Synthesis of Ferrocene Based Organometallic Compounds & Antimicrobial Activity

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Abstract: The synthesis, characterisation, spectral studies, antibacterial and fugal studies of some transition metal ions like Mn^{++} , Co^{++} , Ni^{++} , Cu^{++} , Pd^{++} and Pt^{++} complexes of ferrocene based Organometallic compounds have been reported. The coordinate bonding of nitrogen to the central metal atom which reduces the electron density in the both azomethine link and thus lower the -HC=N- absorption. The elemental analysis data exhibit the formation of 1:1 [M: L] ratio with coordination number six in the all complexes. The complexes have with octahedral geometry and D_4h symmetry. The ferrocene based organometallic compound shows a molecular ion peak at m/z 482.4 which is equal to theoretical molecular weight. The molar conductance value indicates that, they are non- electrolytic in nature. These complexes were tested with some bacteria and fungi. **Keywords:** ferrocene based organometallic compounds, IR, Mass spectra, electronic spectra, Electron Spin Resonance and antimicrobial activity.

I. Introduction:

The fields of organometallic compounds have been fast developing on account of the wide variety of possible structures for the ligands depending upon the Aldehydes and amines. Organometallic compounds are considered as a very important class of ferrocene &organic compounds, which have wide applications in many biological aspects [1-2]. Transition metal complexes of organometallic compounds are one of the most adaptable and thoroughly studied systems. These complexes have also applications in clinical and medicinal in addition to their important roles in catalysis and organic synthesis [3-7]. Studies of a new kind of chemotherapeutic organometallic compounds were now attracting the attention of biochemists. Organometallic compounds metal complexes can now be considered a widely studied subject due to their industrial and biological applications [8-9]. Earlier work reported that some drugs showed increased activity when administered as metal complexes rather than as organic compounds [10]. Organometallic compounds derived from 3-ethoxy-2-hydroxybezaldehyde and 1,1'-diaminoferrocene and characterized them by various analytical methods IR, UV-VIS, ESR, mass spectra. The present aim of the work is to synthesized a new series of ferrocene based organometallic compounds from 3-ethoxy-2-hydroxybezaldehyde and 1,1'-diaminoferrocene at to prepare some transition metal complexes, characterize them and study of antibacterial and anti fungal activities

II. Experimental

2.1 *Materials and methods*: All reagents and chemicals were of analytical grade, used without any further purification. The ferrocene diamine compounds were obtained from Merck Ltd. All solvents were purified & distilled by distillation before using.

2.2 *Preparation of ferrocene based organometallic compounds and metal complexes*: ferrocene based organometallic compounds prepared by mixing of (0.05M) methanoic solution of the 1,1'-Diaminoferrocene with (0.02M) ethanolic solution of 3-ethoxy-2-hydroxybenzaldehyde were reflux for five hours using water condenser at 80°C. After complete refluxation, the solution were cooled at room temperature, keep in dark place for 24 hours, solid separates and dry at 70 °C. The 0.02M Solution of Mn acetate, Co acetate ,Ni acetate , Cu acetate, PdCl₂ and PtCl₂ salt solutions were prepared in double distilled water. The solutions of 0.04m ferrocene based organometallic compounds and 20 cm³ solution of metal acetate and chloride solutions were refluxed for 3 hours using water condenser, by using few drops of alcoholic ammonia solution. This solution will keep for 24 hours in dark place, the coloured solid residue formed and dried at 60°C in oven. The yields of complexes were obtained in range between 44-52%.

 $\label{eq:construction:1,1'-Diaminoferrocene+3-ethoxy-2-hydroxybenzaldehyde \rightarrow 2-ethoxy-6-(\{2'-[(E)-(3-ethoxy-2-hydroxybenzylidene)amino]-1,1'(ferrocene-2,4-dien-1-yl)-2-yl\} carbonimidoyl) phenol$

2.3 Instrumental techniques: The elemental analyses were determined by using micro analytical technique. IR spectra were carried out by using KBr pellets by Perkin Elmer spectrophotometer. The electronic spectra were recorded using ethanol, DMSO and water as a solvent. Melting points of the ligand and decomposition temperature of complexes were determined in our laboratory.

III. Result and Discussion:

The physical and analytical data are listed in table No.1. The metal contains were estimated by volumetrically using EDTA , Pd(II) and Pt(II) metals estimated by AAS method . Iron metal estimated by gravimetrically [11]. All the complexes are soluble in DMSO and DMF. Melting point taken in open capillary and which is uncorrected. All the complexes are non-electrolytic in nature [12-13] and stable at room temperature.

3.1 IR Spectra: The IR spectral bands of ferrocene based organometallic compound and their complexes are given in table No.2. The IR spectra provide valuable information regarding the nature of functional group and its bonding where the group is present. The bonding mode of in the ferrocene based organometallic compound metal ion complexes. A band at 1690 cm⁻¹ in ferrocene based organometallic compound is due to >C = N vibration. The shifting of these groups at lower frequency in the range 1620-45 cm⁻¹ in the metal complexes, when these values compared to ferrocene based organometallic compound. Hence it suggests that the bonding through metal ion with nitrogen atom of azomethine group [14]. The coordinate bonding of nitrogen to the central metal atom which reduces the electron density in the both azomethine link and thus lower the -HC=N absorption[15]. A band at 3380 cm⁻¹ is assigned to Ar-OH frequency in the spectrum of ferrocene based organometallic compound, but in the complexes both bands does not appears in the complexation, which means that involvement of both oxygen atom of hydroxyl group of Ar-OH group in bonding with metal ions [16-17].

New bands were observed in the metal ion complexes, but bands are not present in the spectrum of ferrocene based organometallic compound. The spectra of complexes in the range of 558-572 cm⁻¹, corresponding to metal- nitrogen bonding [18-19] and 412-443 cm⁻¹ corresponding to metal-oxygen bonding respectively[20]. The appearances of vM-N and vM-O vibrations support the involvement of N and O atoms in complexation with metal ions[21-22]. The vC-O (Phenol) stretching frequency of ferrocene based organometallic compound have seen at 1365 cm⁻¹ gets shifted to a lower frequency region in the complexes in the range of 1318-33, it indicates that bonding through phenolic –Oxygen. Therefore the infrared spectral data indicates that the coordination sites of the metal ions are -HC=N and Ar-OH.

3.2 Electronic spectra: The electronic spectral data of the ferrocene based organometallic compound organometallic compounds and its complexes were recorded in DMF and Ethanol. (0.001 Mole/ dm³) the nature of electronic spectra of all the complexes indicates an octahedral geometry around the central metal ions in the complexes. The electronic spectra of cobalt (II) complex have shows the d-d transition bands at 9,546, 17325 and 21985 cm⁻¹. These transitions may be assigned to the ${}^{4}T_{1g}(F) \rightarrow {}^{4}T_{1g}(F) \rightarrow {}^{4}A_{2g}(F)$ and ${}^{4}T_{1g}(F) \rightarrow {}^{4}T_{1g}(P)$ respectively. The spectra of nickel (II) complex have shows three d-d transition bands at 11945, 18,874 and 23923 cm⁻¹. The transitions correspond to the ${}^{3}A_{2g}(F) \rightarrow {}^{3}T_{2g}(F)$, ${}^{3}A_{2g}(F) \rightarrow {}^{3}T_{1g}(F)$ and ${}^{3}A_{2g}(F) \rightarrow {}^{3}T_{1g}(F)$ respectively. The spectra of copper (II) complex have shows the d-d transition bands at 13534, 18874 and 25712 cm⁻¹. These bands correspond to ${}^{2}A_{1g} \rightarrow {}^{2}B_{1g}$, ${}^{2}B_{2g} \rightarrow {}^{2}B_{1g}$ and ${}^{2}Eg \rightarrow {}^{2}B_{1g}$ transitions respectively. The complexes having six coordination number with octahedral geometry and D₄h symmetry. [23-24].

3.3 Electron Spin Resonance: The ESR spectra of Co(II) &Cu (II) complexes were recorded in nitrogen temperature, when the spectra were compared to that of room temperature in exhibiting all the hyperfine lines. The calculated parameter values are given in table .3 [25-26].

3.4 Mass spectra: The mass spectra of the ferrocene based organometallic compound and its nickel complex were recorded show figure 4&5. The ferrocene based organometallic compound shows a molecular ion peak at m/z 482.4. The molecular ion peak for the Nickel complex, observed at m/z 561.03 it is confirmed from its theoretical value. This composition is also supported by the mass spectra of other complexes. It is in good agreement with the micro analytical data [27-28].

3.5Antmicrobial Activity: The antimicrobial tests were performed by the standard disc diffusion method [29]. The complexes were screened for their antifungal activity against fungi viz. *Aspergillus niger* and *Fusarium oxysporum*. The cultures of the fungi were purified by single spore isolation technique. A concentration of 2 mg/cm³ of each metal complex compound in DMF solution were prepared for testing against spore germination of each fungus. Filter paper discs of 10 mm in size, prepared by using Whatmann filter paper no. 41 were saturated with 5 μ l of the metal complex compounds dissolved in DMF solution or DMF as negative control.

The fungal culture plates were inoculated and incubated at $25\pm 20^{\circ}$ C for 72 h. The plates were then observed and the diameters of the inhibition zones (in mm) were measured and tabulated. The antibacterial activity of the complexes was studied against Gram-positive bacteria *Staphylococcus aureus* and Gram-negative bacteria *Escherichia coli*. Each of the metal complex compounds dissolved in DMF at a concentration of 2 mg/ cm³ was prepared. Paper discs of Whatmann filter paper no. 41 were cut and sterilized in an autoclave. The paper discs were saturated with 5µl of the metal complex compounds dissolved in DMF solution or DMF as negative control and were placed aseptically in the Petri dishes containing Nutrient agar media inoculated with the above mentioned two bacteria separately. The petridishes were incubated at 37 0C and the inhibition zones were recorded after 24 h of incubation.

Antifungal activity the ferrocene based organometallic compound and their complexes were screened against E.Coli (bacteria Gram negative) S.Aureus (bacteria Gram positive) A.Nigar (fungus) F.oxysporum (fungus) and the values are given in Table 4. The complexes shows less activity as compare ferrocene based organometallic compound. However, ferrocene based organometallic compound ligand and their complexes showed lower activity as compared to standard drug. Antifungal activity studies of ferrocene based organometallic compound and its complexes against A.Nigar (fungus) F.oxysporum (fungus) shows that all the complexes are less activity than the ferrocene based organometallic compound. It is known that chelation tends to make the ferrocene based organometallic compound act as more powerful and potent antimicrobial agent, thus inhibiting more of the microbes than the parent ligand [30].

IV. Figures and Tables

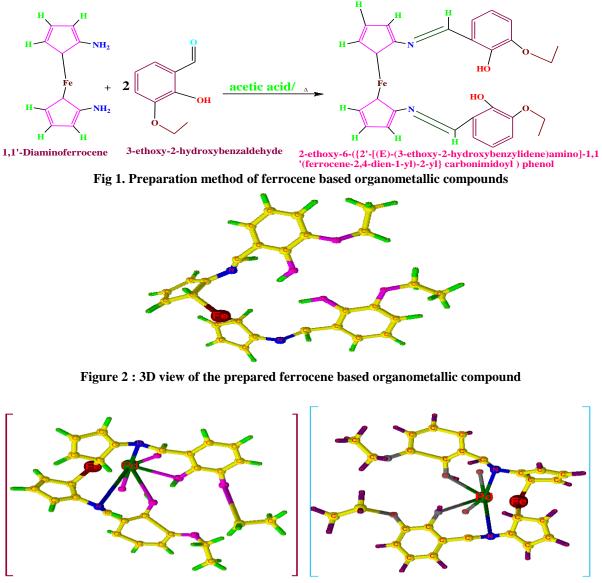


Figure 3: 3D view of the prepared Pd Complex of ferrocene based organometallic compound

Synthesis of Ferrocene Based Organometallic Compounds & Antimicrobial Activity

	% yield	MP/DP°C	C%	N%	Fe%	M%	BM.µeff
$(C_{26}H_{24}N_2O_4Fe)$	71%	235-238	64.84	5.78	11.53		
			(64.52)	(5.58)	(11.25)		
$[Mn(C_{26}H_{22}N_2O_4Fe).2H_2O]$	52%	199-201	56.04	5.03	10.02	9.86	5.45
			(55.78)	(4.81)	(9.83)	(9.67)	
$[Co(C_{26}H_{22}N_2O_4Fe). 2H_2O]$	54%	192-194	55.64	4.99	9.95	10.05	4.49
			(55.39)	(4.71)	(9.74)	(9.82)	
$[Ni(C_{26}H_{22}N_2O_4Fe). 2H_2O]$	52%	182-184	55.66	4.99	9.95	10.46	3.25
			(55.35)	(4.75)	(9.78)	(10.22)	
$[Cu(C_{26}H_{22}N_2O_4Fe). 2H_2O]$	48%	188-190	55.18	4.95	9.87	11.23	1.85
			(54.93)	(4.70)	(9.63)	(11.01)	
$[Pd(C_{26}H_{22}N_2O_4Fe). 2H_2O]$	47%	177-179	51.3	4.61	9.17	17.48	
			(51.07)	(4.38)	(8.95)	(17.23)	
[Pt(C ₂₆ H ₂₂ N ₂ O ₄ Fe). 2H ₂ O]	44%	172-174	44.78	4.02	8.01	27.97	
			(44.53)	(3.83)	(7.84)	(27.71)	

Table .1: Analytical data and Physical Data ferrocene based organometallic compound and Its Complexes

Schiff base /Complexes	vC-OH	vC=N	vC-O	vM-N	vM-O	2H ₂ O
$(C_{26}H_{24}N_2O_4Fe)$	3380	1690	1365	-	-	-
$[Mn(C_{26}H_{22}N_2O_4Fe).2H_2O]$	-	1625	1322	559	417	3445,3538
[Co(C ₂₆ H ₂₂ N ₂ O ₄ Fe). 2H ₂ O]	-	1633	1318	568	435	3457, 3522
[Ni(C ₂₆ H ₂₂ N ₂ O ₄ Fe). 2H ₂ O]	-	1622	1328	572	427	3438, 3510
[Cu(C ₂₆ H ₂₂ N ₂ O ₄ Fe). 2H ₂ O]	-	1645	1333	560	445	3432, 3522
[Pd(C ₂₆ H ₂₂ N ₂ O ₄ Fe). 2H ₂ O]	-	1635	1325	557	439	3435, 3527
[Pt(C ₂₆ H ₂₂ N ₂ O ₄ Fe). 2H ₂ O]	-	1630	1331	563	412	3452, 3507

Table 2 : IR Spectral Data Of ferrocene based organometallic compound and Its Complexes in Cm⁻¹

complexes	g _{II}	gı	\mathbf{g}_{av}	G	A _{II}	AI
[Co(C ₂₆ H ₂₂ N ₂ O ₄ Fe). 2H ₂ O]	2.289	2.059	2.135	4.61	0.0137	0.0011
[Cu(C ₂₆ H ₂₂ N ₂ O ₄ Fe). 2H ₂ O]	2.295	2.065	2.142	4.47	0.0133	0.0014

 Table 3: Electron spin resonance spectral parameters

sample	Inhibition zone diameter(mm/mg Sample)						
	E.Coli (bact.G-)	S.Aureus(bact. G+)	A.Nigar(fungus)	F.oxysporum(fungus)			
Control: DMF	0.0	0.0	0.0	0.0			
Tetracycline Antibacterial Agent(Std)	-	-	-	-			
Amphotericin B Antifungal agent	-	-	15	17			
$(C_{26}H_{24}N_2O_4Fe)$	24	27	10	11			
$[Mn(C_{26}H_{24}N_2O_4Fe).2H_2O]$	15	14	0.0	0.0			
$[Co(C_{26}H_{24}N_2O_4Fe).2H_2O]$	17	19	0.0	0.0			
$[Ni(C_{26}H_{24}N_2O_4Fe). 2H_2O]$	12	11	0.0	0.0			
[Cu(C ₂₆ H ₂₄ N ₂ O ₄ Fe). 2H ₂ O]	11	17	0.0	0.0			
$[Pd(C_{26}H_{24}N_2O_4Fe).2H_2O]$	20	19	05	06			
$[Pt(C_{26}H_{24}N_2O_4Fe) . 2H_2O]$	22	21	05	07			

Table : 4 Antimicrobial activity

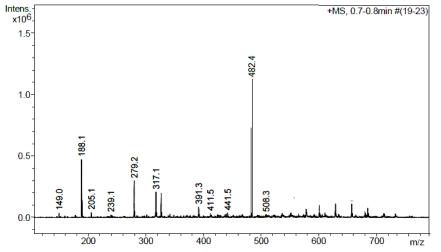
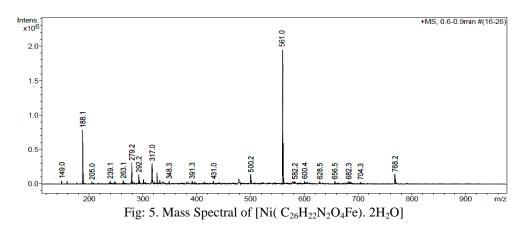


Fig: 4. Mass Spectral of ferrocene based organometallic compound (C₂₆H₂₄N₂O₄Fe)



V. Conclusion:

The ferrocene based organometallic compound and its metal complexes of Mn-acetate , Co- acetate , Ni- acetate , Cu- acetate , PdCl₂ and PtCl₂ have been prepared and characterized on the basis elemental analysis, molar conductance, magnetic moment, infrared, electronic spectra, electron spin resonance, mass spectra and their microbial activity . The physical and analytical data show that the metal- ligand ratio of all complexes is 1:1. Complexes are non-electrolytes in nature, the ligand act as neutral and tetra coordinating through oxygen atoms of hydroxyl group , nitrogen atom of the azomethine group of 2-ethoxy-6-({2'-[(E)-(3-ethoxy-2-hydroxybenzylidene)amino]-1,1'(ferrocene-2,4-dien-1-yl)-2-yl} carbonimidoyl) phenol. Complexes are octahedral geometry with coordination number six. The antimicrobial activity results indicate that, the metal complexes are less active as compared ferrocene based organometallic compound. We are proposed the following probable structure of the complex [M ($C_{26}H_{22}N_2O_4Fe$). 2H₂O].

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