



SYNTHESIS AND PHYSICO-CHEMICAL STUDIES OF COMPLEX OF CO (II) WITH CINNAMYLIDENE ACETOPHENONE LIGAND (CHALCONE)

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ABSTRACT

New Mn (II), Fe (II), Co (II), Ni (II), Cu (II) and Zn (II) coordination compounds with Cinnamylidene acetophenone (Chalcone) ligand were prepared. The present study includes the synthesis and characterization of Cobalt (II) complex by elemental analysis, IR spectra, electronic spectra, magnetic studies, conductivity measurement etc. It was found that the chalcone here acts as an olefinic ligand. The spectral and magnetic data revealed the formation of high spin octahedral complex.

Keywords: Cinnamylidene acetophenone, Chalcones, Metal (II) complexes, High spin complexes, Olefinic complexes.

1. INTRODUCTION

The field of coordination chemistry is now the most active field of inorganic chemistry. The progress in studies of metal complex chemistry has been rapid, perhaps partly because of the utility and economic importance of metal chemistry, the intrinsic interest of many of the compounds, and the intellectual challenge of the structural problems to be solved.

Synthesis is one of the pillars to chemistry and there has been an enormous successful attempt in the preparative side, followed by useful characterization by various Physico - Chemical methods.

Chemists are getting attracted towards chalcones as ligands for the synthesis of metal complexes due to their easy methods of preparation, having large number of replaceable hydrogens, thereby having significant biological activities.

Chalcones are naturally occurring flavonoids consisting of two aromatic rings connected by α , β - unsaturated carbonyl groups. The presence of a α , β -unsaturated bond and the absence of the central C-ring are two specific characteristics of chalcones, making these compounds chemically different from the other flavonoids [1].

The α , β -unsaturated ketone (enone) moiety is responsible for the biological performances and also is significant in defining the geometry of coordination complexes. The enone consists of two key functionalities, a carbon-oxygen double bond (carbonyl

group) and carbon-carbon double bond adjacent to the carbonyl group [2].

Anti-bacterial, anti-inflammatory, anti-parasitic activity, antitumoral, anti-malarial, anti-HIV, antioxidant, all these important biological activities are shown by chalcones [3-6].

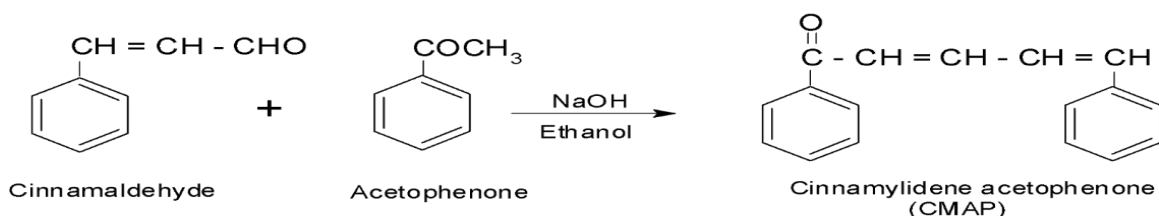
2. EXPERIMENTAL

2.1. Chemicals

The chemicals used were of analytical grade. Water and ethyl alcohol were doubly distilled.

2.2. Synthesis of ligand

The ligand used in the present work is not commercially available. However, it was prepared by the method reported earlier [7] as below. 0.16 mol of acetophenone was taken in a 500 ml beaker. To this 0.16 mol of cinnamaldehyde was added. The reaction mixture was cooled in an ice bath. To this cold solution 60 ml of ethyl alcohol and 100 ml of 0.27 mol of NaOH were added with continues stirring. Temperature of the solution was kept between 15- 30°C. Stirring was continued for about half- one hour. A lot of yellow sediment was separated out. The mixture was then allowed to stand for overnight. It was then filtered, washed several times with water and dried. The crude product was recrystallized from ethyl alcohol. It was then weighed and melting point was noted. The melting point of cinnamylidene acetophenone was found to be 101°C.



2.3. Synthesis of metal complex

Manganese acetate was dissolved in minimum quantity of ethyl alcohol and 2 to 3 drops of acetic acid was added to get its clear solutions. A hot ethanolic clear solution of ligand was gradually added to the hot ethanolic clear solution of metal salt in the molar proportion of 1:1 with constant stirring. The reaction mixture was then digested on water bath for about 2 hours. A coloured complex was filtered, washed several times with hot water and ethyl alcohol and dried in a desiccator over calcium chloride.

2.4. Analysis of the complex

2.4.1. Elemental analysis

Estimation of metal content has been carried out by classical method [8]. Estimation of elements (C,H) has been carried out at RSIC, Punjab University, Chandigarh. Elemental analysis provides information about the percentage of basic elements like carbon, hydrogen, nitrogen and sulphur, which form the skeletal backbone of the ligand and the metal complexes. For this about 0.1 to 0.2 g of complex was weighed accurately in a clean dry platinum crucible and heated strongly in air for about 5-6 hours to attain the constant reduced weight and metal was weighed in the form of the stable oxide.

2.4.2. Infrared Spectra

Infrared spectra of both ligand and complex are recorded in solid, liquid or as Nujol mull emulsions of a sample. In the solid state, the most common material used for making the pellets is KBr for studies in the range 4000-400 cm^{-1} . In the present study, infrared

spectra of ligand and its complex as KBr pellets were scanned on Shimadzu 8101 A FTIR Spectrophotometer from department of pharmacy, RTMNU, Nagpur for the range of 4000-400 cm^{-1} .

2.4.3. Electronic Spectra

In the present study, absorption spectra of ligand was recorded in DMSO on a Shimadzu UV 3101 PC spectrophotometer at department of chemistry, RTMNU, Nagpur and diffused reflectance spectra of complex was recorded on Cintra spectrophotometer at department of chemistry, RTMNU, Nagpur.

2.4.4. Molar conductance measurement

The electrical conductance measurement has been carried out in DMSO using a Toshniwal conductivity bridge and a dip type cell calibrated with KCl solution.

2.4.5. Magnetic susceptibility measurement

Magnetic susceptibility measurement at room temperature were carried out by a Gouy's method.

3. RESULTS AND DISCUSSION

3.1. Elemental analysis

In the present investigation it was observed that Co (II) forms the coordination complex with CMAP. It was pink in colour. It was insoluble in common organic solvent like benzene, CCl_4 , alcohol, chloroform, nitrobenzene etc. Molecular weight of the complex could not be determined by conventional methods like osmometry, viscometry etc., due to solubility problems. Elemental analysis (Table 1) suggests metal to ligand ratio of this complex was found to be 2: 2.

Table 1: Analytical and Physical data for the ligand and Co(II) complex

Analytical and Physical data		$\text{C}_{17}\text{H}_{14}\text{O}$ (CMAP)	$[\text{Co(II)}_2(\text{C}_{17}\text{H}_{14}\text{O})_2(\text{CH}_3\text{COO})_2] \cdot 3\text{H}_2\text{O}$
FW		234	757
Colour		Pale Yellow	Pink
% Analysis found (Cal)	Co	-	15.44 (15.57)
	C	87.12 (87.17)	59.56 (60.23)
	H	5.78 (5.98)	4.99 (5.28)
Geometry of complex		-	Octahedral
Molar Conductance $\times 10^{-4}$ mhos $\text{cm}^2 \text{mole}^{-1}$			4.81

3.2. Infrared Spectra of CMAP and its Co(II) complex

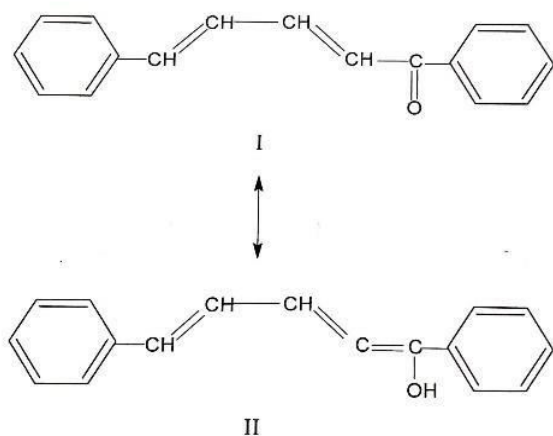
Various significant bands of CMAP and its Co(II) complex have been assigned with the aid of literature data and these assignments are given in table 2.

Table 2: Infrared Spectral data of CMAP and Co(II)-CMAP Complex

Bands	CMAP	Co - CMAP
C=C	1599 st	1456s
(COO ⁻) asym		1550s
(COO ⁻) sym		1419s
$\Delta(\text{COO})$		131
C=O	1655 st	1610vw
(-CH=CH-)trans	997 st	-
$\nu(\text{H}_2\text{O})$		3450b
$\delta(\text{H}_2\text{O})$		-
Co - O		613w
Co - C		410w

m - medium, *w* - Weak, *b* - broad, *s* - Sharp, *vw* - Very weak

It can be concluded from the table that the C=C bonds are involved in the metal- ligand bonding in Co(II) complex. IR spectrum of ligand (CMAP) displays broad medium intensity band at 3450 cm⁻¹ assignable to ν (O-H) vibration along with a strong, sharp band at 1655 cm⁻¹ assignable to C=O vibration. Therefore, it can be concluded that the ligand exists in the following tautomeric forms.



The spectrum displays a sharp and strong intensity band at 1599 cm⁻¹ assignable to C = C stretching vibration in ligand. The shifting of this band to lower frequency side 1456 cm⁻¹ in the complex suggests strong coordination through C = C bond. The coordination through C=C bond is further supported by the disappearance of a strong band at 997 cm⁻¹ corresponding to out of plane

C- H bending in conjugated trans- trans system. Nakamoto [9] reported that the carboxylate gives a strong asymmetric stretching band near 1650-1550 cm⁻¹ and a weaker stretching band near 1400 cm⁻¹. The difference in these frequencies (Δ) was correlated to the nature of metal - ligand bonding of carboxylate group. It was concluded that as the covalent character of the Metal-O bond increases; the carbonyl group becomes more asymmetrical which results in the greater difference in the stretching frequencies. As the strength of O- Metal bond increases, the symmetry of the COO⁻ group increases and the difference (Δ) decreases. In the present investigation a band observed at 1550cm⁻¹ can be assigned to asymmetric stretching of COO⁻ group and a band at 1419 cm⁻¹ can be assigned to symmetric stretching vibration of COO⁻ group. Further comparatively small separation value, Δ (COO), of 131 cm⁻¹ suggests the bidentate nature of the acetate group [10]. The IR spectrum of this metal complex displays a weak band in 410 cm⁻¹ region which can be assignable to Co-C bond [11]. Similarly, weak to medium intensity bands in 613 cm⁻¹ can be assigned to Co-O bond.

In general water of hydration absorbs at 3300-3450 cm⁻¹ [12]. A broad band observed in the metal complex at 3450 cm⁻¹ can be assigned as lattice water in this complex. IR spectra (wavenumbers are in cm⁻¹) of the ligand and Co(II) complex are shown in Fig 1 and 2 resp.

3.3. Magnetic moment and Electronic Spectra

The electronic spectra of the complex was recorded in DMSO solution. The magnetic and electronic spectral data are given in table 3.

3.4. Magnetic Property

A magnetic susceptibility of Co (II) complex was measured at room temperature using Guoy method. From the knowledge of magnetic susceptibility, magnetic moment was calculated. The magnetic moment value of Co (II) chelate was found to be closed to 4.4 B.M. The sub abnormal value of magnetic moment than that of expected spin only value might be attributed to direct Co-Co interaction indicating high spin octahedral geometry [13].

Electronic properties: Diffused reflectance spectra of Co (II) complex, under present investigation was studied in the range of 250-750 nm. This spectrum is incorporated in Fig. 4. Observed transitions and their probable assignments are shown in table 1.3. The reflectance

spectrum of this complex found to be exhibited two main absorption maxima. An unsymmetrical band near 21 kK and a band near 17.8 kK which corresponds to two spin allowed ${}^4T_{1g}(F) \rightarrow {}^4T_1(P)$ (ν_3) and ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ (ν_2) transitions. This is in accordance with the observations of Thakur and Singh [14] indicating high spin octahedral geometry to the Co (II) complex.

Table 3: Magnetic moment and Assignment of Solid State Reflectance Spectra of Co CMAP complex

μ_{eff} (B.M.)	Absorption Bands		Assignments
	nm	kK	
4.4	476	21.0	${}^4T_{1g}(F) \rightarrow {}^4T_1(P)$
	560	17.8	${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$

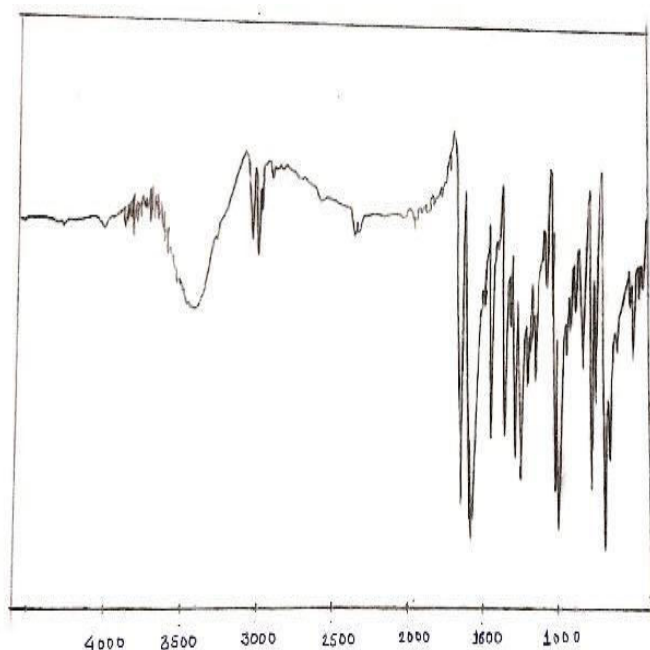


Fig. 1: IR Spectra of CMAP

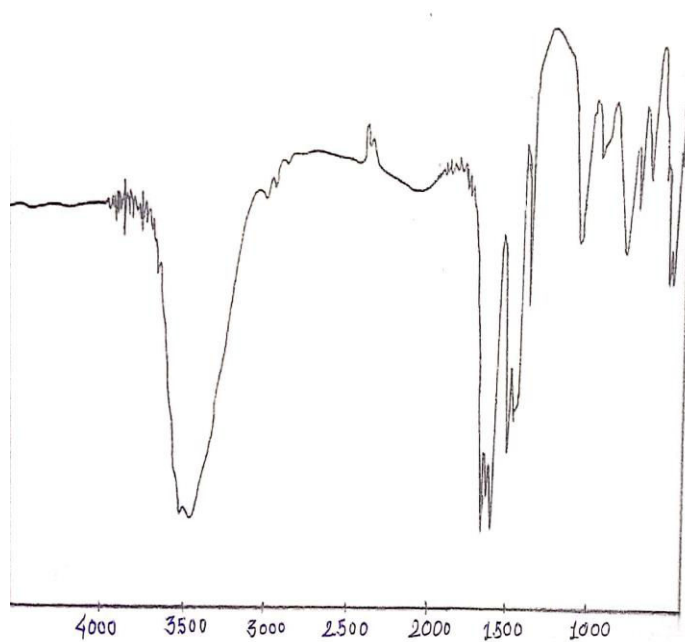


Fig. 2: IR Spectra of Co-CMAP

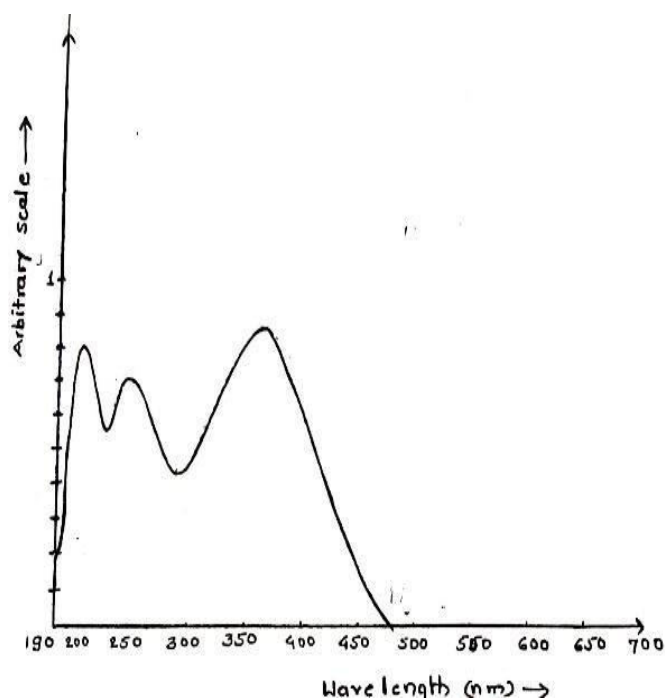


Fig. 3: Absorbance spectra of CMAP

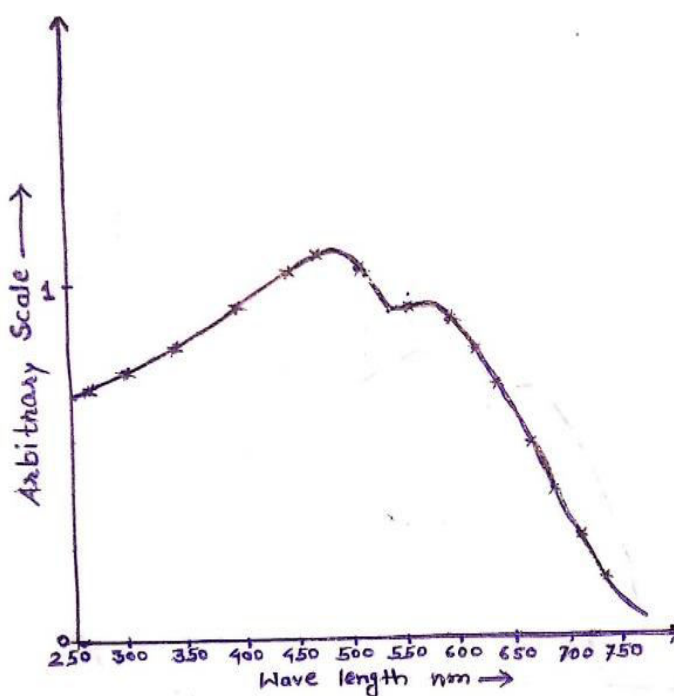


Fig. 4: Reflectance spectra of Co-CMAP Complex

4. CONCLUSION

Elemental analysis of Co (II) shows the composition 2:2 (M: L). Its non electrolytic nature has been indicated by the low values of molar conductance in DMSO. The magnetic moment value of this complex suggested to have octahedral geometry. Octahedral geometry is also supported by electronic spectra of the complex. The changes in stretching frequencies in the IR spectra of the ligand and its complex indicates that C=C bonds of ligand are involved in coordination. As well as acetate groups are also found to be involved in coordination with the metal ion. Co-oxygen and Co- Carbon bond formation is further ascertained by the appearance of new bands in the low frequency region. Thus, on the basis of elemental analysis, conductance measurements, magnetic, spectral and IR data, the complex is suggested to have octahedral stereochemistry. Higher percentage of metal in the complex indicates its dimeric nature. On the basis of above findings, the most probable structure for the complex is as shown in Fig 5.

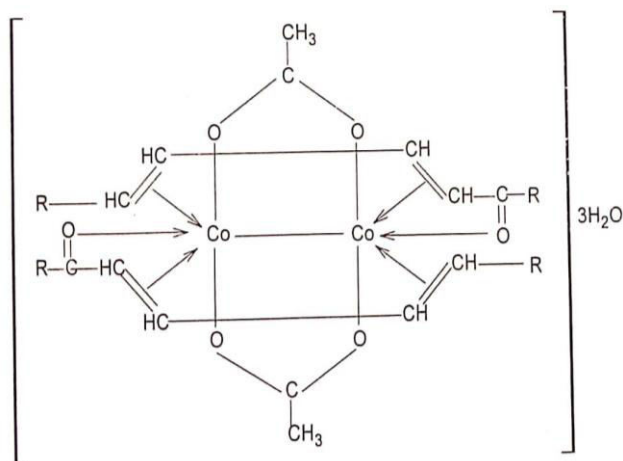


Fig. 5: Probable structure for the complex

Conflict of Interest Statement

The author declares that there is no conflict of interest.

5. REFERENCES

1. Kozłowski D, Trouillas P, Calliste C, Marsal P, Lazzaroni R, Duroux J. *The Journal of Physical Chemistry A*, 2007; **111**(6):1138-1145.
2. Johnson J, Yardily A. *Journal of Coordination Chemistry*, 2019; **72**(15):2437-2488.
3. Dalla Via L, Gia O, Chiarello G, Ferlin MG. *European Journal of Medicinal Chemistry*, 2009; **44**(7):2854-2861.
4. Kumar D, Maruthi Kumar S, Akamatsu K, Kusaka E, Harada H, Ito T. *Bioorganic & Medicinal Chemistry Letters*, 2010, **20**(13):3916-3919.
5. Carvalho L, Tavares et al, *European Journal of Medicinal Chemistry*, 2011; **46**(9): 4448-4456.
6. Aly M, Fodah H, Saleh S Y. *European Journal of Medicinal Chemistry*, 2014; **76**: 517-530.
7. Fan JF, Xiao H M. *Chinese Journal of Structural Chemistry*, 1999; **18**:348.
8. Kalsi PS. *Spectroscopy of Organic Compounds*. 5th ed. New Edge International Publishers; 2002.
9. Nakamoto K. *Infrared spectra of Inorganic and Coordination Compounds*; 3rd ed. Wiley - Interscience, New York: 1977. p. 227
10. Rana K, Shah, N R, Patil M S, Karampurwala A M, Shah J R, *Makromol Chem*, 1981; **182**:3387.
11. Pruchnic F. *Organometallic Chemistry of the Transition Elements*, 1990.
12. Mukharjee P, Jha, R.R. *Asian Journal of Chemistry*, 2006; **16**(2):793.
13. Singh N, Arora R, Chaudhari S. *Asian Journal of Chemistry*, 2004; **16**(2):654.
14. Thakur S N, Singh S B, Kumar S. *Asian Journal of Chemistry*, 2002; **14**(1):383.