

Electrical Conductivity of Co (II), Ni(II) and Cu(II), Complexes derived from bidentate thiazole Schiff base.

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ABSTRACT

The new thiazole Schiff base have been synthesized by condensing 2-hydroxy-5-chloro acetophenone and 4-(p-hydroxyphenyl)-2-aminothiazole. The metal complexes were obtained as a result of interaction of Schiff base ligand and metal ions Co(II), Ni(II) and Cu (II). The complexes have been characterized on the basis of elemental analysis, infrared, molar conductance, magnetic Susceptibilities, and Elctrical conductivity.

Keywords: Thiazole Schiff Base, Molar conductance, Electrical conductivity.

INTRODUCTION

Schiff bases are compounds containing azomethine linkage ($>C=N$) and are formed by condensation of primary amines with the active carbonyl compounds. The present reference research paper focus on synthesis, characterisation and various methods of Schiff base derived from sulphanilic acid and salicylaldehyde and Comparative study of Schiff base using various synthesis methods and their theoretical prediction of activities[1] Synthesis, characterization and antifungal activity of manganese (II) complex with Schiff Base derived from acetylacetone andl leucine [2] The newly synthesized Schiff bases, 2-acetylthiophene thiosemicarbazone and thiophene-2-aldehyde thiosemicarbazone and their metal complexes with Co(II), Cu(II), Zn(II) and Ni(II) complexes and Their Schiff bases metal complexes were tested for antibacterial activity.[3]

There is the combination of the azo group, the imidazole unit and the Schiff base fragment to studies the synthesis, characterization, and optical properties of four different Schiff bases ligands. They are reported the possible use of such systems in biological applications for their antifungal properties and antioxidant activities.[4] Synthesis and structural diversity transition metal coordination complexes with diverse Schiff base ligands and macrocyclic systems [5] This paper discusses the electrical conductivity and the accompanying compensation effect for Schiff base complexes of Co (II), Ni (II) and Cu (II).

METHODOLOGY

All the chemicals were of A.R. grade and used as received. 2-hydroxy-5-chloro acetophenone (HCA) and 4-(p-hydroxyphenyl)-2 amino thiazole was prepared by known methods.[6-9] The solvents were purified by standard methods[10]

Synthesis of 2-hydroxy-5-chloro acetophenone 4-(p-hydroxyphenyl)-2 imino thiazole [HCA]: A solution of 4-(p-hydroxyphenyl)-2 imino thiazole (0.02M) in 25ml of ethanol was added to an ethanolic solution(25ml) of 2-hydroxy-5-chloro acetophenone (0.02M) and the reaction mixture was refluxed on a water bath for 4h. After cooling a pale yellow coloured crystalline solid was separated out. It was filtered and washed with ethanol, crystallized from DMF and dried under reduced pressure at ambient temperature. The purity of ligand was checked by elemental analysis shown in Table 1. and m.p. It was also characterized by IR and ^1H NMR spectral studies. Yield:70%; m.p. 310°C

Preparation of complexes: All the metal complexes were prepared in a similar way by following method. To a hot solution of ligand HCA (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 metal chloride content of complexes were analyzed by standard methods.[11] 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. The molar conductance of the complexes at 10^{-3}M dilution in DMF were determined using equiptronic digital conductivity meter EQ-660 with a cell constant 1.00 cm^{-1} at room temperature. The magnetic moment measurement were made on a Gouy balance at room temperature using $[\text{HgCo}(\text{SCN})_4]$ as the calibrant. The thermogravimetric analysis were performed on laboratory set up apparatus in air atmosphere at $10^\circ\text{C min}^{-1}$ heating rate. The molecular weights of the complexes were determined by Rast method are shown in Table 2.

RESULTS AND DISCUSSION

The Schiff base ligand HCA and its complexes have been characterized on the basis of ^1H NMR, IR spectral data, elemental analysis, molar conductance, magnetic susceptibility measurements and electrical conductivity analysis data. All these values and analytical data is 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 (Table 2) shows all the complexes are non electrolytes¹¹ The ^1H NMR spectra of ligand HCA shows signals at δ 12.09, (1H, s phenolic OH), δ 9.51 (1H, s, phenolic OH), δ 7.55, 7.54, 7.53 and 7.52 (4H, m, phenyl) δ 6.81, 6.80, and 6.78(3H, s Phenyl), 6.68 (1H s thiophene), and 2.56(3H, s, methyl) [12-15] IR spectra of ligand and metal complexes shows $\nu(\text{C}=\text{N})$ peaks at 1620cm^{-1} and absence of $\text{C}=\text{O}$ peak at around $1700\text{--}1750\text{ cm}^{-1}$ indicates the Schiff base formation.[16-18] IR spectra of complexes are shown in Table 3.

Electrical Conductivity

The electrical resistivity of the different metal chelates can be measured either with a.c. or d.c. methods.

However, in the present work the d.c. method is used for resistivity measurements, over a wide range of temperature. The electrical conductivity of metal complexes varies with their nature and temperature.[19-23] The variation of electrical conductivity of the metal complexes with temperature is the basis of their classification as semiconductors or metallic conductors. The electrical conductivity of metallic conductors decreases with increasing temperature (i.e. temperature coefficient is negative) and their resistivity ranges from 10^{-6} to 10^{-3} .

The electrical conductivity and activation energy of HCAT complexes are cited in Table 4

1. Electrical conductivity of the complexes lies in the range of 2.10×10^{-9} to $6.69 \times 10^{-7} \Omega^{-1} \text{cm}^{-1}$ at 373 K.
2. The electrical conductivity of these complexes at 373 K follows the order Ni > Cu > Co.
3. The activation energy of electrical conduction of the complexes has been found to increase in the order Ni < Cu < Co.

Table1: Analytical data of the Ligands.

Ligand	Molecular Formula	Formula Weight	Color and nature	Elemental Analysis				
				C% found (Cal.)	H% Found (Cal.)	N% Found (Cal.)	Cl% Found (Cal.)	S% Found (Cal.)
HCAT	$\text{C}_{17}\text{H}_{13}\text{N}_2\text{O}_2\text{SCl}$	344.6	Yellow Crystalline	59.38 (59.19)	03.70 (03.77)	08.5 (08.12)	10.11 (10.30)	09.22 (09.31)

Table 2: Analytical data and molar conductance of the compounds.

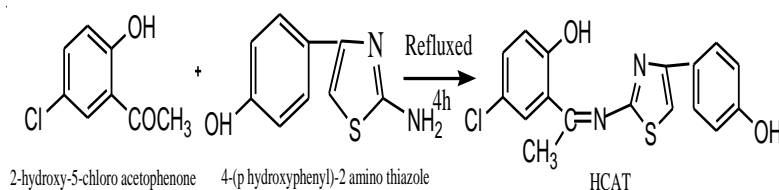
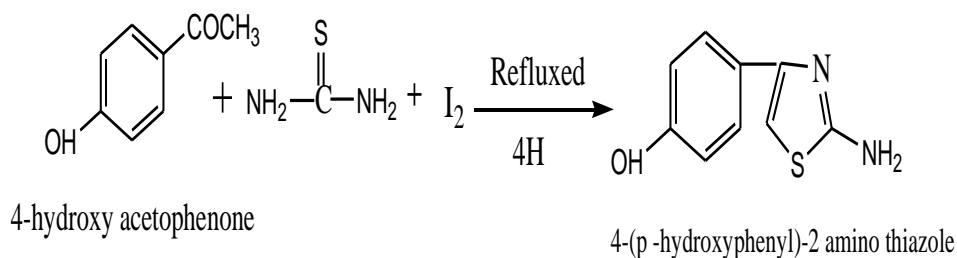
Compounds	Colour	Mol.wt.	Analysis % Found (calc.)					μ_{eff} B.M.	Λ_{M} ($\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$)
			M	C	H	N	Cl		
			[CoL ₂ (H ₂ O) ₂] H ₂ O	Brown	800.1	7.25 (7.36)	50.86 (50.99)		
[NiL ₂ (H ₂ O) ₂] H ₂ O	Green	799.9	7.30 (7.33)	50.78 (51.00)	3.68 (3.75)	6.95 (7.00)	8.72 (8.87)	3.2	7.9
[CuL ₂ (H ₂ O) ₂] H ₂ O	Brown	804.7	7.70 (7.89)	50.60 (50.70)	3.65 (3.72)	6.82 (6.95)	8.72 (8.82)	1.70	8.3

Table 3: IR spectra of ligand and metal complexes.

Compound	$\nu(\text{O}-\text{H})$ hydrogen bonded	$\nu(\text{C}=\text{N})$ imine	$\nu(\text{C}=\text{O})$ phenolic	$\nu(\text{M}-\text{O})$	$\nu(\text{M}-\text{N})$	$\nu(\text{C}-\text{S})$
HCAT	3119	1620	1514	--	--	1122
[CoL ₂ (H ₂ O) ₂] H ₂ O	--	1608	1504	470	430	1098
[NiL ₂ (H ₂ O) ₂] H ₂ O	--	1585	1465	468	422	1090
[CuL ₂ (H ₂ O) ₂] H ₂ O	--	1610	1504	509	410	1110

Table 4: Electrical Conductivity (σ) at 373 K and Activation Energy (E_a) of the complexes

Metal		Co(II)	Ni(II)	Cu(II)
HCAT	σ ($\Omega^{-1} \text{cm}^{-1}$)	2.10×10^{-9}	1.28×10^{-8}	4.10×10^{-8}
	E_a (eV)	0.0824	0.0147	0.0399

Synthesis of 4-(p hydroxyphenyl)-2 amino thiazole;**CONCLUSION**

The D.C. Electrical conductivity of the synthesized complexes were measured in the temperature range 298-423 K. All the complexes indicating their semiconducting behaviour

Conflicts of interest: The authors stated that no conflicts of interest.

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