

SYNTHESIS AND CHARACTERIZATION OF BINUCLEAR Fe(III) CHELATES OF 2,4-DIHYDROXY-5-ACETYLACETOPHENONEDIOXIME

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Chelates of Iron (III) of the type $[\text{Fe}_2(\text{DAAPDO})(\text{L}_1)_4\text{Cl}_4]$ where $\text{L}_1 =$ pyridine, H_2O , aniline, methylamine and triphenylphosphine has been synthesized by the interaction of Iron (III) with the ligand (DAAPDO) i.e., 2,4-dihydroxy -5-acetophenonedioxime in 2:1 molar ratio in refluxing methanol solution. The resulting products have been characterized by elemental analysis and spectral analysis as well as magnetic susceptibility measurements. Structures of the Iron (III) complexes are also proposed the unusual yet stable bimetallic centered complexes.

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1. Introduction

Iron (III) chelates¹ of oxime and substituted pyridine, triphenylphosphine, aniline, amine are of great importance due to their biological, pharmacological, clinical and analytical applications. Iron (III) ion in aqueous solution is its tendency to hydrolyze and to form stable complexes. Some of the most interesting complexes of O, N donors are formed by salen (N,N^1 – ethylene bis (salicylideneiminato)) and related ligands being prepared^{2,3}. The coordinating nature of metal with an organic moiety forming complexes depends upon the structural and electronic factors in the ligand. Nitrogen atoms easily coordinate to the metal ion because of its basic nature. Iron (III) complexes of the ligands 2,4-dihydroxy-5-acetophenonedioxime⁴ $[\text{Fe}_2(\text{DAAPDO})(\text{L}_1)_4\text{Cl}_4]$ are synthesized and characterized with the help of conductivity, magnetic susceptibility, infrared spectra and elemental analysis are undertaken. The infrared spectra will give an idea of the geometry of the complexes.

2. Materials and methods

All the chemicals used and solvents were of A.R. (B.D.H) grade. The solvents used at various stages in this work were purified by the usual procedures.⁵ Elemental analysis (C H N O) were carried out RSIC, CDRI, Lucknow, India. Iron content of the complexes was estimated by incinerating the complex to iron oxide. Molar conductance of the complexes were done in nitromethane solution using platinised platinum electrode (cell constant 0.1). Electronic absorption spectra of the complexes were recorded in the UV – Visible region on a systronics 107 spectrophotometer, Magnetic moment using vibrating magnetometers and IR (200-4000 cm^{-1}) on perkin Elmer 783 doublebeam IR spectrophotometer at RSIC, IIT, Madras.

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2.1 Synthesis of ligand ⁶

Anhydrous Zinc (II) Chloride was dissolved in acetic anhydride and dry resorcinol was added, boiled for 15 min., at about 140°C, a viscous oily red solution formed are allowed to cool and 1:1 HCl was added, an orange red crystalline was separates out. The product obtained is 2,4-dihydroxy-5-acetophenone (96.5%pure, m.pt.,180°C). The ligand (DAAPDO) 2,4-dihydroxy-5-acetophenonedioxime⁶ were synthesized by refluxing (for 8 hrs)a mixture of equal amount of the above prepared product 2,4-dihydroxy -5-acetophenone and hydroxylamine hydrochloride in methanol medium on water bath. The resulting product further recrystallised using alcohol (m.pt.181 °C).

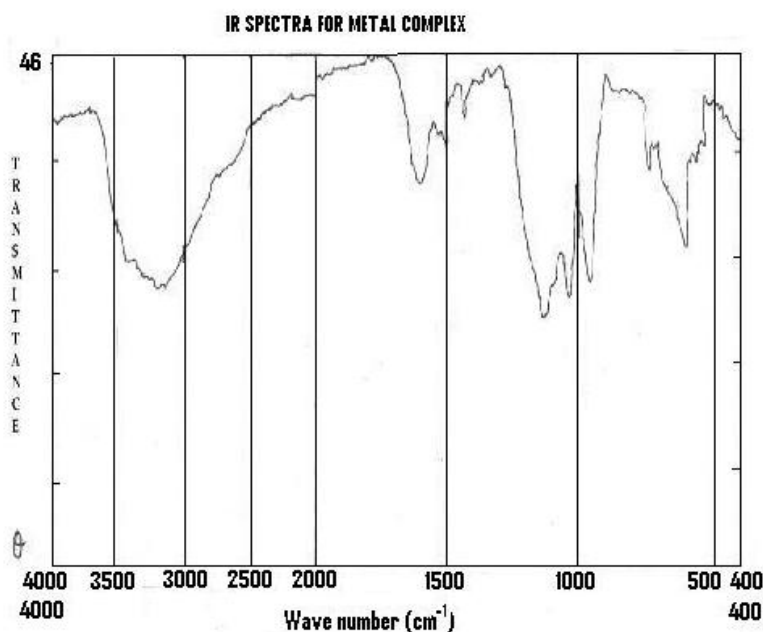


Fig. 1 The IR spectra for the metal complex

2.2 Synthesis of Complexes

[(μ -2,4-Dihydroxo-5-Acetylacetophenonedioximato)Bis(diaquadichloroiron(III))]

$[\text{Fe}_2(\text{DAAPDO})(\text{L}_1)_4\text{Cl}_4]$ where $\text{L}_1 = \text{H}_2\text{O}$ were prepared by the reaction mixture of Ferric Chloride and corresponding ligands (DAAPDO) in 2:1 molar ratio in 20ml methanol and refluxed for 30 minutes, maintained pH(\sim 10), filtered and washed with water and the complex was dried over anhydrous calcium chloride in vacuum. (Yield = 63%). This complex was dissolved in methanol and substituted excess of corresponding ligands $\text{L}_1 = \text{C}_6\text{H}_5\text{NH}_2$, CH_3NH_2 , $\text{P}\Phi_3$ in 1:2 molar ratio followed by the above procedure, obtained the Binuclear Iron (III)complexes of $[\text{Fe}_2(\text{DAAPDO})(\text{L}_1)_4\text{Cl}_4]$ where $\text{L}_1 = \text{C}_6\text{H}_5\text{NH}_2$, CH_3NH_2 , $\text{P}\Phi_3$ respectively. All the synthetic and analytical details are given in table.1. The structures of representative complexes are given in Fig 2.

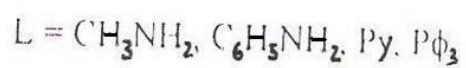
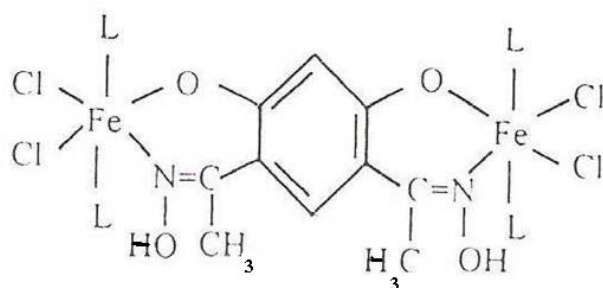
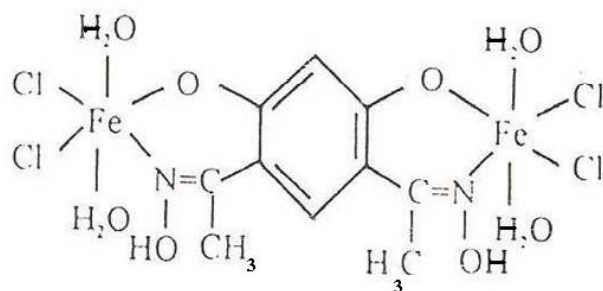
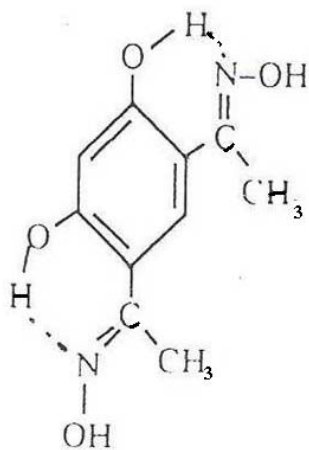
(1) 2,4-dihydroxy-5-acetylphenonedioxime (DAAPDOH₂)

Fig. 2 The DAAPDOH₂ complex

3. Results and discussion

The new binuclear chelates¹ have been synthesized by the reaction of FeCl₃ with the corresponding ligand (L₁) in methanol and the reaction product obtained are represented by the schematic Fig.2.

The ligand DAAPDO are solid and orange colour (Table.2). These complexes are microcrystalline, non-hygroscopic, air stable solids and colour ranges from orange to brown. The complexes are homogenous on TLC and 2D paper chromatography. They are soluble in H₂O, methanol, acetone, methylenechloride, CCl₄, chloroform, acetone, methanol. The complexes do not melt or decomposed upto 225^oC. The yield varied 60-70%. Molar conductance of the complexes (in nitro methane)⁷ and solubility reveals their non electrolytic nature. A plot of yield % Vs the molar excess of the ligand reveals the metal- ligand stoichiometry of the complexes.

Table.1. Infrared Spectral Data

SAMPLE	Significant IR bands (cm ⁻¹)
DAAPDOH ₂	3400(s),3150(w),1650(s), 1510(s),1350(s),900(w)
[Fe ₂ DAAPDO(H ₂ O) ₄ Cl ₄]	3300(b),1610(s),1310(s),1450(m)
[Fe ₂ DAAPDO(CH ₃ NH ₂) ₄ Cl ₄]	3300(b),1610(s),1310(s),1450(m), 1050(s),950(s),850(s),700(s)
[Fe ₂ DAAPDO(C ₆ H ₅ NH ₂) ₄ Cl ₄]	3300(b),1610(s),1310(s),1450(m), 1250(m),780(s),850(m),600(s)
[Fe ₂ DAAPDO(Py) ₄ Cl ₄]	3300(b),1620(s),1450(m), 640(s),610(m)
[Fe ₂ DAAPDO(PΦ ₃) ₄ Cl ₄]	3300(b),1620(s),750(m),530(s)

DAAPDOH₂ - 2,4 – dihydroxy -5- acetylacetophenone dioxime

Py - pyridine

PΦ₃ - triphenyl phosphine

3.1 Magnetic moment

The complexes in the present work shows the magnetic moment⁸ in the range 2.2- 2.7 B.M. (table.2) and suggesting the complexes are low spin in an octahedral coordination sphere⁹.

Table.2. Physical and electronic spectral data.

Sample	colour	M.pt °C	M _{eff} (BM)	Λ _m in Nitromethane mho cm ⁻¹ /equiv.	v _{max} cm ⁻¹
DAAPDOH ₂	Orange	182	-	-	-
[Fe ₂ DAAPDO(H ₂ O) ₄ Cl ₄]	Reddish brown	224	2.5	8	22000
[Fe ₂ DAAPDO(CH ₃ NH ₂) ₄ Cl ₄]	Brown	226	2.2	11	22200, 36400
[Fe ₂ DAAPDO(C ₆ H ₅ NH ₂) ₄ Cl ₄]	Dark brown	222	2.7	14	22600, 36100
[Fe ₂ DAAPDO(Py) ₄ Cl ₄]	Brown	196	2.4	12	22800, 36300
[Fe ₂ DAAPDO(PΦ ₃) ₄ Cl ₄]	Light brown	198	2.5	9	22700, 36200

3.2 Electronic spectra

The electronic spectral data for the complexes which are soluble in common solvents show a broad band in the range 20000-23000 cm^{-1} and the ϵ value in the range 100 (table.2). There is no any significant change in the band among the different complexes. The absence of multiplicity of bands indirectly suggests the absence of the tetragonal geometry and implies Iron (III) are octahedral complexes. In addition to that, Triphenylphosphine ($\text{P}\Phi_3$) existing as a co-ligand are proved by the strong absorption^{10,11} in the range of 260 cm^{-1} due to $\pi - \pi^*$ transition of phenyl ring.

3.3 IR spectral studies

The IR Spectra of the ligand DAAPDO shows band range 1650-1600 cm^{-1} (ν C=N) and for the complexes $\sim 1650 \text{ cm}^{-1}$ revealed the coordination of nitrogen atom of oxime to the Fe^{3+} ion.(table.3). The stretching frequency region of the ligand observed strong and broad bands at around 3000 cm^{-1} due to hydrogen bonding between the phenolic -OH group and the oximic -OH group¹². In complexes these bands are absent shows replacement of hydrogen of phenolic -OH and the lowering of C=N frequency due to the $\pi -$ electron back donation of metal ion to the nitrogen atom leads to the lowering of the ionic character of C=N of oxime¹³. A typical vibration due to pyridine^{14,15} and triphenyl phosphine¹⁶ are observed in the complexation when these monodentate ligands are present as co-ligand, lack of IR band in the finger print region can also assigned to be indication of a symmetrical structure of the complexes. The IR spectra was not recorded below 400 cm^{-1} where normally for the direct linkages M-L vibration¹⁷ shows there is no attempt is made for direct linkages. The IR spectral datas are given in the Fig.1.

4. Conclusions

A series of new iron (III) complexes of the type $[\text{Fe}_2(\text{DAAPDO})(\text{L}_1)_4\text{Cl}_4]$ where DAAPDO is the quadridentate 2,4-dihydroxy-5-acetylacetophenonedioxime⁴ derived from the mixture of Resacetophenone and hydroxylamine hydrochloride and L_1 represents pyridine, H_2O , aniline, methylamine and triphenylphosphine have been synthesized. The molar conductivity measurements pointed out to the non-electrolytic nature of the complexes.

The infrared spectra support the facts that the nitrogen atom group and the oxygen atom of the phenolic -OH group are bonded to Fe (III).In all the complexes the coordination number of iron is six, corresponding to octahedral complex. Another significant conclusion from this study points out that the ligands have two symmetrical oxygen atom^{18,19} of phenolic -OH in 2,4 position and two symmetrical nitrogen atom of oximic group in 1,5 position ligating the two Fe^{3+} ions forming in effect of binuclear complexes²⁰. From the electronic spectrum and magnetic moment, it can be shown that the complexes formed are low spin octahedral structures.

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