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SYNTHESIS AND CHARECTERIZATION OF IRON (II) COMPLEX WITH 1,5-DIPHENYLPENTA-2,4-DIEN-1-ONE

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Abstract:
Some novel transition metal [Mn(II), Fe(II), Co(II), Ni(II), Cu(II) and Zn (II)] complexes of 1,5-diphenylpenta-2,4-dien-1-one **(**chalcone) were prepared. The present study is based on the synthesis and characterization of Iron (II) complex with 1,5-diphenylpenta-2,4-dien-1-one. It was found that the chalcone here acts as an olefinic ligand. The spectral and magnetic data revealed the formation of octahedral structure of the complex.

Keywords: Chalcone, Iron (II) complex, ferrous acetyl acetonate, Diamagnetism, Octahedral geometry

Introduction:

The field of coordination chemistry has grown in last fifty years from a readily defined and limited area into what is now the most active field of inorganic chemistry. In recent years, it has received not only a large amount of experimental studies but also a rather extensive theoretical treatment. Synthesis is one of the pillars to chemistry and there had been an enormous successful attempt in the preparative side, followed by useful characterisation by various Physico – Chemical methods. The so much progress in studies of metal complex chemistry had been rapid, perhaps partly because of the utility and economic importance of metal chemistry, the intrinsic interest of many of the compounds, and intellectual challenge of the structural problems to be solved.

The chalcone metal complexes have enough potential as efficient photosensitizer for photodynamic therapy[1]. Chalcones are very reactive compounds and owe their reactivity to keto – enol type (O = C – C = C) of conjugated double bond system present in the molecule. Chalcones have extensive usefulness in various biological area such as antibacterial, antitumor, antioxidant, antimalarial, anti-inflammatory, anti-HIV[2-9]. In the present work, transition metal complex is prepared by using 1,5-diphenylpenta-2,4-dien-1-one with Iron (II). To study the structural aspects of this metal chelate various physico-chemical methods have been used i.e. infrared spectra, electronic spectra, magnetic studies, conductivity measurement etc.

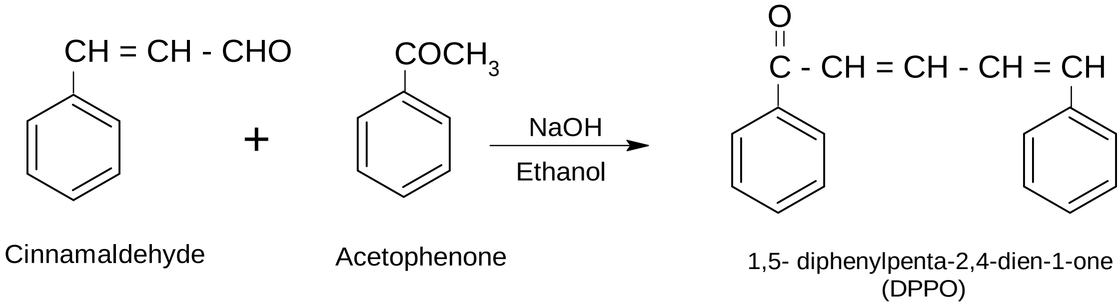
Experimental

Chemicals:

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

Synthesis of Ligand (DPPO):

The ligand used in the present work is not commercially available. However, it was prepared by the method reported earlier[10] 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 ligand 1,5-diphenylpenta-2,4-dien-1-one (DPPO) was found to be 101^0C.



Preparation of ferrous acetyl acetonate:

0.2 mol of acetyl acetone was gradually added to an aqueous solution (0. 1 mol) of ferrous ammonium sulphate. To this solution, ammonia was added drop by drop with constant stirring. A reddish coloured ferrous acetyl acetonate was separated out. The mixture was then digested on water bath. The colour of ferrous acetyl acetonate changed to dark red. It was then cooled, filtered, washed several times with hot water, dried and then used for complexation[11].

$$FeSO_4.\,(NH_4)_2SO_4.6H_2O + CH_3COCH_2COCH_3 \xrightarrow[\Delta]{NH_3} Fe\,(CH_3COCH_2COCH_3)_2$$

Synthesis of metal complex: Iron (II) was taken in the form of ferrous acetyl acetonate. It 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.

Analysis of the complex:

A) Elemental analysis: Estimation of metal content has been carried out by classical method[12]**.** 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.

B) Infrared Spectra: Infrared spectra of both the ligand and complex were 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 DPPO 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}.

C) Electronic Spectra: In the present study, absorption spectra of ligand DPPO 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

D) 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

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

Results and Discussion:

Elemental analysis: Iron (II) complex is red - brown in colour. Elemental analysis (Table 1.1) suggests a 2:2 metal DPPO stoichiometry. The Iron (II) complex was found to be insoluble in common organic solvents like chloroform, carbon tetrachloride, benzene, alcohol, nitrobenzene etc. molecular weight of the complex could not be determined due to solubility problem.

Table 1.1: Analytical and Physical data for the ligand (DPPO) and Iron (II) complex

Analytical and Physical data		$C_{17}H_{14}O$ (DPPO)	$[Fe(II)_2(C_{17}H_{14}O)_2(CH_3COCH_2COCH_3)]\ 2H_2O$
FW		234	816
Colour		Pale Yellow	Reddish Brown
% Analysis found (Cal)	Fe	-	13.56 (13.72)
	C	87.12 (87.17)	64.33 (64.7)
	H	5.78 (5.98)	4.97 (5.88)
Geometry of complex		-	Octahedral

Molar Conductance X 10^{-4} mhos cm^2 $mole^{-1}$		5.34

Infrared Spectra of DPPO and its Iron(II) complex: Various significant bands of DPPO and its Iron(II) complex have been assigned with the aid of literature data and these assignments are given in table 1.2

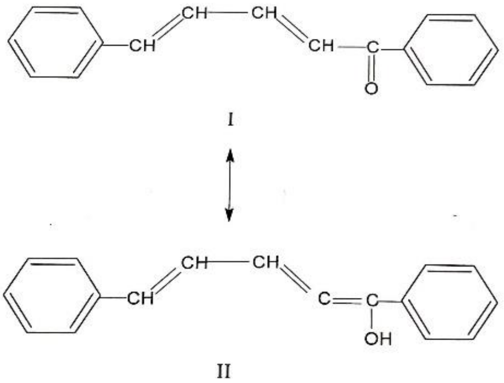
Table 1.2: Infrared Spectral data of DPPO and Iron (II) – DPPO Complex

Bands	DPPO (Ligand)	Fe - DPPO
C=C	1599 st	1527s
(COO^-) asym		-
(COO^-) sym		-
Δ(COO)		-
C= O	1655 st	1650vw
(- CH= CH-)trans	997 st	-
$\upsilon(H_2O)$		3420b
δ (H_2O)		-
Fe – O		610w
Fe - C		445m

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- DPPO bonding in Fe(II) complex. IR spectrum of DPPO ligand displays broad medium intensity band at 3450 cm assignable to v (0-H) vibration along with a strong, sharp band at 1655 cm

assignable to C=O vibration. Therefore, it can be concluded that the DPPO exists in the following tautomeric forms.



A band at 1650 cm^{-1} indicate the non involvement of C = O group in complexation. The spectrum displays a sharp and strong intensity band at 1527 cm^{-1} assignable to C = C stretching vibration. The coordination through C=C bond is further supported by the disappearance of a strong band at 997 cm corresponding to out of plane C- H bending in conjugated trans- trans system. In case of Iron(II) complex, the intensity of υ (C = O) becomes very weak suggesting coordination through oxygen atom of C = O group. A band at 580 cm^{-1} can be assigned to

Fe – O bond that appears due to formation of bond between Fe and acetyl acetonate oxygen atom. Similarly, weak intensity band at 610 cm^{-1} can be assigned to Fe – O bond. In the present investigation the IR spectrum of this metal complex displays a weak band at 445 cm^{-1} which can be assignable to Fe – C bond**[13].** In general water of hydration absorbs at 3300-3450 cm^{-1} **[14]** A broad band observed in the metal complex at 3420 cm^{-1} can be assigned to lattice water in this complex. IR spectra (wavenumbers are in cm^{-1}) of the DPPO and Iron(II) complex are shown in Fig 1.1 and 1.2 resp.

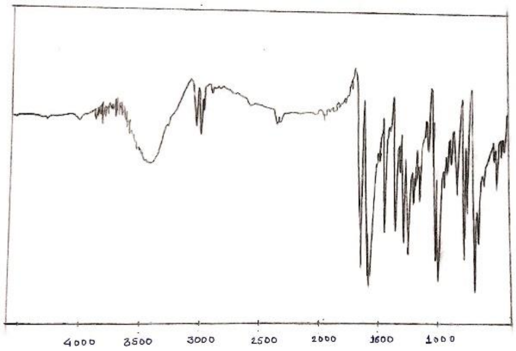


Fig 1.1: IR Spectra of DPPO

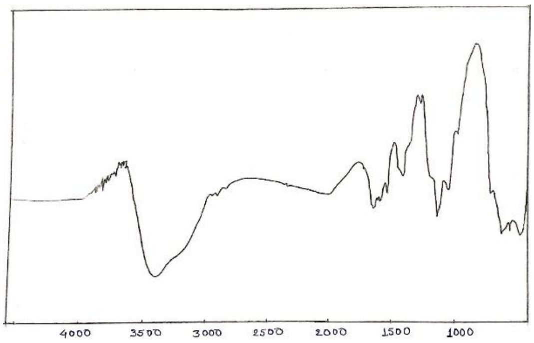


Fig 1.2: IR Spectra of Fe – DPPO

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 1.3

Magnetic Property: A magnetic susceptibility of Iron (II) complex was measured at room temperature using Guoy method. The iron (II) complex was found to be diamagnetic.

Electronic properties: Diffused reflectance spectra of Iron (II) complex, under present investigation was studied in the range of 250- 750 nm. The spectrum is shown in Fig. 1.4. Observed transitions and their probable assignments are shown in table 1.3. The spectrum exhibits two absorption bands in the region 28571 cm^{-1} and 36363 cm^{-1}. The first band near 28 kK can be assigned to the $^{1}A_{1(g)} \rightarrow {}^{1}T_{1(g)}$ transition and band near 36 kK may be ascribed to $^{1}A_{1}g \rightarrow {}^{1}T_{2}(g)$ which are characteristic bands for low spin octahedral geometry**[15]**.

Table 1.3: Magnetic moment and Assignment of Solid State Reflectance Spectra of Iron-DPPO complex

μ_{eff} (B.M.)	Absorption Bands		Assignments
	nm	kK	
Diamagnetic	350	28.57	$^{1}A_{1(g)} \rightarrow {}^{1}T_{1(g)}$
	275	36	$^{1}A_{1}g$ (G) $\rightarrow {}^{1}T_{2}(g)$

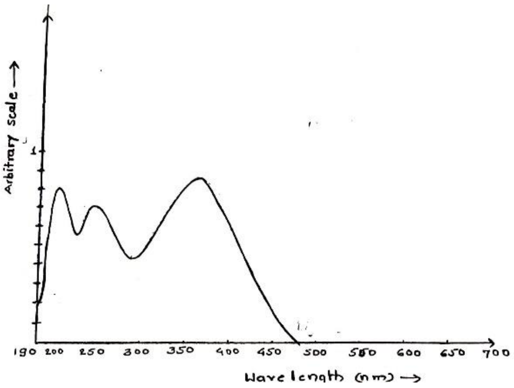


Fig 1.3: Absorption spectra of DPPO

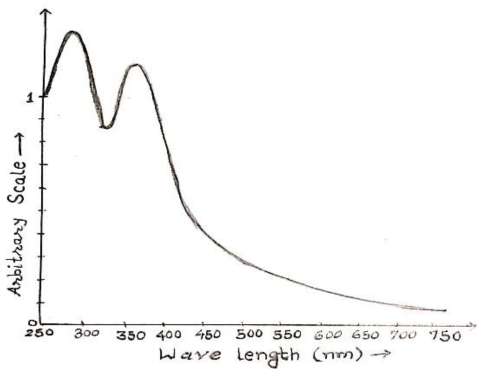
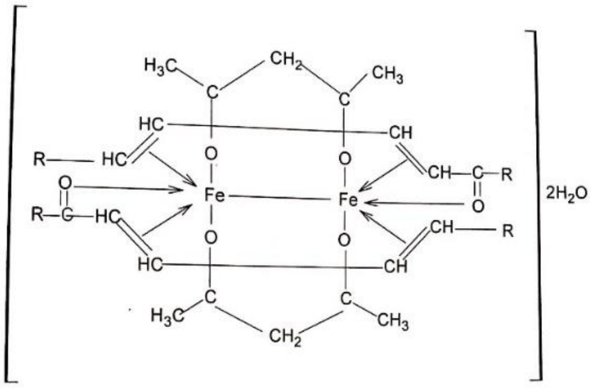


Fig 1.4: Solid State Reflectance Spectra of Fe – DPPO complex

Conclusion:

Elemental analysis of Iron (II) shows the composition 2:2 (M: L). Its non-electrolytic nature has been indicated by the low values of molar conductance in DMSO. Zero magnetic moment value confirms its diamagnetic nature. Octahedral geometry is supported by electronic spectra of the complex. The changes in stretching frequencies in the IR spectra of the DPPO and its complex indicates that C=C bonds and C = O bonds of DPPO are involved in coordination. In this complex acetyl groups are found to be involved in the coordination with the metal ion. Fe -O and Fe- 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.



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