Structural Analysis of Newly Synthesized NO Donor Schiff Base Complexes of Cu(II), Ni(II), Co(II) and Fe(III) Metal Ions by Conventional Method

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Abstracts: Transition metal complexes of Cu(II), Ni(II), Co(II) and Fe(III) Containing Bidentate Schiff base, derived from the condensation of salicylaldehyde and 2-aminophenol were synthesized and characterized by IR, UV- Vis., and some physical measurements. IR spectral studies show the binding sites of the Schiff base ligand with the metal ion. Molar conductance data and magnetic susceptibility measurements give evidence for monomeric and electrolytic nature of the complexes. Structural studies showed that Cu(II), Ni(II) and Co(II) ion complexes are tetrahedral and Fe(III) ion complex is octahedral.

Keywords: Transition Metal Complex, Bidentate Ligand, Schiff Base

1. Introduction

Schiff bases are condensation products of primary amines with carbonyl compounds and they were first reported by Hugo Schiff in 1864. These compounds containing a general formula $RHC=N-R'$ where R and R' are alkyl, aryl, cyclo alkyl or heterocyclic groups are also known as anils, imines or azomethines [1]. Because of the relative easiness of preparation, synthetic flexibility, and the special property of C=N group, Schiff bases are generally excellent chelating agents, especially when a functional group like -OH or -SH is present close to the azomethine group so as to form a five or six membered ring with the metal ion [2,3]. Schiff bases are well known for their biological applications as antibacterial, antifungal, anticancer and antiviral agents [4, 5]. Also, Schiff base metal complexes have been widely studied because they have industrial, antifungal, antibacterial, anticancer herbicidal applications, [6] antitubercular activities [7] and chelating abilities which give it attracted remarkable attention [8].

Recently, we studied few mixed ligand complexes containing heterocyclic amine as secondary ligands and few

Schiff base containing complexes [9-15]. In the present work, transition metal complexes of Cu(II), Ni(II), Co(II) and Fe(III) containing bidentate Schiff base, derived from the condensation of salicylaldehyde and 2-aminophenol were synthesized and characterized by conventional method.

2. Experimental

2.1. Reagents and Chemicals

All the reagents used were of analar or chemically pure grade. Solvents were purified and dried according to standard procedures.

2.2. Physical Measurements

The melting or decomposition temperatures of all the prepared metal complexes were observed in an electro thermal melting point apparatus model No.AZ6512. The SHERWOOD SCIENTIFIC Magnetic Susceptibility Balance was used for the present investigation. Infrared spectra as KBr disc were recorded in a SIMADZU FTIR-8400 (Japan) infrared spectrophotometer, from 4000-400 cm^{-1} . The absorbances of the complexes were recorded on SHIMADZU

Spectrophotometer.

3. Synthesis

3.1. Synthesis of Schiff Base 2-[(2-Hydroxy-Phenylimino)-Methyl]-Phenol, ($C_{13}H_{10}NO_2$)

The Schiff base was prepared by mixing salicylaldehyde in ethanol with ethanolic solution of 2-aminophenol. Salicylaldehyde (0.611 g, 5 mmol) in absolute ethanol (20 mL) was added to an ethanolic (30 mL) solution of 2-aminophenol (0.545 g, 5 mmol). An orange precipitate was observed. The precipitate was filtrated on a Buchner funnel and dried in a vacuum desiccator over anhydrous $CaCl_2$. The structure of the synthesized Schiff base is shown in Figure-1.

Figure 1. 2-[(2-Hydroxy-phenylimino)-methyl]-phenol.

3.2. Preparation of $[Cu(C_{13}H_{10}NO_2)_2]$

0.741 g (2 mmol) of $Cl_2CuO_8 \cdot 6H_2O$ was dissolved in 5 mL ethanol in a conical flask. 1.482g of Schiff base was taken in another small beaker and was dissolved in 10 ml ethanol. Then the solution was poured in the conical flask containing copper salt solution and stirred for 4 hours at ambient temperature and allowed to stand for half an hour. A green precipitate was observed. The precipitate was filtrated off on a Buchner funnel and dried in a vacuum desiccator over anhydrous $CaCl_2$.

3.3. Preparation of $[Ni(C_{13}H_{10}NO_2)_2]$

0.731 g (2 mmol) of $Cl_2NiO_8 \cdot 6H_2O$ was dissolved in 5 mL ethanol in a conical flask. 1.463g of Schiff base was taken in another small beaker and was dissolved in 10 ml ethanol. Then the solution was poured in the conical flask containing nickel salt solution and stirred for 4 hours at ambient temperature and allowed to stand for half an hour. A greenish yellow precipitate was observed. The precipitate was filtrated off on a Buchner funnel and dried in a vacuum desiccator over anhydrous $CaCl_2$.

3.4. Preparation of $[Fe(C_{13}H_{10}NO_2)_3]$

0.541 g (2 mmol) of $FeCl_3 \cdot 6H_2O$ was dissolved in 5 mL ethanol in a conical flask. 1.082g of Schiff base was taken in another small beaker and was dissolved in 10 ml ethanol. Then the solution was poured in the conical flask containing

iron salt solution and stirred for 4 hours at ambient temperature and allowed to stand for half an hour. A black precipitate was observed. The precipitate was filtrated off on a Buchner funnel and dried in a vacuum desiccator over anhydrous $CaCl_2$.

3.5. Preparation of $[Co(C_{13}H_{10}NO_2)_2]$

0.498g (2 mmol) of $Co(CH_3COO)_2 \cdot 4H_2O$ was dissolved in 5 mL ethanol in a conical flask. 0.996g of Schiff base was taken in another small beaker and was dissolved in 10 ml ethanol. Then the solution was poured in the conical flask containing cobalt salt solution and stirred for 4 hours at ambient temperature and allowed to stand for half an hour. A brown precipitate was observed. The precipitate was filtrated off on a Buchner funnel and dried in a vacuum desiccator over anhydrous $CaCl_2$.

4. Results and Discussion

All the complexes were characterized by elemental analysis, conductance measurements, magnetic moment and spectroscopic studies. The elemental analysis of C, H and N (Table-2) of the complexes are consistent with the proposed formula. The conductance (Table-1) values of the complexes reveal that the complexes are non-electrolytic in nature [16].

The spectral components of the complexes (Table-3) showed a strong absorption band at $(1580-1640) \text{ cm}^{-1}$ for $\nu(C=N)$ stretching. Band at $(3020-3165) \text{ cm}^{-1}$ due to aromatic $\nu(C-H)$ stretching. The Band at $(500-600) \text{ cm}^{-1}$ due to $\nu(M-N)$ stretching, which indicated the co-ordination through N atom to the metal. Band at $(460-500) \text{ cm}^{-1}$ due to $\nu(M-O)$ stretching, which indicated the complexation have taken place to the metal through the deprotonated O atom of phenolic OH moiety. A band at $(3400-3590) \text{ cm}^{-1}$ due to $\nu(O-H)$ stretching.

The UV-visible spectrum (Table-4) for the complexes shown absorbance at 286.50 nm (3.87), 334 nm (2.30), 452nm (3.01) and 415nm (3.03) for Cu(II), Ni(II), Fe(III), and Co(II) ion complexes respectively. The electronic spectra show bands in the region 200-400 nm due to charge transfer only [17]. The observed magnetic moment values of the complexes at ambient temperature are given in Table-3. The observed magnetic moment value of Cu(II) complex is 1.87 B.M. corresponding to one unpaired electron. It appears from the magnetic moment data of Cu(II) complex display paramagnetic behavior and hence, is of high spin tetrahedral complex [17]. The observed magnetic moment value of Ni(II) complex is 2.95 B.M. corresponding to two unpaired electron. It appears from the magnetic moment data of Ni(II) complex display paramagnetic behavior and hence, is of high spin tetrahedral complex [17]. The observed magnetic moment value of Fe(III) complex is 5.94 B.M. corresponding to five unpaired electrons. It appears from the magnetic moment data of Fe(III) complex display paramagnetic behavior and hence, is of high spin octahedral complex [17]. The magnetic moment value of Co(II) complex is 4.08 B.M. corresponding to three unpaired

electrons. It appears from the magnetic moment data of Co(II) complex display paramagnetic behavior and hence, is of high spin tetrahedral complex [17].

5. Conclusion

Here, M = Cu(II), Ni(II) and Co(II)

Figure 2. Tetrahedral structure of Cu(II), Ni(II) and Co(II) ion complexes.

Figure 3. Octahedral structure of Fe(III) complex.

On the basis of the elemental analysis, magnetic moment, conductance measurements, IR spectra, UV-visible spectra and other physical properties, the suggested structures of the Cu(II), Ni(II) and Co(II) ion complexes are tetrahedral and Fe(III) ion complex is octahedral in nature as shown in Fig.-2 and 3 respectively.

Table 1. Analytical data and physical properties of the complexes.

Complexes	Colour	Melting point or decomposition tem. ($\pm 5^\circ\text{C}$)	% Yield	Molar conductance ($\text{ohm}^{-2} \text{cm}^2 \text{mol}^{-1}$)
[Cu(C ₁₃ H ₁₀ NO ₂) ₂]	Green	280(d)	68	0.20
[Ni(C ₁₃ H ₁₀ NO ₂) ₂]	Greenish yellow	300 (above)	63	2.2
[Fe(C ₁₃ H ₁₀ NO ₂) ₃]	Black	300 (above)	64	6.8
[Co(C ₁₃ H ₁₀ NO ₂) ₂]	Brown	300 (above)	65	1.2

Where, d = decomposition.

Table 2. Elemental analysis data of the complexes.

Complexes	% Carbon		% Hydrogen		% Nitrogen	
	Calculated	Found	Calculated	Found	Calculated	Found
[Cu(C ₁₃ H ₁₀ NO ₂) ₂]	63.98	63.62	4.13	4.02	5.74	5.64
[Ni(C ₁₃ H ₁₀ NO ₂) ₂]	64.63	64.46	4.17	4.06	5.78	5.69
[Fe(C ₁₃ H ₁₀ NO ₂) ₃]	67.64	67.50	4.37	4.29	6.07	5.97
[Co(C ₁₃ H ₁₀ NO ₂) ₂]	64.60	64.47	4.17	4.05	5.79	5.67

Table 3. Selected infrared spectral bands of the complexes (as KBr disc).

Complexes	$\nu(\text{O-H})$, cm^{-1}	$\nu(\text{C}=\text{N})$, cm^{-1}	$\nu(\text{C-H})$ of aromatic cm^{-1}	$\nu(\text{M-O})$ cm^{-1}	$\nu(\text{M-N})$ cm^{-1}	μ_{eff} in B.M.
[Cu(C ₁₃ H ₁₀ NO ₂) ₂]	3437	1614	3058	487	538	1.87
[Ni(C ₁₃ H ₁₀ NO ₂) ₂]	3435	1620	3058	482	523	2.95
[Fe(C ₁₃ H ₁₀ NO ₂) ₃]	3437	1601	3018	478	532	5.94
[Co(C ₁₃ H ₁₀ NO ₂) ₂]	3436	1605	3058	492	516	4.08

Table 4. UV-visible spectral bands of the complexes in dimethyl sulfoxide (DMSO).

Complexes	λ_{max} (nm)	Absorbance
[Cu(C ₁₃ H ₁₀ NO ₂) ₂]	286	3.87
[Ni(C ₁₃ H ₁₀ NO ₂) ₂]	334	2.30
[Fe(C ₁₃ H ₁₀ NO ₂) ₃]	452	3.01
[Co(C ₁₃ H ₁₀ NO ₂) ₂]	415	3.03

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