

Synthesis and Structural Studies of Complexes of Coumarin Derivative

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ABSTRACT

A bidentate chalcone namely 3-[3-(3'-bromo phenyl)-prop-2-enoyl]-4-hydroxy-6-methyl-2H-chromene-2-one(2) was synthesized by condensing 3-acetyl-4-hydroxy-6-methyl-coumarin with 3-bromo benzaldehyde. Cu(II), Ni(II), Co(II) and Mn(II) complexes of this chelating ligand were synthesized using hydroxides of these metals. The ligand and the complexes were characterized by elemental analyses, ¹H NMR, UV-Vis and IR spectra, conductance and magnetic susceptibility measurements. All these studies determines the metal-ligand stoichiometry.

Keywords : Coumarin, Chalcone, Transition metal complexes and Structural studies.

I. INTRODUCTION

4-Hydroxy-6-methyl-coumarin, its chalcone derivatives and their metal complexes find a variety of synthetic^{1,2}, analytical^{3,4} and biological^{5,6} applications and have been studied extensively. Structural studies on the complexes⁽³⁾ of bivalent metal ions such as Cu(II), Ni(II), Co(II) and Mn(II) have been carried out by using various techniques. The coordination of the ligand to the metal ion is found to be through carbonyl oxygen and phenolic oxygen of the chalcone⁽²⁾ of 4-Hydroxy-6-methyl-coumarin in the octahedral environment. The literature survey reveals a wealth of data on the transition metal complexes but complexes of chalcone have been less investigated as ligand, it was therefore proposed to investigate the ligation properties of chalcone and their metal complexes with transition metal(II) ions.

II. METHODS AND MATERIAL

All the reagents were of AR Grade and received from BDH, England, Merck, Germany and Sigma-Aldrich chemical company, USA. Melting points of the complexes were determined on open capillary tubes and are uncorrected. Molar conductance were determined using Toshniwal Conductivity bridge on direct reading digital conductivity meter. IR spectra were recorded in the solid state (KBr pellets) in the range 400-4000 cm⁻¹ using Shimadzu 435 FT-IR spectrophotometer by KBr technique. Magnetic susceptibility measurements were

done using Gouy balance consisting of the type NP-53 electrometer with DC power supply type NP-1053. ¹H NMR spectra were recorded on Bruker FT 300 MHz NMR spectrometer in CDCl₃ + DMSO-d₆ solvent using TMS as an internal standard. Elemental analysis was done on Thermofinigan elemental analyzer.

3-[3-(3'-Bromo phenyl)-prop-2-enoyl]-4-hydroxy-6 methyl-2H-chromen-2-one(2).⁷

A mixture of 3-acetyl-4-hydroxy-6-methyl coumarin (2.52 gm, 0.01M); 3'-bromo benzaldehyde (4.62gm, 0.025 M) and piperidine (1 ml) were added into ethanol (50 ml). The reaction mixture was refluxed on water bath for 4 h., cooled and solid was separated. Then it was crystallized from suitable solvent, reddish yellow coloured compound was obtained. Compound(2) : m. w. 385, yield 70%, m.p. 210°C. Anal Calcd for C₁₉H₁₃O₄Br requires, C, 54.10%, H, 3.22%, O, 16.54%, Br, 20.68%. Found: C, 54.22%, H, 3.37%, O, 16.62%, Br, 20.77% IR bands v_{max} (KBr, cm⁻¹): 1667 (C=O Str. of Carbonyl group), 1591 (CH=CH Str. of Ethylene, aromatic C=C), 1014(C-O-C Str of ether linkage), 1740 (C=O Str. of δ-lactone ring), 3420 (OH Str. of phenol), 729(C-Br Str.). ¹H NMR(CDCl₃, DMSO-d₆) : δ ppm : 2.50 (s, 3H, CH₃), 7.65(d, 1H, -CH=CH), 7.39 (d, 1H, -CH=CH), 3.91 (s, 1H, -OH), 7.11 to 8.45 (m, 6H, Ar-H).

Bis [3-[3-(3'-bromo phenyl)prop-2-enoyl] 4-hydroxy-6- methyl-2H-chromen-2-one]copper(II)complex
[Cu(C₁₉H₁₂O₄Br)₂(H₂O)₂] (3)

Copper chloride solution (10.0ml., 0.01M) diluted to 50 ml. and excess of ammonium hydroxide was added to get the pH between 10.5-11.0. It was refluxed with excess of alcoholic solution of 3-[(3-(3'-bromophenyl)prop-2-enoyl]4-hydroxy-6-methyl-2H-chromen-2-one (0.01M) on a water bath for half an hour when reddish yellow precipitates of copper complex were obtained. The precipitates were filtered, washed with distilled water and dried at 100^o C. The complex was crystallized from DMF. Compound (3a) Yield :74%, Anal Calcd for [Cu(C₁₉H₁₁O₄Br)₂(H₂O)₂] requires, C, 52.50%, H, 3.16%, O, 18.30%, Cu, 7.25%. Found : C,52.56%, H, 3.22%, O,18.44%, Cu, 7.32% IR bands ν_{max} (KBr, cm⁻¹): 1685 (C=O Str. of Carbonyl group), 1625 (CH=CH Str. of Ethylene, aromatic C=C), 1112 (C-O-C Str. of ether linkage), 1732 (C=O Str. of δ - lactone ring), 590-500 (Cu-O band), 785 (C-Br Str.).

Similarly other metal complexes were prepared. The complexes did not show clear melting point. They charred at temperature above 290^o C.

III. RESULTS AND DISCUSSION

The newly isolated metal complexes are insoluble in acetone, benzene and chloroform. They are freely soluble in di methyl sulphoxide di methyl formamide and 1,4-dioxane. The structure of the metal complexes and the ligand are shown in scheme. The solids do not melt sharply and undergo decomposition above 290^oC temperature. All the compounds gave satisfactory elemental analyses values and are close with the calculated value.

Molar Conductivity Measurements :

The conductivity of metal complexes was determined using Thoshniwal Conductivity Bridge. It was dissolved in DMF and conductivity was measured.

Conductivity of the DMF along was measured and solution of the complexes in DMF with different concentration was measured.

The conductivity data are in (Table-I) and the data indicates that the complexes are non- electrolyte in nature⁸

IR Studies :

The ligand peaks at 1623 and 1626 cm⁻¹ corresponding to C=O have been shifted to +15-23 cm⁻¹ in the complexes, which indicate coordination through oxygen atom of the carbonyl group⁹. One new band in infrared appears at 560-580cm⁻¹ which is probably due to M-O band¹⁰. The peak at 1720 cm⁻¹ is attributed to δ -lactone ring of coumarin. Only a sharp band between 3200-3400 cm⁻¹ is disappeared in the spectra of metal complexes, these peaks can be assigned to OH stretching and bending vibration, the broadness of the peak indicate the presence of coordinated water molecule in the complexes. In short, most of the bands appeared in the spectra of corresponding ligand are observed at the similar position in the IR spectra of metal complexes. (Table-II)

¹H NMR Studies :

The ¹H NMR spectra of ligand have been recorded in CDCl₃. In the ligand -OH group appeared at 3.91 δ ppm while -CH₃ proton appeared at 2.50 δ ppm. Two doublets appeared at 7.65 and 7.39 δ ppm due to two ethylenic protons of chalcone. The rest of the protons appeared in the aromatic range at 7.11 to 8.45 δ ppm. An examination of NMR spectra of the ligand reveals that these are on expected lines according to their structures.

Magnetic Studies and Electronic Spectra :

The magnetic susceptibility measurements of the complexes were obtained at room temperature using Gouy balance. Pure Hg[Co(SCN)₄] was synthesized used as calibration standard¹¹.

The Copper, Nickel, Cobalt and Manganus complexes are paramagnetic in nature. The magnetic moment μ_{eff} values suggest that the complexes have high spin octahedral geometry¹².

The UV-Vis spectral data of this ligand and it's metal complexes in DMF include absorption regions with band assignments data. The absorption spectrum of the ligand and metals are characterized mainly by three absorption

bands in the region 260-325 nm, which may be assigned to \rightarrow^* , $n\rightarrow^*$ and charge transfer transition, the longer wavelength band is assigned to intra molecular charge transfer, while other due to \rightarrow^* , and $n\rightarrow^*$ transition within the C=O bonds influenced by charge transfer interaction¹³.

The two absorption bands are observed in the region 15600-15890 cm^{-1} and 22225-24695 cm^{-1} , in electronic spectra of Cu(II) metal complex of the ligand may assigned to $2B_{1g} \rightarrow 2A_{1g}$ and charge transfer transition respectively¹⁴. The diffuse reflectance spectra of Ni(II) coordination compound shown two bands at 15385 and 24394 cm^{-1} assigned to the transitions $3A_{1g}(F) \rightarrow 3T_{1g}(F)$ and $3A_{1g}(F) \rightarrow 3T_{1g}(P)$ respectively. The electronic spectral data of Co(II) observed in the range 15625-16650 and around 23000 cm^{-1} may be attributed to $4T_{1g}(F) \rightarrow 4T_{1g}(P)$ and $4T_{2g}(F) \rightarrow 4T_{2g}(F)$ transitions respectively¹⁵. The absorption bands of Mn(II) complex are found to occur around 16225 cm^{-1} and 24050 cm^{-1} attributed to $6A_{1g} \rightarrow 4T_{1g}(G)$ and $6A_{1g} \rightarrow 4T_{2g}(G)$ transitions respectively.

From the study of these data it is confirmed that all the complexes possess octa hedral geometry.

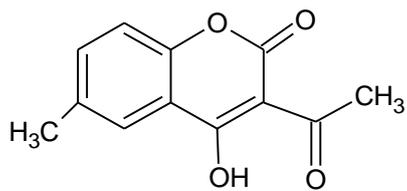
IV. CONCLUSION

The structural study of these M(II) complexes reveals that all complexes are paramagnetic and non-electrolyte in nature and having octahedral geometry. The ligand can be used as an analytical reagent for some metal ions. The synthesized metal complexes may also have some biological activities

V. REFERENCES

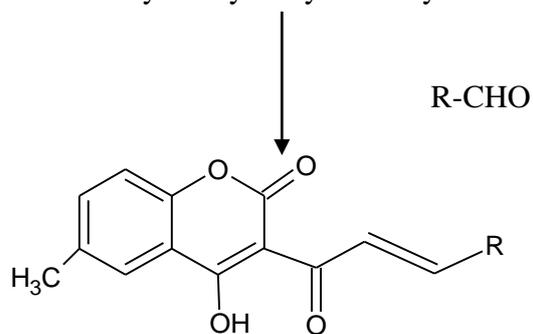
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Scheme-1



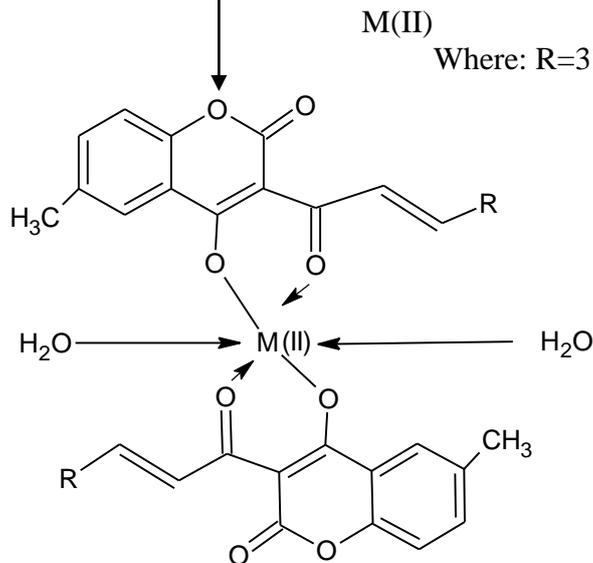
(1)

3-Acetyl-4-hydroxy-6-methyl-2-benzopyranone



(2)

3-[(3-(Aryl substituted))-prop-2-enyl]-4-hydroxy-6-methyl-2H-chromen-2-one



(3)

Bis-(3-[(3-(Aryl substituted))-prop-2-enyl]-4-hydroxy-6-methyl-2H-chromen-2-one)M(II)(H₂O)₂ complex Where, M(II): Co(II), Cu(II), Ni(II), Mn(II)

Table I. Analytical Data of Metal (II) Complexes

Sr.	Molecular formula	M. W.	% OF Carbon		% OF Hydrogen		% OF Metal		Cond. Ω^{-1}	μ Eff B.M.
			Calcd	Foun	Calcd	Foun	Calcd	Foun		
				d		d		d		
3a	$\text{Cu}[\text{C}_{19}\text{H}_{12}\text{O}_4\text{Br}]_2(\text{H}_2\text{O})_2$	867.54	52.56	52.4	3.22	3.1	7.32	7.2	7.5	1.78
3b	$\text{Ni}[\text{C}_{19}\text{H}_{12}\text{O}_4\text{Br}]_2(\text{H}_2\text{O})_2$	864.71	52.73	52.6	3.23	3.1	6.78	6.6	9.1	2.80
3c	$\text{Co}[\text{C}_{19}\text{H}_{12}\text{O}_4\text{Br}]_2(\text{H}_2\text{O})_2$	864.93	52.72	52.6	3.23	3.1	6.81	6.7	8.9	3.83
3d	$\text{Mn}[\text{C}_{19}\text{H}_{12}\text{O}_4\text{Br}]_2(\text{H}_2\text{O})_2$	860.93	52.96	52.8	3.25	3.1	6.38	6.2	10.8	5.90

Table II. Spectral Data of Metal (II) Complexes

Sr.	Metal complexes	Frequencies Cm^{-1}						
		Alkane -CH ₃	Aromatic -CH	Ketone -C=O	Alkene CH=CH	M-O Band	Ether C-O-C	Halogen C-Br
3a	$\text{Cu}[\text{C}_{19}\text{H}_{12}\text{O}_4\text{Br}]_2(\text{H}_2\text{O})_2$	2928	1511	1650	1609	590-	1112	785
		2834	1249	1710		500		
		1443	832					
		1383						
3b	$\text{Ni}[\text{C}_{19}\text{H}_{12}\text{O}_4\text{Br}]_2(\text{H}_2\text{O})_2$	2920	1562	1697	1612	590-	1130	781
		2858	821	1715		500		
		1456	1222					
		1384						
3c	$\text{Co}[\text{C}_{19}\text{H}_{12}\text{O}_4\text{Br}]_2(\text{H}_2\text{O})_2$	1922	1554	1689	1584	590-	1138	782
		2853	1222	1715		500		
		1460	833					
		1375						
3d	$\text{Mn}[\text{C}_{19}\text{H}_{12}\text{O}_4\text{Br}]_2(\text{H}_2\text{O})_2$	2933	1562	161	1602	590-	1072	782
		2858	1227	1732		500		
		1464	821					
		1383						