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Synthesis and Characterization of Copper (II) Chelates of some Tetra Dentate Schiff Bases

Abstract

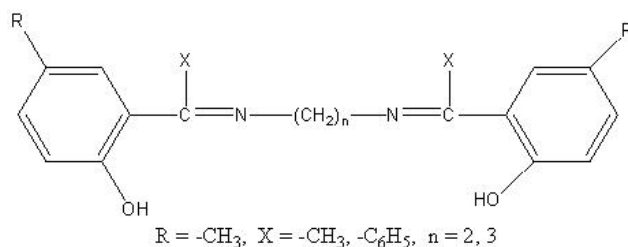
A series of chelates of tetra dentate schiff bases, obtained from condensing 2-hydroxy-5-methyl acetophenone and 2-hydroxy-5-methyl benzophenone with aliphatic diamines, then the chelates were prepared by refluxing the mixture of schiff bases solution and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ solution at definite pH range. The chelates have been isolated in solid state and structural features were obtained from their elemental analysis, Conductivity, Magnetic susceptibility and UV and IR spectroscopic studies, the ligands have general formula $L = (\text{HMPXM})_2\text{RDM}$ where $(\text{HMPXM})_2\text{RDM} = \text{N}^1, \text{N}^2$ -bis (2'-hydroxy-5'-methyl phenyl substituted methylidene) diamine, where $R = -\text{CH}_3$ and $X = -\text{CH}_3, -\text{C}_6\text{H}_5$. The schiff base chelates have 1:1 composition and structures for these chelates are suggested.

Keywords: Chelates, Vibronic, Spectral studies, Magnetic moment, Schiff bases

Introduction

The oxygen bridged bidentate, tridentate and tetra dentate chelates have attracted much attention due to their interesting spectral and magnetic properties and their use in biochemical processes and homogeneous catalysis¹⁻⁴. Metal chelates of Schiff bases have been the subject of intensive research because they not only have interesting spectral and magnetic properties, but they also possess a diverse spectrum of biological and pharmaceutical activities⁵⁻⁹.

A literature survey reveals that most of the studies on the binary and ternary complexes of transition metal ions with a number of schiff bases are carried out in aqueous -organic or mixed organic solvent media and studies of such reactions in micellar media are considerably less. It is despite the fact that many chemical reactions are reported 10-14 to be effected by the presence of micelles on the systems. The solubility and compartmentalizing actions of micelles on the reactants strongly modify complex and acid base equilibria, redox properties and reaction rates. The complexes of Cu(II), Ni(II), Co(II), and Fe(II) with the Schiff base derived from 2-hydroxy-5-methyl-3-nitroacetophenone with ethylene diamine, propylene diamine have been studied earlier¹⁵. In the present study, we have been prepared tetra dentate chelates directly by the reaction of Schiff bases derived from 2-hydroxy-5-methylacetophenone and 2-hydroxy-5-methylbenzophenone with aliphatic diamines then refluxed with metal chloride. The obtained chelates are of type $[\text{ML}]$ where L is a Schiff base molecule.



Experiment

All the chemicals used were of AR grade (BDH or FLUKA); 2-hydroxy-5-methylacetophenone and 2-hydroxy-5-methylbenzophenone was prepared by Fries migration reaction of the paracresyl acetate¹⁶⁻¹⁷. The Schiff bases were prepared by refluxing 2:1 molar quantities of acetophenone and benzophenone and substituted aliphatic diamines in ethanol with catalytic quantity of acetic acid for 3.5 hours, solidification occurred after concentrating and cooling. The resulting crystalline product is filtered, dried and purified by recrystallisation in ethanol and then purity is checked by TLC using silica gel-G. The analytical and physical data of $(\text{HMPXM})_2\text{RDM}$ are given in Table-1. All the Schiff bases have yellowish color and crystalline in nature. Melting points were determined in open capillaries and are uncorrected.

The complexes were prepared by refluxing ethanolic solutions of the metal chloride and ligands in 1:1 ratio for 2-3 hrs. After cooling and adjusting the pH between 9.5-11.00 with dilute alcoholic ammonium solution the complex has precipitated out as dark green solid, the resulting mass was filtered and washed with hot ethanol and dried. The complexes were analyzed for metal ions by standard method¹⁸. The analytical data of compounds are given in Table- 2.

TABLE -1
ANALYTICAL AND PHYSICAL DATA OF $(\text{HMPXM})_2\text{RDM}$

Ligand No.	X	R	Ligand (M.F.)	M.W.	M.P. $^{\circ}\text{C}$	% Found (Calcd.)		
						C	H	N
L1	-CH ₃	-CH ₃	C ₂₀ H ₂₄ O ₂ N ₂	324	202	74.01 (74.04)	7.41 (7.46)	8.60 (8.63)
L2	-CH ₃	-CH ₃	C ₂₁ H ₂₆ O ₂ N ₂	338	110	74.48 (74.52)	7.71 (7.74)	8.24 (8.28)

L3	-C ₆ H ₅	-CH ₃	C ₃₀ H ₂₈ O ₂ N ₂	448	230	80.29 (80.33)	6.26 (6.29)	6.21 (6.24)
L4	-C ₆ H ₅	-CH ₃	C ₃₁ H ₃₀ O ₃ N ₂	478	126	80.47 (80.49)	6.52 (6.54)	6.02 (6.06)

TABLE -2
ANALYTICAL DATA OF Cu (II) CHELATES

Complex No.	M.W.	Conductivity Ohm ⁻¹ Cm ² mol ⁻¹	% Found (Calcd.)			
			C	H	N	Cu
[Cu L ₁]	374.42 (387.97)	9.0	61.89 (61.92)	6.18 (6.23)	7.18 (7.22)	16.34 (16.38)
[Cu L ₂]	389.92 (402.0)	9.2	62.69 (62.74)	6.49 (6.52)	6.92 (6.97)	15.78 (15.81)
[Cu L ₃]	498.38 (512.11)	9.7	70.31 (70.36)	5.47 (5.51)	5.42 (5.47)	12.39 (12.41)
[Cu L ₄]	512.42 (526.14)	8.8	70.72 (70.77)	5.72 (5.75)	5.28 (5.32)	11.99 (12.08)

TABLE-3
MAGNETIC SUSCEPTIBILITY DATA OF Cu (II) CHELATES

Complex No.	M.W.(M)	Amount of comp. in gms.(m)	Force of magnetic field (F) in g	χ	χ_M C.G.S	χ_{corr} M C.G.S	μ_{eff}
[Cu L ₁]	387.97	0.6299	3.4317	4.3284	1679.28	1788.01	2.08
[Cu L ₂]	402.00	0.6542	3.3460	4.0656	1634.38	1857.44	2.12
[Cu L ₃]	512.11	0.6764	2.5857	3.0568	1565.42	1719.89	2.04
[Cu L ₄]	526.14	0.8025	3.4581	3.4231	1801.02	1964.06	2.18

Result and Discussion

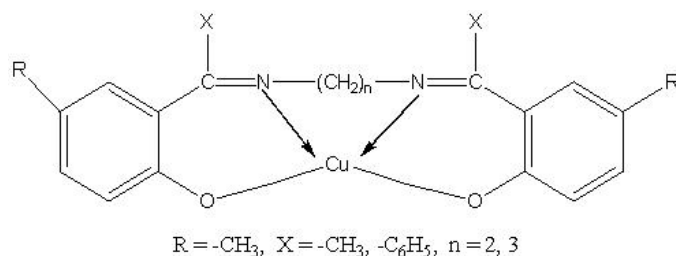
All the Chelates are very much stable, having high m.p. and sparingly soluble in common organic solvents. The analytical data of the complexes are recorded in Table-2 and Table-3. The elemental analysis implies that the metal and ligands is in 1:1 stoichiometric. The conductance measurements were carried out at room temperature using a Thoshniwal conductivity bridge. The electrical conductivity values of 10⁻³ M solutions in DMF (Table-2 and 3) were in the range 8.0-10.0 ohm⁻¹ cm² mole⁻¹ reveals non electrolytic nature of the complexes.

The electronic spectra of the ligand and complexes were measured by using Shimadzu UV-265 instrument. The ligand and complexes exhibit bands at 300 to 325 nm due to the vibronic structure of the metal, which seems to be overlapped by the strong ligand to metal charge transfer bands. The intensity of the absorption characteristics of Cupper (II) ion is much weaker than that of K type of bands. From the experimental data, the influence of the metal ion on the characteristic absorption is much weaker than the ligands, which has a large conjugated system¹⁹⁻²⁰.

The IR spectra²¹⁻²² of the ligands and complexes were recorded in KBr on Shimadzu 435-IR spectrophotometer between 4000-400 cm⁻¹. In the IR spectra of ligands, bands were obtained in the range 1660-1575 cm⁻¹ for ν (C=N) at 1300-1080 cm⁻¹ for ν (C-O) and at about 2900- 2800 cm⁻¹ for ν (C-H). The broad weak band in the region 3450-3400 cm⁻¹ is due to the intra molecular H-bonded OH. This band totally disappeared in the complexes suggesting the involvement of OH group in coordination. The shift of lower or higher wave numbers of ν (C=N) or ν (C-O) respectively in the complexes indicates participating of nitrogen atom of the azomethelene group and phenolic (C-O) in coordination after deprotonation 23-24. This was further supported by the disappearance of (OH) stretching vibration in the complexes. The formation of the (M-N) and (M-O) bonds were further supported by appearance of ν (M-N) and ν (M-O) in the regions 430-460 cm⁻¹ and 530-550 cm⁻¹ respectively in the spectra of the complexes.

Magnetic susceptibility of all the compounds was measured at room temperature (300K) by Gouy balance method. The value of specific susceptibility (χ) and molar susceptibility (χ_M) of all the complexes were determined (Table-3). The molar magnetic susceptibilities of the complexes were computed using Pascal's additivity law and the value of susceptibilities for Cupper ions required for this purpose were taken from the literature.

The Cupper chelates are paramagnetic having one unpaired electron. Generally, the magnetic moment for Cupper (II) complexes is of the order of 2.04-2.18 B.M., which is attributed to the mixing of the higher ligand field terms in to the ground (²A_{1g}) by spin orbit coupling²⁵⁻²⁶ to give some orbital contribution to the moment. However, the remarkably high moments of the Cupper (II) square planer complexes could not be explain satisfactorily. Generally, the magnetic moment value can not be helpful to decide the symmetry of the Copper chelates i.e. tetrahedral or octahedral but from the electronic spectra, tetragonal structure is assigned to the Copper chelates. However, in present case Cupper (II) might have stabilized due to conjugation of the ligand attached to it. The possible structures of Cupper (II) chelates are as under.

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