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Synthesis and Characterization of Cobalt (II), Nickel (II), and Copper (II) Complexes of Some 2'- Hydroxychalcones

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ABSTRACT

A series of metal complexes of Co (II), Ni (II) and Cu (II) have been synthesized with newly synthesized biologically active ligands. These ligands were prepared by the condensation of substituted 2'- Hydroxyacetophenones and 3, 5 dibromosalicylaldehyde. The structures of the complexes have been proposed by the analytical data, conductivity measurement, magnetic moment, IR, electronic spectral data and thermal studies. Analytical data confirmed 1:2 stoichiometry and the electronic spectral data suggest that all Co (II), Ni (II) complexes have octahedral geometry whereas Cu (II) complexes have square planar geometry. Presence of coordinated water molecules in Co (II) and Ni (II) complexes is confirmed by TGA studies. The conductivity data show that all these complexes are non electrolytes.

Keywords: - Transition metal complexes, IR, ESR spectra and TGA.

INTRODUCTION

Chalcones are open chain flavonoids whose basic structure includes two aromatic rings bound by an α , β - unsaturated carbonyl groups. They are usually obtained from natural products with extractive techniques[1-2] or by several homogeneous [3-4] and heterogeneous[5-6] synthetic methods. The importance of chalcones lies in the wide range of pharmacological activities such as antioxidant, antitumor[7], antimalarial[8], anticancer[9], antiinflammatory[10], antileishmanial[11] and antimicrobial[12].

2'-Hydroxychalcone known to be pharmacologically active possess co-ordinating sites and are expected to form complexes with different metal ions. Lense et.al[13] reported that O-Hydroxychalcones are much more reactive with metal ions than the ketones and aldehydes from which they are synthesized several of the chalcones have been employed as useful analytical reagent.

The chelating tendency of these compounds is little known except for a few publications involving similar ligands. We report here the synthesis of a series of Co (II), Ni (II) and Cu (II) with substituted 2'-Hydroxychalcones and their characterization based on analytical, conductance, magnetic moment, IR, electronic spectra and thermal studies are reported.

EXPERIMENTAL SECTION

All the reagents used were chemically pure and are of AR grade. Solvents were dried and distilled before use according to standard procedure[14]. The ligands selected in the preparation of metal complexes are 1-(2'-Hydroxy phenyl)-3-(1-Hydroxy, 2, 4-Dibromo phenyl)-2-propen-1-one and 1-(2'-Hydroxy-3'-Iodo-5'-methyl phenyl)-3-(1-Hydroxy 2, 4-dibromo phenyl)-2-propen-1-one.

Synthesis of metal complexes

The ligand (0.002 mole) and the metal salt (0.01 mole) in 50 ml methanol was reflux for 2 hour. In all the cases the ligand concentration was in slight excess of the 1:2 metal ligand molar ratio. The solid mass separated was filtered through a sintered glass crucible (G4) and the residue was washed several times with hot methanol until the washings were free of the excess of ligand. These complexes were finally dried under vacuum desiccator over fused CaCl_2 . Analytical and physical data is given in TABLE-1. Molar conductance measurements were carried out in 10^{-3} M in DMF solution using an Elico digital conductometer model-180. The magnetic susceptibility measurements of the complexes in the solid state were made on Guoy balance at room temperature using Hg $[\text{Co}(\text{NCS})_4]$ as standard. Diamagnetic corrections were applied using pascals constant. The IR spectra of the metal in KBr pellets in the range of $4000\text{-}350\text{ cm}^{-1}$ were recorded making use FTIR-SHIMADZU8400S spectrometer.

UV-Visible spectra in DMF were recorded on a SHIMADZU multipurpose recording spectrophotometer model 1601 and TGA and DTA analysis of metal complexes were carried out in nitrogen atmosphere in the range $25\text{-}1200\text{ }^\circ\text{C}$ on shimadzu DTG-50 with a heating rate $10\text{ }^\circ\text{C min}^{-1}$ using alumina as a standard.

RESULT AND DISCUSSION

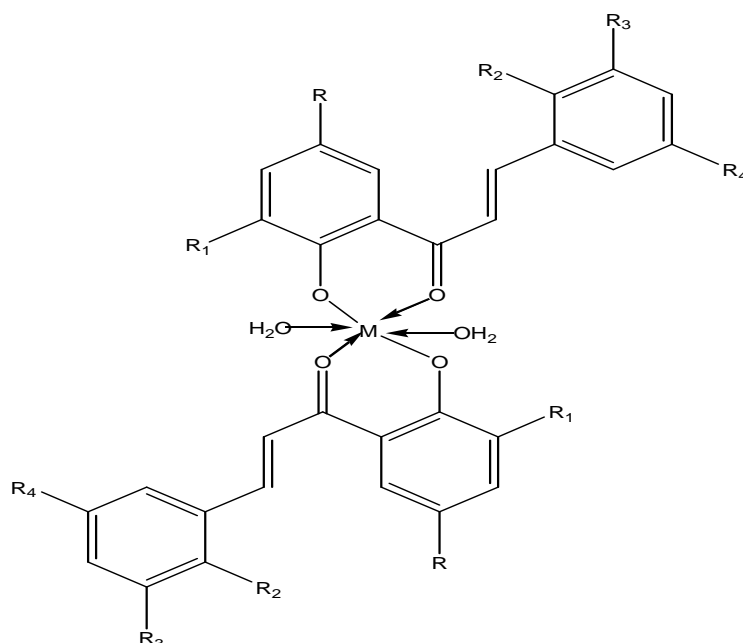
All the complexes are stable at room temperature insoluble in water and most of the common organic solvents but soluble in DMF and DMSO. The analytical data of the complexes (TABLE-1) indicates that their stoichiometry may be represented as 1:2 metal to ligand ratio. The molar conductance values of the complexes in DMF solvents are in the range of $6.45\text{-}26.25\text{ ohm}^{-1}\text{ cm}^2\text{ mol}^{-1}$ suggesting their non-electrolytic nature[15].

IR spectra

The ligand showed a weak broad band around $2890\text{-}3068\text{ cm}^{-1}$, but the IR spectra of Ni (II) and Co (II) complexes exhibited intense broad band near $3300\text{-}3400\text{ cm}^{-1}$ due to ν OH of coordinated water molecule[16]. In the IR spectra of all the ligands an intense band appearing around 1647 cm^{-1} is attributed to $\nu(\text{C}=\text{O})$ [17]. This band is shifted to lower wave number in the spectra of the complexes indicating coordination through oxygen of (C=O) group. The medium intensity band appearing around $1533\text{-}1569$ in the ligands and the complexes are assigned to $\nu(\text{C}=\text{C})$ (aromatic). The $\nu(\text{M}-\text{O})$ band was observed in the complexes around 445 cm^{-1} [18].

TABLE-1:-Magnetic moment, Conductivity and analytical data of Co (II), Ni (II) and Cu (II) complexes

Sr. No.	Molecular Formula	Colour	M.P/D.P. °C	Elemental Analysis		Molar Conductivity Ohm-1 Cm ² Mol-1×10 ⁻³	μ_{eff} B.M.
				Halogen Found (Calcd)	Metal Found (Calcd)		
1.	C ₃₀ H ₂₂ O ₈ Br ₄ Ni	Yellow	276	37.48 (37.16)	6.88 (6.54)	25.27	2.41
2.	C ₃₀ H ₂₂ O ₈ Br ₄ Co	Green	236	37.25 (37.86)	6.97 (6.18)	18.64	4.36
3.	C ₃₀ H ₁₈ O ₆ Br ₄ Cu	Bluish	278	37.27 (37.92)	7.41 (7.86)	21.48	1.67
4.	C ₃₂ H ₂₄ O ₈ I ₂ Br ₄ Ni	Green	264	26.21 (26.78)	5.18 (5.69)	12.16	2.96
5.	C ₃₂ H ₂₄ O ₈ I ₂ Br ₄ Co	Yellow	234	25.80 (25.16)	5.20 (5.38)	11.32	4.92
6.	C ₃₂ H ₂₀ O ₆ I ₂ Br ₄ Cu	Bluish Green	268	27.22 (27.58)	5.59 (5.62)	7.48	1.89



M= Ni (II), Co (II)

Complex No.	R	R ₁	R ₂	R ₃	R ₄
1.	H	H	OH	Br	Br
2.	H	H	OH	Br	Br
3.	H	H	OH	Br	Br
4.	CH ₃	I	OH	Br	Br
5.	CH ₃	I	OH	Br	Br
6.	CH ₃	I	OH	Br	Br

Thermal analysis

The thermogram of [Ni(L₂)₂]₂H₂O complex shows that the complex starts decomposing gradually, till it attains the temperature corresponding to 70-85 °C which corresponds to two moles of hydrated water. After 250 °C the anhydrous complex starts to decompose. Total mass loss up to 750 °C is found to be 88.60% (calc 87.72) which shows finally the formation of NiO. The residue left after 750 °C is 8.10 (calc. 8.32%) which resembles the theoretical

values (TABLE-2). Hence from TGA, it is clear that the complex under study contains two water molecules which are coordinated to central metal ion[19].

TABLE-2:- Thermo analytical result of [Ni (L₂)₂ (H₂O)₂] complex.

Metal Comp	Temperature C	Weight loss in %	
		Found (Calcd)	Fragment removed
[Ni (L ₂) ₂ (H ₂ O) ₂]	230	3.29(3.86)	Two water molecule
	700	88.60(87.72)	Organic part
	>700	8.10(8.32)	Metal Oxide

Magnetic moment

The μ_{eff} values at room temperature for Cu (II) complexes are in the range of 1.78-1.84 B.M. usually observed for square planar Cu (II) complexes [20-21]. Ni (II) and Co (II) complexes have magnetic moment values in the range of 2.92-3.14 and 4.38-4.90 B.M. respectively. These values are expected for octahedral geometry of Ni (II) [22-23] and Co (II) complexes at 25°C.

Electron spin resonance study

The ESR spectra of Cu (II) complexes in the polycrystalline state shows two peaks, one of intense absorption at high field and the other of less intensity at low field. From these spectra the values of g_{\parallel} and g_{\perp} have been calculated by Kneubehls method [24] and are given in TABLE-3. The observed g -values point to the presence of the unpaired electron in the dx^2-y^2 orbital with $g_{\parallel} > g_{\perp}$ characteristic of square planar or elongated tetragonal geometry. The g_{\parallel} obtained for the Cu (II) complexes is less than 2.3 indicating covalent character of the metal-ligand bond[25]. The axial symmetry parameter (G) for the complexes is found to be greater than 4, as shown in TABLE-3. This shows absence of interaction between copper centers in the solid state[26].

TABLE-3:- ESR Spectral data of Cu (II) Complexes

Sr.No.	Complex	g_{\parallel}	g_{\perp}	g_{av}	G axial Symmetry Parameter
1.	Cu (L ₂) ₂	2.2810	2.0577	2.1321	4.3387
2.	Cu (L ₂) ₂	2.2650	2.0634	2.1306	4.3284

CONCLUSION

The Cu (II), Ni (II) and Co (II) complexes are coloured, insoluble in most of the organic solvent but soluble in DMF and DMSO. The stoichiometry of the metal complexes obtained has been found to be 1:2. The infrared spectral data indicate that all the ligands act as mononegative bidentate species towards Cu (II), Ni (II) and Co (II) complexes. The electronic spectral data suggested that Co (II), Ni (II) complexes have octahedral, while Cu (II) complexes have square planar geometry.

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