

α, α -DIMETHYL-4-[1-HYDROXY-4-[4 (HYDROXYDIPHENYLMETHYL)-1-PIPERIDINYL]BUTYL] BENZENEACETIC ACID HYDROCHLORIDE AS A CHELATING AGENT IN SOME METAL COMPLEX

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ABSTRACT

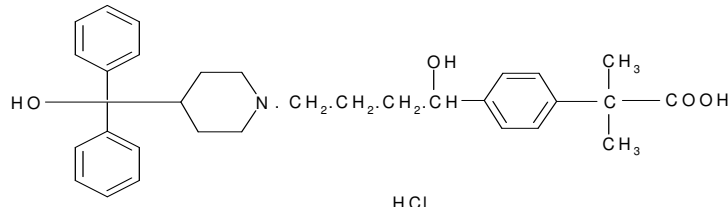
α, α -Dimethyl-4-[1-hydroxy-4-[4-(hydroxydiphenylmethyl)-1-piperidiny]butyl] benzeneacetic acid hydrochloride treated with metal ion solutions of Fe(II), CO(II), Cu(II) using different experimental conditions, there is formation of metal complexes. After the purification of metal complexes, they are characterized by analytical, thermal, magnetic, Infrared, X-ray diffraction methods. After analysis of the metal complexes, expected geometry and structure of prepared metal complexes were determined.

Key Words:- synthesis of Fe (II), Co (II), Cu (II) metal complexes, Analytical, IR, XRD study.

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INTRODUCTION

α, α - Dimethyl-4- [1-hydroxy-4-[4- (hydroxydiphenylmethyl) -1-piperidiny] butyl]benzeneacetic acid hydrochloride (DHB) having molecular formula $C_{32}H_{39}NO_4.HCl$.



Considering the presence of oxygen donor atom we have used α, α -Dimethyl-4-[1-hydroxy-4-[4-(hydroxydiphenylmethyl)-1-piperidiny] butyl]benzeneacetic acid hydrochloride (DHB) as a complexing agent to prepare the metal complexes of Fe(II), Co(II), Cu(II). Presence of oxygen donor atom provides a magnitude of bonding possibilities¹. The pH of compound is acidic. When the solution of this compound is treated with transition metal ion solution at different pH and different laboratory conditions, the precipitate appears indicating the formation of complex. The prepared complexes are filtered, purified and washed with different solvents. Precipitate is dried in oven at 70 to 80⁰C .

The physical parameters of the prepared metal complexes like colour, yield, nature, decomposition point, M:L ratio, conductance, magnetic susceptibility were recorded. Also chemical parameters like estimation of metal ions, estimation of chloride were carried out by standard methods².

The coordinate bonding between donor atom and the metal ion is interpreted by IR spectra³. The electronic spectrum of the complexes also used to find out different transitions. X-ray diffraction method is used to find out the crystal structure of the prepared complexes. After considering physical, chemical, spectral parameters, the proposed structure of prepared complexes is given.

EXPERIMENTAL

0.1 M alcoholic solution (60 ml) of Metal salt were mixed with 0.1 M alcoholic solution (120 ml) of DHB in round bottom flask. The pH of reaction mixture is adjusted to 7.2 by adding alcoholic ammonia.

The long vertical water condenser is connected to water bath and the round bottom flask containing reaction mixture kept in water bath for refluxion. It is refluxed for 3 hours. The precipitate appears and it is filtered through ordinary filter paper and is washed with alcohol for three times. Obtained product is dried and stored in sample glass bottle.

RESULTS AND DISCUSSION

Characterization of the prepared complexes

After preparation of metal complexes yield physical characterization like nature, colour, decomposition point μ_{eff} of the prepared complexes are measured.

The M:L ratio of prepared complexes were determined by heating known weight of complex slowly at beginning later on strong flame. To determine M:L ratio, TGA graphs are also used. Elemental analysis of the prepared complexes was obtained from IICT Hyderabad. The results of elemental analysis are given in the table For Estimation of chloride vollards method is used². Non coordinated water present in the metal complexes was recorded by keeping the known weight of complex in previously weighed crucible in oven at 80°C for one hour. The difference in weight gives the amount of non coordinated water in the complex.

Thermal study of complexes

Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) techniques are used to determine the decomposition nature of the complex. The samples were heated in the temperature ranges room tempt-1000°C. The range of temperature and the experimental and calculated mass losses of the decomposition reactions are given in the Table-2.

Thermal study of Fe (II) complex

Thermogram of Fe (II) complex shows weight loss corresponds to one mole of hydrated water molecule in the temperature range 45-98°C. After this Fe (II) complex shows sharp decrease in weight indicating decomposition of organic part of complex corresponds to 82.88 percent which is comparative with the theoretical value. In the temperature 827-1000°C horizontal nature of thermograph indicates stable residual metal oxide as Fe₂O₃⁴. The percentage weight of metal oxide was found to be 15.08 percent which is close to theoretical value 14.92.

Thermal study of Co (II) complex

TGA of Co (II) complex shows weight loss corresponding to one mole of lattice water in temperature range 50-96°C. Decomposition beyond this temperature in the range 96 – 231°C corresponds to mass loss of 6.83% in the TG curve assigned to expulsion of two water molecules from the complex⁵. This temperature range also indicates that they are present in coordination sphere. The decomposition occurs in the temperature 231-800°C indicates the loss of organic part content of complex. This loss is found to be 78.79percent. The end product of decomposition is formation of CoO, weight corresponds to 11.27 percent which is equal to theoretical value 11.50.

Thermal study of Cu(II) complex

The first step of decomposition in the case of Cu (II) complex occurs in the temperature range 50-89°C, Corresponds to mass loss 2.89%. This loss corresponds to loss of one mole of lattice water. The decomposition of organic part of complex occurring with weight loss continues up to 790°C. The total loss in this temperature range is found to be 83.98 percent. It is clear that the final product of decomposition as computed from thermogram corresponds to metal oxide 12.57percent⁶. It is in agreement with theoretical value.

IR spectra of metal complex

The IR of ligand and its complexes with Fe(II), Co(II), Cu(II) metal ions were obtained from SAIF, IIT ,Chennai. The IR spectra of ligand is compared with the metal complexes. There are changes in IR spectra of metal complexes gives donor site of ligand. Infra Red spectral data of ligand (DHB) and metal complexes are given in the Table-3.

IR spectrum of ligand shows strong band at 3297cm^{-1} attributed to $\nu(\text{O-H})$ alcoholic stretching vibration. Intense band at 1705cm^{-1} attributed to stretching vibrations of $\nu(\text{C=O})$. Ligand also exhibits strong bands at 2936cm^{-1} , 1167cm^{-1} assigned to stretching vibration of $\nu(\text{C-H})$ and $\nu(\text{C-N})$ groups⁷ respectively.

Study of IR spectra of Fe (II) complex

IR spectra of Fe (II) complex reveals that, the band observed in the range $3000\text{-}3297\text{cm}^{-1}$ due to stretching vibration of primary and secondary alcoholic $\nu(\text{O-H})$ group in ligand and is shifted in complex towards higher stretching vibration appears at 3407cm^{-1} attributed to involvement in coordinate bond. The weak band in ligand at 2946cm^{-1} due to $\nu(\text{O-H})$ of carboxylic group is shifted in complex and merge in the range $3407\text{-}2950\text{cm}^{-1}$ indicated participation in coordination⁸. New band in complex observed at 455cm^{-1} indicating formation of $\nu(\text{M-O})$ bond.

If the comparison is made between spectrum of ligand and Co (II) complex gives very useful information. A broad band observed at $3000\text{-}3297\text{cm}^{-1}$ due to primary and secondary $\nu(\text{O-H})$ group shifted to higher frequency appears at 3402cm^{-1} indicating coordination of alcoholic (OH). Similarly band at 2946cm^{-1} in ligand due to carboxylic $\nu(\text{OH})$ shifted appear at 3407cm^{-1} indicates involvement in coordination. Formation of $\nu(\text{M-O})$ ⁹ bond in complex is supported by the appearance of band at 445cm^{-1} . Similarly comparison is made between IR spectra of ligand and Cu (II) complex. Ligand exhibits broad band in the region $3000\text{-}3297\text{cm}^{-1}$ which can be assigned to $\nu(\text{O-H})$ stretching vibration which may be due to intermolecular hydrogen bonding. This broad in complex is shifted and appears in at $3640\text{-}3400\text{cm}^{-1}$ region¹⁰. Band at 449cm^{-1} due to $\nu(\text{Cu-O})$ band¹¹.

The stretching vibration in the ligand appears at 1705cm^{-1} due to carbonyl group¹². These vibrating bands were not observed in complex in Fe (II), Co (II) and Cu (II) similarly $\nu(\text{C-N})$ band stretching in ligand is at 1167cm^{-1} and in all complex they observed in the range $1165\text{-}1087\text{cm}^{-1}$. In case of Co (II) and Cu (II) complexes band observed at 322 and 347cm^{-1} respectively in the far infra red spectrum is due to $\nu(\text{M-Cl})$ vibration which indicates the presence of chloride bridge¹³.

X-ray diffraction study

X-ray diffraction study of Fe (II), Co (II) and Cu (II) were scanned in the range $2\theta = 10 - 80^\circ\text{C}$. With the help of X-ray diffraction technique it is possible as certain the special arrangement of the structural units substance in crystalline state and employed in investigating the interior of a crystal. Value 'd' is calculated by using Bragg's equation¹⁸ $n\lambda = 2d \sin \theta$

The crystal lattice parameters and complete powder diffractogram data Fe (II) complex is given in the Table-4.

From the cell data and crystal lattice parameters one can conclude that Fe (II) complex is having monoclinic crystal system.

Cell data and crystal lattice parameter of Cu (II) complex attributed to Orthorhombic crystal system¹⁴.

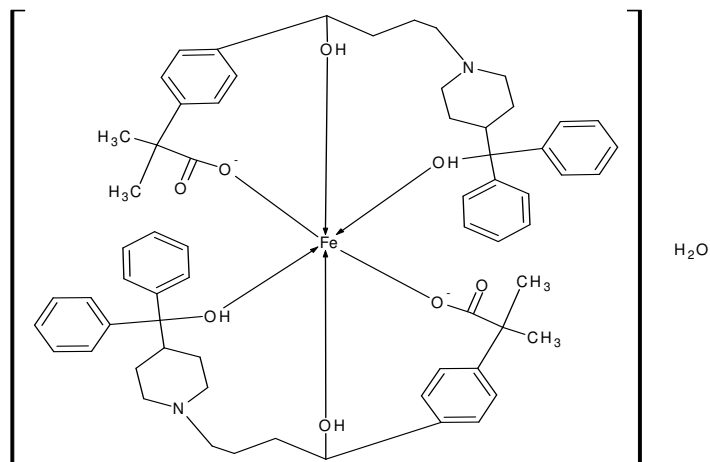
CONCLUSION

On the basis of crystal lattice parameters, analytical, spectral data of Fe (II), Co (II) and Cu (II) complex, the proposed structure for complexes are as shown in following figure.

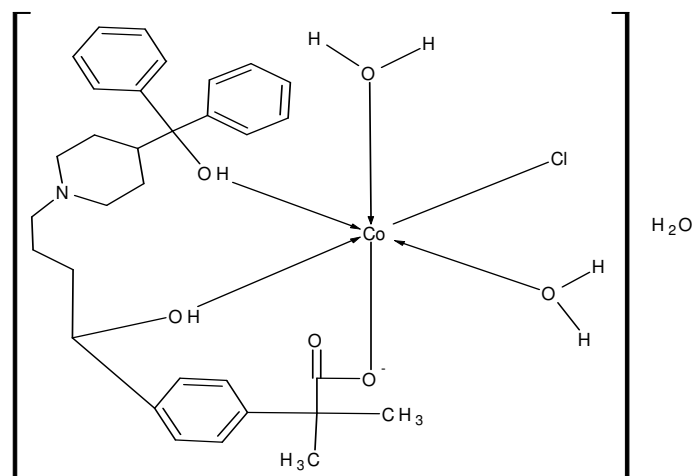
Table-1: Analytical data and other physical properties of metal complexes.

Metal Complex	Mol. Wt.	Colour	D.P $^\circ\text{C}$	% of yield	M.L. ration	Molar Cond. ($\text{S cm}^2 \text{mol}^{-1}$)	μ eff BM	Elemental analysis Found (Calcd)		
								C	H	N
[Fe (DHB) ₂] H ₂ O	1074	Orange	247	79	1:1	12.56	4.93	70.64 (70.50)	7.08 (7.26)	2.61 (2.60)
[Co(DHB)Cl 2H ₂ O].H ₂ O	647.5	Light green	259	87	1:1	14.96	3.85	59.82 (59.30)	6.83 (6.64)	2.41 (2.16)

[Cu(DHB)Cl] H ₂ O	616	Light green	281	85	1:1	16.30	2.15	62.02 (62.33)	6.73 (6.33)	2.46 (2.27)
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Bis α,α -Dimethyl-4-[1-hydroxy-4-[4-(hydroxydiphenylmethyl)-1-piperidinyl]butyl]benzeneacetic acid hydrochloride (DHB) Fe (II) complex [Molecular formula = C₆₄H₇₆N₂O₉.Fe; Mol. wt. = 1072]



Monochloro α,α -Dimethyl-4-[1-hydroxy-4-[4-(hydroxydiphenylmethyl)-1-piperidinyl]butyl]benzeneacetic acid hydrochloride (DHB) diaquo Co (II) complex. [Molecular formula C₃₂H₄₃NO₇ Cl Co; Mol. wt. = 647.5]

Table-2: Thermoanalytical results of Fe (II), Co (II), Cu (II) complexes

Complex	Total loss		Tempt. Range °C	Loss (%)
	Theoretic al	Expt.		
[Fe (DHB) ₂].H ₂ O	85.08	84.82	45-98 98-827 827-1000	1.92 82.88 15.08(residue) 14.92 (calcd.)
[Co (DHB) Cl 2H ₂ O]. H ₂ O	88.50	88.60	50-96 96-231 231-800 800-1000	2.98 6.83 78.79 11.27 (residue) 11.50 (calcd.)
[Cu (DHB).Cl] H ₂ O	87.10	86.91	50-89	2.89 (2.93)

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