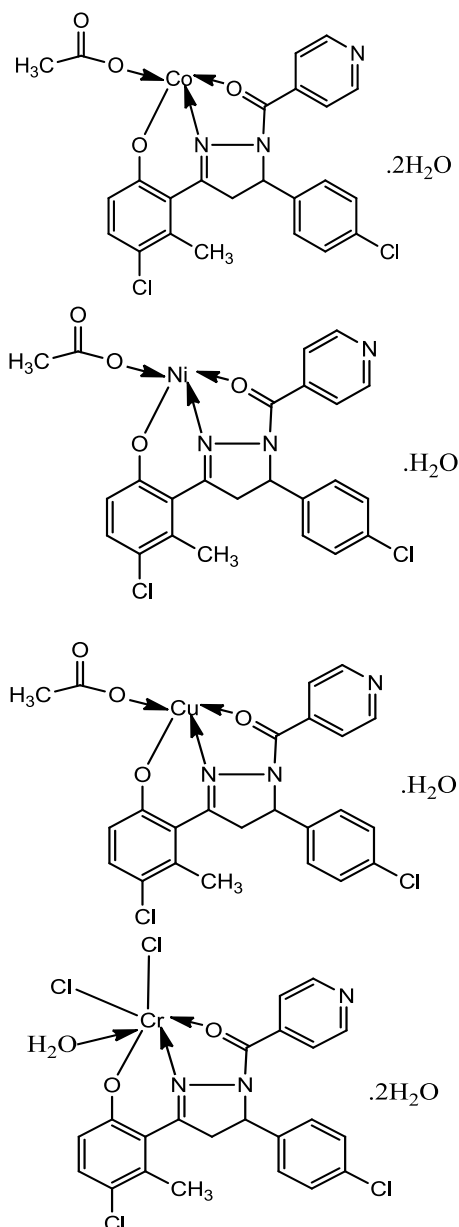


Fig 3: Probable Structures of Co(II), Ni(II), Cu(II) and Cr(III) complexes

Conclusion

The metal complexes were synthesized by condensing Schiff base ligand with respective metal salts and characterized by different spectral techniques. The spectral data indicates that ligand act as monobasic tridentate towards all metal ion. Lower values of molar conductivity indicate that all complexes are act non-electrolyte. The activation energy calculated by the Freeman-Carroll and Sharp-Wentworth methods are in good agreement with each other. Thermodynamic parameters have been calculated on the basis of thermal activation energy and values are given in Table 2. The thermal stability of the compounds can be correlated with the substituent group attached to the ligands.

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