

PHYSICAL, CHEMICAL AND SPECTRAL PARAMETERS OF SOME NEWLY SYNTHESIZED Cu (II), Co (II), Fe (II) COMPLEXES WITH (RS)-4-(7-CHLORO-4-QUINOLYL AMINO) PENTYLDIETHYLAMINE DIPHOSPHATE

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ABSTRACT

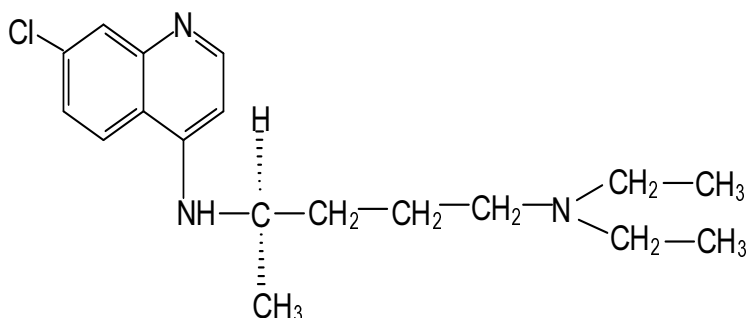
(RS)-4-(7-chloro-4-quinolyl amino) pentyldiethylamine diphosphate (CPH2) is an active chelating agent due to presence of different donor atoms. The Transition metal Complexes of Fe (II), Co (II) and Cu (II) of CPH2 have been prepared and characterized by physical and chemical methods. To determine the nature of bonding in the complexes Infrared, UV-Visible spectra's are used. The thermal decomposition was studied by TGA-DTA.

Key Words: Complexes, Infrared spectra, TGA-DTA study.

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INTRODUCTION

Generally, the chelating agents are polyfunctional molecules which have tendency to form metal chelates. Transition metal ions such as Fe (II), Co (II) and Cu (II) etc. form complexes with (RS)-4-(7-chloro-4-quinolyl amino) pentyldiethylamine diphosphate. Literature survey indicates that a metal complex plays an important role in the development of co-ordination chemistry^{1,2}. They have received much importance in recent years because of their diverse biological activity and synthetic utility. Transition metal complexes have been used in antituberculosis, antibacterial, antifungal, hypotensive and hypothermic^{3,4} reagents. Some copper complexes are known to possess anticancer⁵, antiinflammatory⁶ functions. Research study indicates that acyclic ligands containing Nitrogen, oxygen, sulphur donor atoms in their structure can act as effective chelating agent for transition metal ion⁷. It is observed that when the drugs are administered as metal chelate there is increase in activity. In the present study we have used (RS)-4-(7-Chloro-4-quinolyl amino) pentyldiethylamine diphosphate as chelating agent for the preparation of complexes. Metal complexes were synthesized by employing various methods. In the present work they are synthesized by refluxing ligand solution and metal ion solution. Structure of ligand is-



Molecular formula: Mol. wt = 515.87

EXPERIMENTAL

Preparation of [Fe (II) (CPH2)₃] HPO₄ complex

0.1 M solution of Ferrous Chloride is prepared in redistilled water. Similarly 0.3 M solution of complexing agent is prepared by dissolving it in distilled water. 25 ml of Fe (II) solution is treated with 25 ml of complexing agent solution. The pH of solution is maintained by the addition of alcoholic ammonia. The reaction mixture is refluxed for three hours using water bath. Obtained solid mass is separated by filtration through sintered glass crucible and the residue was washed with hot alcohol until the washing is free from excess of ligand. The prepared complexes were dried under vacuum desiccator's over fused calcium chloride.

Preparation of [Co (II) (CPH2)₃] HPO₄

Aqueous 25 ml of cobalt chloride (0.1 M) solution is treated with 25 ml (0.2 M) aqueous solution of ligand with constant stirring. pH of solution is maintained at 7 by the addition of alcoholic ammonia solution. The reaction mixture is refluxed in water bath for three hours using vertical water condenser. Precipitate is formed; it is filtered through sintered glass crucible. Residue was washed with hot ethanol. The residue was dried in vacuum desiccators over fused calcium chloride yield were recorded.

Preparation of [Cu (II) (CPH2)₂] HPO₄

Aqueous 25 ml (0.1 M) solution of copper chloride were prepared in redistilled water and is added drop wise to 25 ml (0.1 M) aqueous solution of (CPH2) ligand with constant stirring. Precipitate is obtained and is refluxed for 2 hours using vertical water condenser. It is filtered through sintered glass crucible, residue is washed with alcohol.

RESULTS AND DISCUSSION

Prepared Fe (II), Co (II) and Cu (II) complexes with (RS)-4-(7-chloro-4-quinolyl amino) pentyldiethylamine diphosphate were characterized by physical, Chemical and spectral analysis. Co lour decomposition point M:L ratios of the prepared complexes are measured. The elemental analysis of the prepared the metal complexes were obtained from IICT Hyderabad, observed values of nitrogen, carbon and hydrogen are matches with the theoretical values. The data regarding elemental analysis is also given in table No.1. Estimation of phosphorus is carried by volumetric method. In this method known volume of standard ammonium molybdate solution is added in known volume of decomposed metal complex solution in nitric acid medium. The volume of ammonium molybdate utilized to from phosphoammonium molybdate is determined by back titration method. The values obtained match with theoretical values.

Table-1: Analytical data and other physical properties of metal complexes

Metal Complex	Mol. weight	Co lour	D.P °C	% of yield	M.L. ratio	Molar Cond. (S cm ² mol ⁻¹)	μ _{eff}	Elemental analysis Found (Calcd)		
								C	H	N
[Fe(CPH2) ₃] HPO ₄	1110.5	Grey	429	90	1:3	11.82	5.14	58.84 (58.35)	7.42 (7.11)	11.25 (11.34)
[Co(CPH2) ₃] HPO ₄	1113.5	Violet	391	78.4	1:3	9.96	3.69	58.87 (58.19)	7.52 (7.09)	11.06 (11.31)
[Cu(CPH2) ₂]HPO ₄	798.5	Light peacock blue	376	87.2	1:2	8.72	1.97	54.40 (54.10)	6.73 (6.63)	10.62 (10.51)

TGA-DTA Study

TGA-DTA study metal complexes of Fe (II), Co (II) and Cu (II) with CPH2 were carried out by thermo gravimetric analysis from ambient temperature to 1000°C in nitrogen atmosphere. Thermal analysis^{9,10} techniques which are dependence on the parameters of any physical and chemical property of a substance on temperature measured. TGA and DTA of samples were obtained by using the Instrument TA instrument USA, Model, -SDT – 2960 simultaneous ESC-TGA range 1500°C.

Thermal study of Fe (II) CPH2 complex

Fe (II) CPH2 complex is thermally stable up to 250°C indicating they are not hydrated. This complex shows two stages during thermal decomposition. The first step of decomposition occurs in the range 250 – 527°C with the loss of 58.29 percent indicating decomposition of some organic part of complex. The second stage of decomposition of occurs in the temperature 527-807°C shows the loss of remaining part of complex corresponds to loss 27.19 percent. Finally from 807-1000°C temperature horizontal nature of thermogram is obtained indicating the formation of metal oxide.

Table-2:Thermo gravimetric results metal ion complexes

Complex	Total loss		Temperature in °C	Loss (%)
	Theoretical	Experiment		
[Fe (CPH2) ₃] HPO ₄	85.60	85.39	250 – 527 527 – 807 807– 1000	58.29 27.10 14.51 (residue) 14.40 (calculate)
[Co (CPH2) ₃] HPO ₄	93.27	93.31	225 – 400 400 – 805 805-1000	38.02 55.29 6.63 (residue) 6.73 (calculate)
[Cu (CPH2) ₂] HPO ₄	90.05	89.27	225 – 525 525 – 810 810-1000	54.43 34.84 10.49 (residue) 9.95 (calculate)

Thermo gravimetric study of [Co (II) CPH₂] complex

There is no loss up to 225°C suggesting absence of lattice water^{11, 12}. The weight loss started slowly after this temperature. The first weight loss was encountered in the temperature range 225-400°C, was 38.02 percent indicating decomposition of some organic part of complex. The presence of exothermic peak in the same region suggests bond breaking. This decomposition of the organic part of complex continues, till metal oxide is remaining in the form of cobalt oxide.

Thermogravimetric study of [Cu (II) CPH₂] complex

The thermogram of Cu (II) complex indicates that, the complex remains stable up to 225°C indicating absence of coordinated water. Above this temperature complex starts decomposition. This decomposition occurs in two stages. First stage of decomposition occurs in the temperature rang 225 to 525°C and second stage decomposition in the temperature range 525-810°C. The total mass loss in this temperature range was found to be 89.27 percent. Finally metal oxide is formed at the temperature 810°C corresponding to weight 10.49 percent identical with theoretical value 10.27 of copper oxide. Thermogravimetric results of Fe (II), Co (II) and Cu (II) metal ion complexes are given in the table No.2

Infra red spectrum study of complexes

IR spectra of complexes were obtained from sophisticated Analytical Instrument facility, Indian Institute of Technology, Chennai. Absorption bands are summarized in table No. 3. The comparison of IR spectral data of Fe (II), Co (II) and Cu (II) complexes with ligand helps in determining the bonding pattern in the complexes.

Table- 3: Infra Red spectral studies of ligand (CPH2) and their Fe (II), Co (II) and Cu (II) complexes.

Compound	ν (N-H)	ν (C-H)	ν (C-N)	ν (C=C) Aromatic	ν (M-N)
CPH2	3430	2943	1092	1614	-
[Fe (CPH2) ₃] HPO ₄	3391	3200-2900	1067	1630	461
[Co(CPH2) ₃] HPO ₄	3412	3155	1015	1643	453
[Cu (CPH2) ₂] HPO ₄	3420	3000-2795	1064	1635	449

In the IR spectrum of ligand strong band is obtained in the region at 3430 cm^{-1} which is assigned to $\nu(\text{N-H})$ stretching vibration. The more intense and sharp band observed at 2943 cm^{-1} due to $\nu(\text{C-H})$ stretching vibration¹³. A relatively strong band appears in the region 1614 cm^{-1} and 1092 cm^{-1} due to $\nu(\text{C}=\text{C})$ and $\nu(\text{C-N})$ stretching vibration respectively.

IR spectra of [Fe (CPH₂)₃] HPO₄ complex

In the IR spectra of ligand $\nu(\text{N-H})$ band observed at 3430 cm^{-1} is shifted toward lower frequency and observed at 3391 cm^{-1} indicates participation of nitrogen atom during chelating. Ligand exhibits $\nu(\text{C-N})$ stretching vibration at 1092 cm^{-1} , in the metal complex this band appears at 1067 cm^{-1} indicates involvement of nitrogen in coordination. In the ligand aromatic $\nu(\text{C}=\text{C})$ appears as an intense band around 1614 cm^{-1} , this band shifted due to stretching and appears at 1630 cm^{-1} support formation of complex compound. Further $\nu(\text{C-H})$ stretching vibration in ligand appears at 2943 cm^{-1} and this band merge in the range $3200\text{-}2900\text{ cm}^{-1}$. The additional band around 461 cm^{-1} assigned to $\nu(\text{M-N})$ stretching vibration. This band is not observed in ligand.

IR spectra of [Co (CPH₂)₃] HPO₄ complex

Ligand show band in the region at 3430 cm^{-1} due to $\nu(\text{N-H})$ stretching vibration. In the spectra of complex this broad band shifted and appears at 3412 cm^{-1} indicating involvement of nitrogen atom in bonding with metal ion. The ligand shows band at 1092 cm^{-1} due to $\nu(\text{C-N})$ stretching vibrations. This band in metal complex is considerably lowered to 1015 cm^{-1} indicating involvement of nitrogen in the complex formation. $\nu(\text{C}=\text{C})$ aromatic stretching vibration in complex appears at 1630 cm^{-1} . This band in ligand appears at 1614 cm^{-1} . The $\nu(\text{C-H})$ stretching vibration in ligand appears at 2943 cm^{-1} . Due to complex formation this broad band appears in the region 3155 cm^{-1} . The weak band appearing in the region at 453 cm^{-1} can be assigned to $\nu(\text{M-N})$ stretching vibration^{14, 15}.

IR spectra of [Cu (CPH₂)₂] HPO₄ complex

The IR spectra of ligand display a band at 3430 cm^{-1} which is due to $\nu(\text{N-H})$ group. This band shifted towards lower frequency and appears at 3420 cm^{-1} . The disappearance of this band indicates involvement in co-ordination with the metal ion under study. The $\nu(\text{C-N})$ mode in complex is shifted to 1064 cm^{-1} in case of Cu (II) complex from the ligand value 1092 cm^{-1} . In the Cu (II) complex both the nitrogen $\nu(\text{NH}_2)$, $\nu(\equiv\text{N})$ may be involved in bonding to the metal atom. Similarly $\nu(\text{C}=\text{C})$ of aromatic ring observed in ligand at 1614 cm^{-1} and is shifted to 1635 cm^{-1} in complex due to complex formation. $\nu(\text{C-H})$ in ligand observed at 2943 cm^{-1} is now merge in the complex in the region $3000\text{-}2795\text{ cm}^{-1}$. The band around 449 cm^{-1} Cu (II) complexes attributed to $\nu(\text{M-N})$.

Electronic spectral study

Electronic spectral data of Fe (II), Co (II) and Cu (II) are shown in the table No.4

Table-4: Electronic spectral data and magnetic moment value of Fe (II), Co (II) and Cu (II) complexes

Compound	Wavelength cm^{-1}	Transition	Magnetic Moment BM
[Fe (CPH ₂) ₃] HPO ₄	12547, 28328	${}^5\text{T}_{2g} \rightarrow {}^5\text{E}_g$, charge transfer	5.14
[Co (CPH ₂) ₃] HPO ₄	14880, 17211, 19230	${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}$, ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{A}_{2g}(\text{F})$, ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})$	3.69
[Cu (CPH ₂) ₂] HPO ₄	20242, 25906, 39036	${}^4\text{A}_2 \rightarrow {}^4\text{T}_1(\text{p})$, charge transfer transition	1.97

For the Fe (II) complex a broad band is observed at 12547 cm^{-1} corresponds to the ${}^5\text{T}_{2g} \rightarrow {}^5\text{E}_g$ transition. The absorption band observed at 28328 cm^{-1} due to charge transfer transition. These bands are specific to octahedral geometry of metal complex. The magnetic moment determined experimentally is of 5.14 BM which support octahedral geometry of Fe (II) complex.

In the electronic spectra of Co(II) complex three band are observed at 14880, 17211 and 19230 cm^{-1} are assignable to the transitions ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$, ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ and ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ receptively. These transitions are characteristics of Co (II) ion in an octahedral coordination and this geometry is supported by value of magnetic moment 3.69 BM.

In the Cu(II) complex two absorption maxima at 20242 cm^{-1} and 25906 cm^{-1} which corresponds to ${}^4A_2 \rightarrow {}^4T_1(P)$ and charge transfer transition respectively. These bands are specific to Cu (II) ion in tetrahedral coordination. The geometry is further supported by magnetic moment value 1.97 B.M.

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