



THERMAL TECHNIQUE AND AGRO-INDUSTRIAL APPLICATION OF CO(II), NI(II) AND CU(II) SCHIFF BASE COMPLEXES DERIVED FROM ETHYLENE DIAMINE

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Abstract:

The synthesized Schiff base metal complexes of Co(II), Ni(II) and Cu(II) with Schiff base derived from 2-hydroxy-5-methyl acetophenone and ethylene diamine have been prepared and characterized on the basis of Infrared, ^1H NMR, elemental analysis and thermogravimetric analysis. The Schiff base commonly coordinates through the oxygen atom of phenolic OH group and the nitrogen atom of azomethine group, which is confirmed by IR spectral data. Further conclusive evidence of the coordination of the Schiff bases with the metal ions was shown by the appearance of new bands due to $\nu(\text{M-N})$ and $\nu(\text{M-O})$ in the metal complexes. Thermal technical data shows that the first order kinetics in all complexes and thermodynamic activation parameters were also computed from the thermal data using Broido, Horowitz-Metzger and Freeman-Carroll method. Applications of Schiff base and its derivatives.

Keywords: Schiff base, Spectral, Thermal, Agro-industrial application.

Introduction

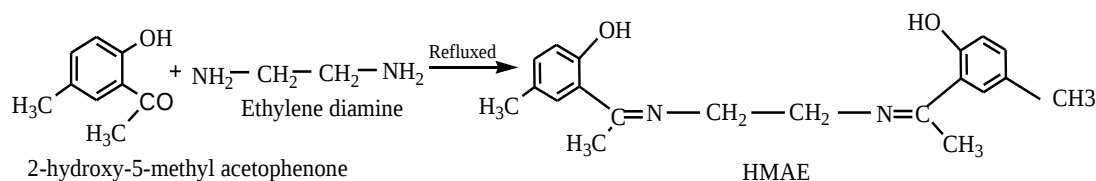
The Schiff bases and its complexes play a significant role in the area of coordination chemistry and applicable in engineering, applied chemistry. The common Schiff bases are crystalline solids, which are in basic nature in the area of engineering, applied engineering, bioinorganic, biotechnology and technical studies in chemistry. Coordination chemistry of Schiff bases possessing two different atoms capable of coordinating to metal ions has long been a subject of particular interest to both the synthetic and theoretical coordination chemist. Synthesis, spectroscopic, quantum, thermal and kinetics, antibacterial and antifungal studies: Novel Schiff base 5-methyl-3-5-bromosalicylidene amino-pyrazole and its transition metal complexes¹ Promising Schiff bases in antiviral drug design and discovery² Schiff bases as analytical tools: synthesis, chemo-sensor, and computational studies of 2-aminophenol Schiff bases³ A review of Schiff base-inorganic complexes and recent advances in their biomedical and catalytic attributes⁴ This study reports how to overcome the challenges experienced in achieving successful synthesized Schiff base via types of Schiff base (chiral and achiral), synthesis, nature of products, and its antibacterial applications⁵. The aim of present investigation is to synthesize transition metal complexes of Co(II), Ni(II) and Cu(II) ions with Schiff base derived from 2-hydroxy-5-methyl acetophenone and ethylene diamine and to study their thermal decomposition technique, pattern as well as to evaluate kinetic parameters by Broido, Horowitz-Metzger and Freeman-Carroll method. Agro-industrial application of Schiff base metal complexes.

Experimental

All the chemicals and solvents were of A.R. grade and used as received, 2-hydroxy-5-methyl acetophenone (HMA) and ethylene diamine was prepared by known methods⁶⁻⁸.

Synthesis of 2-Hydroxy-5-methyl acetophenone-N, N'-ethylenediimine (HMAE):

A hot ethanolic solution of ethylene diamine (0.05 mol) was added to an ethanolic solution of respective acetophenone (0.05 mol). The reaction mixture was refluxed in a water-bath for 3-4 h. The colour product was filtered and recrystallised. The purity of the ligand was checked by elemental analysis, m.p. and TLC. Yield 90%, m. p. 262°C



Scheme 1. Synthesis of HMAE

Table1. Analytical data of the Ligands.

Sr No	Ligand	Molecular Formula	Formula Weight	Color and nature	Elemental Analysis		
					C% found (Cal.)	H% Found (Cal.)	N% Found (Cal.)
1.	HMAE	C ₂₀ H ₂₄ N ₂ O ₂	324	Yellow Crystalline	70.38 (74.07)	07.10 (07.40)	08.14 (08.64)

Preparation of complexes:

All the metal complexes were prepared in a similar way by following method. To a hot solution of ligand HMAE (0.02M) in 25ml of ethanol a suspension of respective metal salts was added drop wise with constant stirring. The reaction mixture was refluxed on a water bath for 4-6 h. The precipitated complexes were filtered, washed with ethanol followed by ether and dried over fused calcium chloride. Yield:45-50%

The complexes are soluble in DMSO and DMF but insoluble in water and common organic solvents. The ¹H NMR spectra of ligand was recorded and obtained from RSIC Chandigarh. IR spectra of the compounds were recorded on Perkin Elmer 842 spectrophotometer in the region 400-4000 cm⁻¹, Carbon, Hydrogen and Nitrogen analysis were carried out at RSIC, Punjab University, Chandigarh. Thermogravimetric analyses were performed on laboratory setup apparatus in air atmosphere at 10°C min⁻¹ heating rate.

Result and Discussion:

The Schiff base ligand HMAE and its complexes have been characterized on the basis of ¹H NMR, IR spectral data and elemental analysis. All these values and analytical data are consistent with proposed molecular formula of ligand. All the compounds are coloured solid and stable in air. They are insoluble in water but soluble in coordinating solvents like DMF and DMSO. The molar conductance values in DMF(10⁻³M) solution at room temperature shows all the complexes are non electrolytes. The ¹H NMR spectra of ligand HMAE shows signals at δ 11.90 (1H, s, phenolic OH); 9.55 (1H, s, phenyl); 8.65 and 8.30(2H, m, phenyl), 3.14(4H, s, CH₂-CH₂); 2.22 ppm (3H, s, methyl)⁹⁻¹⁶ IR spectra of ligand and metal complexes summarized in Table 2. As per observation ν (C=N) peaks at 1630cm⁻¹ indicates the Schiff base formation¹⁷⁻¹⁸.

Table 2. IR spectra of ligand and metal complexes.

Compound	ν (O-H) hydrogen bonded	ν (C=N) Imine	ν (C-O) phenolic	ν (M-O)	ν (M-N)
C ₂₀ H ₂₄ N ₂ O ₂	2918	1630	1475	--	--
[CoL(H ₂ O) ₂] H ₂ O	--	1589	1444	520	452
[NiL] H ₂ O	--	1583	1458	510	492
[CuL(H ₂ O) ₂] 2H ₂ O	--	1582	1442	580	490

Thermal technique: The nature of thermograms of HCAE and its metal complexes indicates that the complexes of Co(II), Ni(II) and Cu(II) decompose in three stage the ligand All the complexes are stable upto 70°C. Elimination of one water molecule from Co(II), Ni(II) upto 130°C and two water molecules from the Cu(II) complexes upto 150°C have been observed (%wt loss obs./calcd. : Co(II) : 3.28/3.20; Ni(II) : 3.54/3.42; Cu(II) : 6.28/6.14; Further loss in weight upto 220-240°C indicating presence of two coordinated water molecule in Co(II) and Cu(II) each (%wt loss obs./calcd.: Co(II) : 6.50/6.38; Cu(II) : 6.27/6.15; In all the complexes rapid weight-loss has been observed above 300°C, indicative of decomposition of the free part of the coordinated ligand, a gradual weight-loss above 400°C corresponding to the degradation of actual coordinated part of the ligand. The half decomposition temperature and the basic parameters calculated for the compounds are given in (Table 3). Thermal activation energy was calculated by Freeman-Carroll¹⁹, Horowitz-metzger²⁰ and Broido²¹ method. On the basis of half decomposition temperature, the relative thermal stability order is found to be The relative thermal stability on the basis of half decomposition temperature is found to be Cu(II)>CO(II)>Ni(II)> HMAE.

Table 3. Thermal decomposition data of HMAE and its complexes.

Compound	Half Decomposition Temperature (°C)	Activation Energy (kJ mole ⁻¹)			Frequency Factor Z (sec ⁻¹)	Entropy Change -ΔS (J mol ⁻¹ K ⁻¹)	Free Energy Change ΔF (kJ mol ⁻¹)
		B*	H-M**	F-C***			
C ₂₀ H ₂₄ N ₂ O ₂₂	263.50	3.39	5.54	4.42	87.32	213.50	127.85
[CoL (H ₂ O) ₂] H ₂ O	398.18	3.59	8.62	8.58	170.95	207.81	158.17
[NiL] H ₂ O	268.36	2.88	5.73	4.84	98.72	213.58	128.74
[CuL (H ₂ O) ₂] 2H ₂ O	594.18	11.56	14.36	11.40	228.40	207.57	199.68

* Broido, ** Horowitz-Metzger and *** Freeman-Carroll

Applications of Schiff base and its derivatives in agro-industries: Action on Insecticides Schiff base ligand was derived from the condensation of 2-hydroxy-5-methyl acetophenone and ethylene diamine. Their metal complexes show high activity against insects²². 2-amino-4-phenylthiazole acts as intermediate in synthesis of photostable pyrrhiod insecticides²³. Fluorination on aldehyde part of Schiff base increases insecto acracicidal activity²⁴. Schiff bases and their metal complexes with Co(II), Ni(II) and Cu(II) show insecticidal activities against bollworm²⁵.

Conclusion:

The thermal decomposition of the complexes is not simple and involves up to three stage decomposition. It is assumed that dehydration of the complexes containing water occurs within an active reaction interface. The compensation technic of thermal decomposition of the complexes indicating the change of sample mass on the estimated values of activation energy and shows some agro-industrial activity.

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