INTERNATIONAL JOURNAL FOR INNOVATIVE RESEARCH IN MULTIDISCIPLINARY FIELD
ISSN(O): 2455-0620 [Impact Factor: 9.47]
Monthly, Peer-Reviewed, Refereed, Indexed Journal with IC Value : 86.87
Volume - 11, Issue - 07, July - 2025

DOIs:10.2015/IJIRMF/202507042 --:-- Research Paper / Article / Review

Thermal studies and Geological Application of of Co(II), Ni(II) and Cu(II) of diamine metal complexes

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Abstract: *The newly synthesized 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 elemental analysis, Infrared, and ^1H NMR 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 v(M-N) and v(M-O) in the metal complexes. TG 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. And studies of geological application*

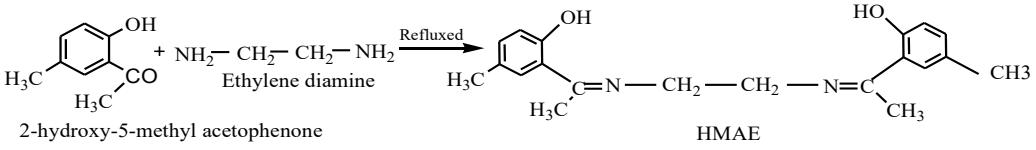
Key Words: *Schiff base, Spectral, Thermal studies, Geological application*

1. INTRODUCTION:

Performance of Schiff Bases Metal Complexes and their Ligand in Biological Activity[1]. Spectral, Structural, and Antibacterial Study of Copper(II) Complex with N_2O_2 Donor Schiff Base Ligand and Its Usage in Preparation of CuO Nanoparticle[2]. These compounds are majorly used in industries and also have significant biological activities, including antioxidant, antibacterial, antifungal, antiviral and antitumor. There is synthesis, characterization and biological activities of new Schiff Base Compound and its lanthanide complexe[3]. Antifungal Activity of Some Mixed Ligand Complexes Incorporating Schiff Bases[4]. Advanced and Biomedical Applications of Schiff-Base Ligands and Their Metal Complexes[5]. 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 pattern as well as to evaluate kinetic parameters by Broido, Horowitz-Metzger and Freeman-Carroll method

2. EXPERIMENTAL:

All the chemicals and solvents were of A.R. grade and used as received, 2-hydroxy-5-methyl acetophenone and ethylene diamine was prepared by known methods[6-8]. 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^{0}C



Scheme 1. Synthesis of HMAE

Table1. Analytical data of the Ligands.

	Ligand			Color	Elemental Analysis

Sr. No		Molecular Formula	Formula Weight	and nature	C% found (Cal.)	H% Found (Cal.)	N% Found (Cal.)
1.	HMAE	$C_{20}H_{24}N_2O_2$	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 ^{1}H 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^{o}C min^{-1} heating rate.

3. RESULT AND DISCUSSION:

The Schiff base ligand HMAE and its complexes have been characterized on the basis of ^{1}H 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^{-3}M) solution at room temperature shows all the complexes are non electrolytes. The ^{1}H NMR spectra of ligand HMAE shows signals at δ11.90 (1H, s, phenolic OH); 9.55 (1H, s, phenyl); 8.65 and 8.30(2H, m, phenyl), 3.14(4H, s, CH_2–CH_2); 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 formation [17-18].

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)
$C_{20}H_{24}N_2O_2$	2918	1630	1475	--	--
[CoL(H2O)2] H2O	--	1589	1444	520	452
[NiL] H2O	--	1583	1458	510	492
[CuL(H2O)2] 2H2O	--	1582	1442	580	490

Thermogravimetric studies: 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^{o}C. Elimination of one water molecule from Co(II), Ni(II) upto 130^{o}C and two water molecules from the Cu(II) complexe upto 150^{o}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^{o}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^{o}C, indicative of decomposition of the free part of the coordinated ligand, a gradual weight-loss above 400^{o}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-Carroll[19], Horowitz-metzger[20] and Broido[21] method. On the basis of half decomposition temperature, the relative thermal stability order is found. 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***			
$C_{20}H_{24}N_2O_{22}$	263.50	3.39	5.54	4.42	87.32	213.50	127.85
[CoL $(H_2O)_2$] H_2O	398.18	3.59	8.62	8.58	170.95	207.81	158.17
[NiL] H_2O	268.36	2.88	5.73	4.84	98.72	213.58	128.74
[CuL $(H_2O)_2$] $2H_2O$	594.18	11.56	14.36	11.40	228.40	207.57	199.68

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

Geological application[22-27]: Cobalt complexes used to develop imaging agents, prodrugs and used as antiviral. antibacterial agents. Nickel and its complexes used to trace the contributions of ultramafic rock and biological activity as it is a vital. Copper is micronutrient for living organisms, and its complexes used in ancient nutrient cycling. Elevated copper levels in modern sediments often indicate industrial contamination, making it a useful marker for both geological and environmental studies.

4. CONCLUSION:

This Geological research is applicable for both geological and environmental studies. As well as 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 effect of thermal decomposition of the complexes indicating the change of sample mass on the estimated values of activation energy.

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