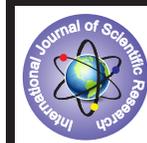


Electronic Spectra, Thermal Analysis, X-Ray Powder Diffraction and SEM Studies of Organometallic Compound



Chemistry

KEYWORDS : Elemental analysis, conductivity, magnetic behavior, Electronic spectra, Thermal, X-Ray Diffraction and SEM.

Gulam Farooq

Department of Chemistry, Sir Sayyad College, Aurangabad-431001(Maharashtra) India

Manohar V Lokhande *

Department of Chemistry, Sathaye College, Mumbai-400057(Maharashtra) India

ABSTRACT

the spectral studies of prepared organometallic compounds like, UV-Visible, Thermal, X-Ray Diffraction and SEM studies of organometallic Compound have been carried out. SEM study indicates that, the size of crystal is 110nm.

The x-ray powder diffraction of the prepared complexes System is Monoclinic-P, A= 19.33 Å, a=18.1919 Å, B= 84.37 Å, b= 8.3856 Å, C= 46.20 Å, c=11.7673 Å, E= 16.09, beta=105.619D, V= 1728.81Å³ and density of complexes in toluene is 1.0974 g/cm⁻³. Electronic spectra of the complex parameters are β=0.9744,δ%=1.323, b1/2=0.08 and η=0.013. According to the study of thermal analysis it indicates that the two coordinated molecules are present in co-ordination sphere

1.Introduction: Organometallic chemistry play an important role in chemistry for energy processing and environmental remediation [1]. The coordination chemistry of complexes of organometallic compounds are filled with opportunities, inspired by Supramolecular chemistry, organ catalysis and Nano science [2-5]. We are describe a new concept for the preparation of Organometallic Schiff bases derivatives via a totally different mechanism than those previously cited above. This new formation of organometallic Schiff bases derivatives is based on the complexation of unsaturated compounds with some transition metal ions. Early transition metal complexes show both types of reactivity and thus, in addition to their utility either as a carbanion source or as a synthetic reagent based on transition metal behavior, it is possible to utilize them for synthetic transformations based on the characteristic Numerous methods for the preparation of organometallic compounds are known in the literature [6] and can be mainly divided into four categories. The first and probably the most important one, is the reaction between an organic halide or pseudo halide and a metal such as the classical oxidative metalation or the halogen-metal exchange, have recently been found to be promising anticancer drug. [7]. The thermal stability and the strong bonding of the ligand to the d- block elements have made the complexes more interesting. These organometallic compounds are synthesized from the condensation of aldehydes with diamine of ferrocene compounds and their complexes [8-9] played an important part in the development of inorganic chemistry, as widely studied coordination compounds are increasingly important as biochemical, analytical, and antimicrobial reagents [10-11]. Also they have been used as anti-bacterial, anti-fungal, anti-cancer, anti-tubercular, hypertensive and hypothermic reagents [12-13]. We have investigated Ni(II), Co(II), Cu(II), Pd(II and Pt(II) prepared from ferrocene aldehydes with amino compounds and their spectral studies like Electronic spectra , Thermal, X-Ray Diffraction and SEM studies were carried out.

2. Method and Material:

All the chemicals are used for the synthesis purpose and the common solvents used at various stages of this work are purified by the standard procedures [8]. All the complexes are soluble in

DMSO at room temperature; Magnetic susceptibility of the complexes was performed on a Sherwood MSB mark Gouy balance. Electronic spectra were obtained by Elico-spectrometer; the SEM images were recorded using JEOL-JSM-840 a scanning electron microscopy and Thermal analysis were carried out at C-met and X-Ray powder Diffraction at TIFR Mumbai.

2.1. Synthesis of organometallic compounds: Organometallic compound synthesized from ferrocene dicarboxyldehyde (1M) and 2-amino benzoic acid (1M) was separately dissolved in 50 cm³ alcohol. Than these solutions were mixed and stirred near about one hour on magnetic plate. The resulting solutions were kept in micro oven near about 180 °C for 30 minutes. After 30 minutes, solutions were cooled at room temperature and kept the solution overnight. The solid product was obtained, this product then filtration, washed several times with ethanol and dried in oven at 60°C. the yield of the product 81 % yields.

2.2 Synthesis of metal complexes :The metal ion complexes of organometallic compounds were prepared by mixing ethanolic equi molar concentration (0.02 M) of 2,2'-{1,1'-(Ferrocene-2,4-dien-1-yl)-2,2'-diylbis[(E)methylidene (E) azanylylidene]} dibenzoic acid with the (0.04M) aqueous solution of metal acetates of Manganese(II) , Cobalt(II), Nickel(II), Copper(II) and Palladium chloride, Platinum chloride salts were used for preparation these complexes. Then the solutions were mixed in 1:1 ratio and refluxed for three hours. After three hours, the solution were cooled at room temperature, solid of complexes were appeared then it will filtered, washed with ethanol and dried at 60°C in oven. The yields of is obtained in between 55-71 %.

3. Result and discussion

The physical and analytical data are given below in table 1. The metal contains are estimated by volumetrically using EDTA and Iron metal estimated by gravimetrically [8]. Complexes are colored, stable at room temperature, soluble in dimethyl sulfoxide and dimethyl formamide. They are decomposed in the range 201-234°C. The melting point and decomposition point reported in open

Table: 1 physical and analytical data

Compound/ Complexes	% Yield	MP/DP °C	N%	Fe%	M%	Ω ⁻¹ mol ⁻¹ cm ²	BM. μeff
(C ₂₆ H ₂₂ N ₂ O ₄ Fe)	81	243-245	05.81	11.58			
			05.18*	11.03*			
[Mn (C ₂₆ H ₂₀ N ₂ O ₄ Fe) .2H ₂ O]	71	223-225	04.90	09.78	09.62	18	5.42
			04.55	09.35	09.31		
[Co (C ₂₆ H ₂₀ N ₂ O ₄ Fe) .2H ₂ O]	63	218-220	04.87	09.71	10.24	22	4.44
			04.45	09.31	09.88		

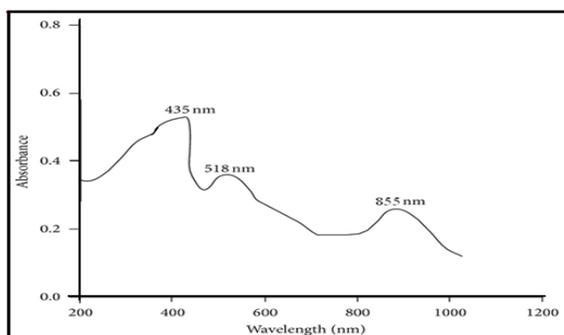
[Ni (C ₂₆ H ₂₀ N ₂ O ₄ Fe). 2H ₂ O]	68	217-219	04.87	09.71	10.21	19	3.22
			04.41	09.24	09.84		
[Cu (C ₂₆ H ₂₀ N ₂ O ₄ Fe). 2H ₂ O]	62	212-214	04.83	09.63	10.96	23	1.81
			04.30	09.19	10.39		
[Pd (C ₂₆ H ₂₀ N ₂ O ₄ Fe). 2H ₂ O]	59	200-202	04.50	08.97	17.09	17	
			04.11	08.55	16.74		
[Pt (C ₂₆ H ₂₀ N ₂ O ₄ Fe). 2H ₂ O]	57	193-195	03.94	07.85	27.42	15	
			03.57	07.44	26.91		

3.1: Electronic Spectra: The electronic absorption spectra were often very helpful in the evaluation of results furnished by other methods of structural investigation. The 'electronic spectral' measurements were used for assigning the stereo chemistries of metal complexes based on the positions & number of *d-d* transition peaks. The 'electronic absorption spectra' of metal ion complexes were recorded in 10⁻⁴ molar concentration of each complex in Dimethyl formamide in the range 300–900 nm at room temperature. The 'electronic absorption spectra' of Nickel (II) in 10⁻⁴ M solutions, the spectra were noisy in both the visible and the UV regions. The results of the electronic spectra are presented in below table.

The electronic spectra of the complexes were recorded in DMF, there spectral parameters and assignment were given in Table 2 & figure 1. The electronic d-d transition bands normally show weak perturbation due to complexation an increase in the intensity, shift to the red region and also splitting of some bands were observed on complex formation. The position, shapes of [Ni (C₂₆H₁₈N₂O₄Fe).2H₂O] were observed in solution phase using water, ethanol and DMF. [Ni (C₂₆H₁₈N₂O₄Fe).2H₂O] complex shows three intense peak, which have acquired lower energies as compared to those of their aqua complexes. The magnitude of the bathochromic shift of the bands in each case meager Nephelauxetic effect (β) [14] Sinha's parameter ($\delta\%$) [15], bonding parameter ($b^{1/2}$) [16] and have been calculated. The bonding parameter reflects the participation of 3d orbital [17]. The $b^{1/2}$ value obtained for the present complexes indicates a decreasing order of 3d- orbital participation in the Cu⁺² and Ni⁺² complexes. The average value of Sinha's parameter ($\delta\%$) obtained in each case is positive and smaller, indicating that, the presence of covalent bonding in the complexes [18].

Figure 1: Electronic spectra of [Ni (C₂₆H₁₈N₂O₄Fe).2H₂O] complex Table 2: electronic Spectral parameters

Complexes	Absorption bands cm ⁻¹	Assignments	Spectral Parameter
[Ni (C ₂₆ H ₁₈ N ₂ O ₄ Fe).2H ₂ O]	22988 19305 11965	${}^3A_g(F) \rightarrow {}^3T_{1g}(F)$ ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ ${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$	$\beta=0.9744$ $\delta\% = 1.323$ $b^{1/2} = 0.08$ $\eta=0.013$



3.2 Thermal analysis: Thermo gravimetric analysis study of [Pt (C₂₆H₁₈N₂O₄Fe).2H₂O] complex shows loss in weight in the

temperature range 40-240°C, which corresponds to loss of coordinated water molecules and some part of the complex [19-20]. The experimental percentage losses, which have been calculated from Thermo gravimetric analysis curve is 9.58%. The values were compared with theoretical percentage loss. The Differential thermal analysis peak is endothermic. In the temperature range at 240-320°C, weight loss some part of complex were also lost. The major part of chelating agent were lost in the temperature range of 320-410°C. The experimental percentage loss is 11.27%, which is obtained from Thermo gravimetric analysis curve. The experimental percentage loss value is comparable with theoretical percentage loss value i.e. 12.19%. The DTA peak is exothermic. The probable leaving part of complex in this temperature range is C₆H₈. The temperature range 500-1000°C leading to the formation of Platinum oxide. The decomposition of complex represented as below:

Table 3: TGA and DTA decomposition Data of the Complexes

Complex	Temp range °C	Calculated Value %	Expt. values %	Possible leaving groups
[P (C ₂₆ H ₁₈ N ₂ O ₄ Fe).2H ₂ O]	40-240	9.58	10.39	H ₂ O, C ₂ H ₈
	240-320	14.37	15.08	C ₆ H ₂ N ₂
	320-410	11.27	12.19	C ₆ H ₈
	500-1000	61.89	62.57	PtO

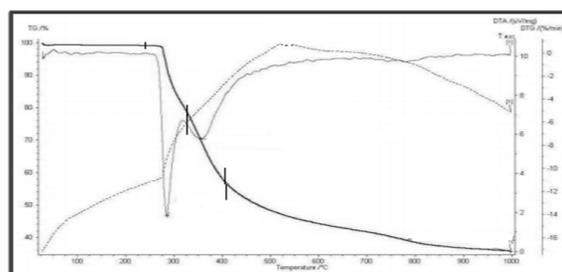


Figure 2: Thermogram [Pt (C₂₆H₁₈N₂O₄Fe).2H₂O] complex

3.3 X-Ray Powder Diffraction of [Co (C₂₆H₁₈N₂O₄Fe).2H₂O] complex: This indexing method also yields the Miller indices (*hkl*), the unit cell parameters and the unit cell volume. The spectra contain 25 intense peaks. The unit cell of Co (II) complex yielded values of lattice constants: $a = 18.1919 \text{ \AA}$, $b = 8.3656 \text{ \AA}$, $c = 11.7673 \text{ \AA}$, density of the complex $D = 1.0974 \text{ g cm}^{-3}$ and a unit cell volume $V = 1728.81 \text{ \AA}^3$. In concurrence with these cell parameters, conditions such as $a \neq b \neq c$ and $\alpha = \gamma = 90^\circ \neq \beta$ required for a monoclinic system were found and it has been satisfactory. Hence, it can be concluded Co (II) complex were monoclinic crystal systems. The experimental density values of the complexes were determined using the specific gravity method by using toluene reagent [21] and found to be 1.0963 g cm^{-3} for the Co (II) complex respectively. Comparison of experimental and theoretical density value shows good agreement within the limits of experimental error [22-23]. *Calculated parameters:* System: Monoclinic-P, $A = 19.33 \text{ \AA}$, $B = 84.37 \text{ \AA}$, $C = 46.20 \text{ \AA}$, $a = 18.1919 \text{ \AA}$, $b = 8.3856 \text{ \AA}$, $c = 11.7673 \text{ \AA}$, $\text{Abita} = 105.619D$, $V = 1728.81 \text{ \AA}^3$, $D = 1.0974 \text{ g/cm}^{-3}$

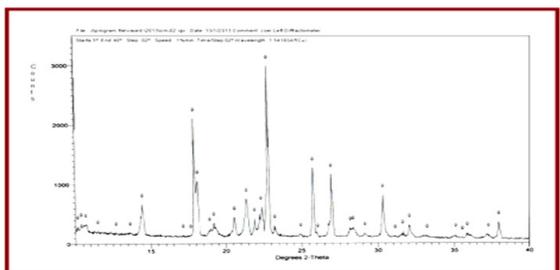
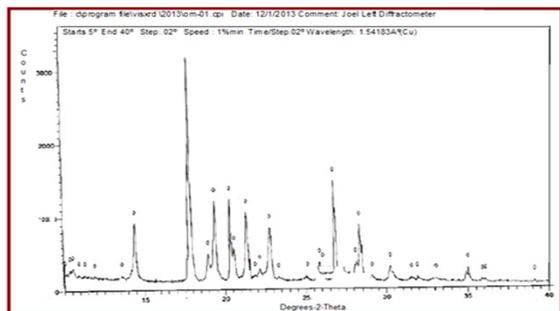


Figure 3: X-Ray Diffraction of [Cu (C₂₆H₁₈N₂O₄Fe).2H₂O] Figure 4: X-ray diffraction of [Co (C₂₆H₁₈N₂O₄Fe).2H₂O]

Table 4: X-ray Powder diffraction of [Co (C₂₆H₁₈N₂O₄Fe).2H₂O] complex

Line No	d-spacing A.		% Intensity	Miller Indices			Sin ² θ		2θ degree		diff
	Obs	Calc		h	k	l	Obs	Calc	Obs	Calc	
1	8.7851	8.7601	18	2	0	0	76.9	77.3	10.06	10.09	-.029
2	8.5314	8.5262	15	1	0	1	81.5	81.6	10.36	10.37	-.006
3	8.3861	8.3856	14	0	1	0	84.4	84.4	10.54	10.54	-.000
4	8.0803	8.0600	17	2	0	1	90.9	91.3	10.94	10.97	-.028
5	7.4181	7.5639	81	1	1	0	107.8	103.7	11.92	11.69	.230
6	6.5053	6.6588	14	1	1	1	140.2	133.8	13.60	13.29	.315
7	6.1245	6.1731	100	2	0	1	158.2	155.7	14.45	14.34	.11
8	4.9593	4.9713	37	2	1	1	241.2	240.1	17.87	17.83	.043
9	4.6717	4.6950	35	0	1	2	271.8	269.2	18.98	18.89	.095
10	4.5739	4.5859	15	2	1	2	283.6	282.1	19.39	19.34	.052
11	4.3623	4.3800	18	4	0	0	311.8	309.3	20.34	20.26	.083
12	4.3120	4.3014	11	1	1	2	319.1	320.7	20.58	20.63	-.051
13	4.1524	4.1375	76	3	1	2	344.1	346.6	21.38	21.46	-.078
14	4.0660	4.0777	31	1	2	0	358.9	356.8	21.84	21.78	.063
15	4.0116	4.0300	63	4	0	2	368.7	365.3	22.14	22.04	.102
26	3.8969	3.8823	52	4	1	0	390.7	393.6	22.80	22.89	-.087
17	3.8080	3.8002	59	2	1	2	409.1	410.8	23.34	23.39	-.048
18	3.5434	3.5484	28	1	1	3	472.5	471.2	25.11	25.07	.036
19	3.4410	3.4442	54	0	1	3	501.1	500.1	25.87	25.85	.025
20	3.4164	3.4129	50	3	2	1	508.3	509.4	26.06	26.09	-.027
21	3.3631	3.3704	57	0	2	2	524.5	522.3	26.48	26.42	.059
22	3.3249	3.3294	35	2	2	2	536.7	535.2	26.79	26.75	.037
23	3.1728	3.1721	57	2	0	3	589.4	589.6	28.10	28.11	-.006
24	3.1421	3.1454	28	3	2	2	600.9	599.7	28.38	28.35	.030
25	3.0660	3.0722	19	4	2	1	631.1	628.6	29.10	29.04	.060

3.3.1: [Cu (C₂₆H₁₈N₂O₄Fe).2H₂O] complex: This indexing method also yields the Miller indices (*hkl*), the unit cell parameters and the unit cell volume. The spectra contain 35 intense peaks. The unit cell of the Cu (II) complex yielded values of lattice constants: *a* = 24.5882 Å, *b* = 4.4656 Å, *c* = 5.8676 Å and a unit cell volume *V* = 627.2087 Å³. Density of the complex *D* = 1.0857 g cm⁻³ and a unit cell volume *V* = 369.2291 Å³. In concurrence with these cell parameters, conditions such as *a* ≠ *b* ≠ *c* and *α* = *γ* = 90° ≠ *β* required for a monoclinic system were found and it have been satisfactory. Hence, it can be concluded Cu (II) complex were monoclinic crystal systems. The experimental density values of the complexes were determined using the specific gravity method by using toluene reagent [21] and found to be 1.0897g/cm³ for the Cu (II) complex respectively. Comparison of experimental & theoretical density value shows good agreement with in the limits of experimental error [22-23].

Calculated parameters : System :Monoclinic-P , A= 20.34 Å, B= 57.47 Å, C= 73.07 Å, a=17.1422 Å, b=10.1601 Å, c= 9.0437 Å, E= 6.55 , beta= 94.875D , = 1569.41 Å³, Density= 1.0857 g /cm⁻³

Table 5: X-Ray Powder Diffraction of [Cu (C₂₆H₁₈N₂O₄Fe).2H₂O] complex

Line No	d-spacing A°		% Intensity	Miller Indices			Sin ² θ		2θ Deg		Diff
	obs.	calc.		h	k	l	obs.	calc.	obs.	calc.	
1	8.7074	8.7320	14	1	1	0	78.3	77.8	10.15	10.12	.029
2	8.5150	8.5401	17	2	0	0	81.8	81.3	10.38	10.35	.031
3	8.2765	8.2650	15	1	0	1	86.6	86.9	10.68	10.69	-.015
4	7.6881	7.7042	21	1	0	1	100.4	100.0	11.50	11.48	.024
5	6.9642	6.7416	45	0	1	1	122.3	130.5	12.70	13.12	-.421
6	6.4863	6.4796	45	2	0	1	141.0	141.3	13.64	13.65	-.014
7	6.1287	6.1389	18	1	1	1	158.0	157.4	14.44	14.42	.024
8	5.1689	5.1351	13	1	1	1	222.1	225.0	17.14	17.25	-.114
9	5.0235	5.0092	19	3	0	1	235.1	236.4	17.64	17.69	-.051
10	4.9566	4.9667	66	3	1	0	241.5	240.5	17.88	17.84	.037
11	4.8915	4.8692	42	1	2	0	248.0	250.2	18.12	18.20	-.083
12	4.6235	4.6384	38	3	0	1	277.5	275.8	19.18	19.12	.062
13	4.3162	4.3279	47	1	2	1	318.5	316.7	20.56	20.50	.056
14	4.1524	4.1325	21	2	0	2	344.1	347.4	21.38	21.48	-.104
15	4.0550	4.0768	29	1	1	2	360.8	357.0	21.90	21.78	.118
16	3.9779	3.9922	45	4	0	1	374.9	372.3	22.33	22.25	.081
17	3.8969	3.8638	42	2	2	1	390.7	397.4	22.80	23.00	-.198
18	3.8258	3.8280	100	2	1	2	405.4	404.9	23.23	23.22	.014
19	3.5672	3.5668	23	3	2	1	466.3	466.3	24.94	24.94	-.002
20	3.4541	3.4674	38	3	1	2	497.3	493.5	25.77	25.67	.100
21	3.4138	3.4160	55	5	0	0	509.1	508.4	26.08	26.06	.017
22	3.3055	3.3220	35	1	3	0	543.0	537.6	26.95	26.81	.136
23	3.1651	3.1702	26	0	3	1	592.2	590.3	28.17	28.12	.046
24	3.1465	3.1482	38	2	3	0	599.3	598.6	28.34	28.32	.016
25	3.0639	3.0694	40	2	2	2	632.0	629.7	29.12	29.07	.053
26	2.9435	2.9435	45	2	3	1	684.8	684.8	30.34	30.34	.000
27	2.8696	2.8791	18	1	1	3	720.5	715.8	31.14	31.04	.104
28	2.8272	2.8229	18	3	2	2	742.3	744.5	31.62	31.67	-.049
29	2.7877	2.7833	12	6	0	1	763.5	765.9	32.08	32.13	-.052
30	2.6953	2.6952	29	1	3	2	816.7	816.8	33.21	33.21	-.002
31	2.5544	2.5613	10	4	0	3	909.3	904.4	35.10	35.00	.097
32	2.5238	2.5264	12	2	2	3	931.5	929.5	35.54	35.50	.038
33	2.5013	2.5046	13	6	0	2	948.3	945.8	35.87	35.82	.049
34	2.4105	2.4123	12	1	4	1	1021.	1019.	37.27	37.24	.028
35	2.3683	2.3648	14	2	4	1	1057.	1060.	37.96	38.02	-.058

3.4 SEM and EDX of the complex: The SEM and EDX of the $[\text{Pd}(\text{C}_{26}\text{H}_{18}\text{N}_2\text{O}_4\text{Fe})\cdot 2\text{H}_2\text{O}]$ complex were recorded. The SEM image $[\text{Pd}(\text{C}_{26}\text{H}_{18}\text{N}_2\text{O}_4\text{Fe})\cdot 2\text{H}_2\text{O}]$ is shown in the figure 3.7-3.9. The SEM of complex shows clearly change which were occurred on the surface of the metalion. The shape of the particles were observed Flake type in case metal complex. Metal Particles were spherical in size quite visible throughout the complex [24-25]. Further the analysis of Pd (II) metal complex shows palladium content along with N which indicates that the formation of metal complex with the organometallic compound and iron atom attached with carbon atom. SEM of the indicate that the size of the particle is near about 110 nm.

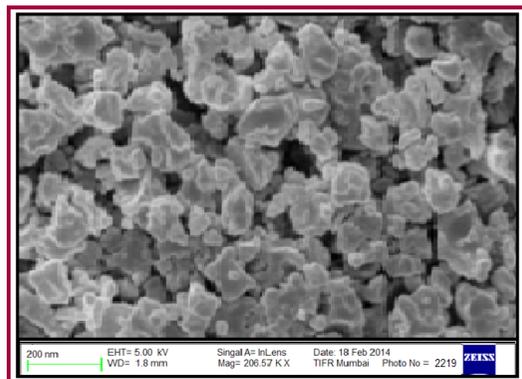


Figure 5: SEM of $[\text{Pd}(\text{C}_{26}\text{H}_{18}\text{N}_2\text{O}_4\text{Fe})\cdot 2\text{H}_2\text{O}]$ complex

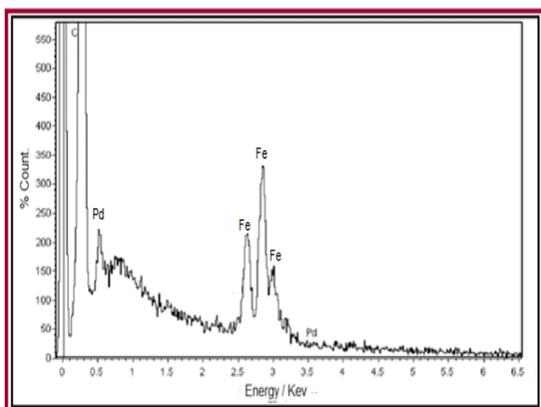


Figure6: EDX of $[\text{Pd}(\text{C}_{26}\text{H}_{18}\text{N}_2\text{O}_4\text{Fe})\cdot 2\text{H}_2\text{O}]$ complex

4. Conclusion: Organometallic compounds were derived from ferrocene aldehyde and amino benzoic acid by microwave technique. The two coordinated water molecule are present in coordination sphere by thermal studies, $[\text{Pd}(\text{C}_{26}\text{H}_{18}\text{N}_2\text{O}_4\text{Fe})\cdot 2\text{H}_2\text{O}]$ complex is 110nm and metal contents were identified by EDX methods.

5. Acknowledgements: The Authors thank to, Director TIFR, C-Met, for providing necessary instrumental facilities. Finally thanks to my friends, colleagues, family members for their co-operation and help.

REFERENCE

- Letko C S, Heiden Z H, Rauchfuss T B (2011) *Inorganic Chemistry*, Vol.50, pp. 5558-5566. | 2. Letko C S, Heiden Z H, Rauchfuss T B (2009) . *Eur J Inorg Chem.*, pp. 4927-4930. | 3. 3.Royer M, Rauchfuss T B , Gray D L, (2009) *Organometallic*,Vol. 28, pp.3618-3620. | 4. Boyer j I, Cundari T R, DeYonker N J, Rauchfuss T B, Wilson S R (2009) *Inorg Chem.*, Vol. 49,pp 638-645. | 5. Rauchfuss T B, Severin K, Atwood J, Steed J,(2008) *Supramolecular Architectures Based on Organometallic Half-sandwich Complexes*, edition, Wiley-VCH, pp.179-201. | 6. Craig P J (2003) *Organometallic Compounds in the Environment*, Wiley Chichester, 2nd edition. | 7. Negishi E (1994) *Organometallics in Organic Synthesis*, Wiley-Interscience, John Wiley & Sons Canada. | 8. Vogel A I (2003) *A Text Book of Quantitative Inorganic Analysis*, Longmans Green, London , 5 th Edition : Sarkara A, Pal S (2008) *Inorg Chim Acta.*, Vol.361,pp.2296-2304. | 9. Oki A R, Hodgson D J (1990) *Inorganica Chim Acta.*, Vol. 170, pp. 65-73. | 10. Mukherjee P, Drew M G B, Estrader M, Diaz C, Ghosh A (2008) *Inorganica Chim Acta.*, Vol. 361, no. 1, pp. 161-172. | 11. Ortiz B Park S M (2000) *Bull Korean Chem Soc.*, Vol.21, no. 4, pp. 405-411. | 12. Ispir E, Kurtoglu M, Purtaş F, Serin S (2005) *Trans Metal Chem.*, Vol. 30, pp. 1042-1047. | 13. Sreedaran S, Bharathi K S, Rahiman A K (2008) *Polyhedron*, Vol. 27, no. 7, pp. 1867-1874. | 14. Housecroft W , Sharpe A(2005) *Inorganic Chemistry*, 2nd Edition, England, Pearson Education Ltd., pp.578-579. | 15. Ajaily M, Abdlseed F, Gweirif A(2007) *E-J. Chemistry*, Vol. 4, No.4, pp. 461-466. | 16. George K A, Lokhande M V, Bhusare S R (2011) *J. Chem.Biol., Physical Sci.*, Vol. 2, No.1, pp.137-144. | 17. Steven Z (2005) *Chemical Principles 5th Edn*. Boston: Houghton Mifflin Company., pp. 550-555. | 18. Cotton F, Wilkinson G(2008) *Basic Inorganic Chemistry*, 3rd Edition, New York: Wiley Interscience., pp 455-512. | 19. Yang V, Thomas B, Ren Z (2000) *Solid Propellant Chemistry, Combustion and Motor Interior.*, Vol.185, pp.423-424. | 20. Brown M (2001) *Introduction to Thermal Analysis: Techniques and Applications*, academic publisher,pp. 55-89. | 21. Shoemaker D, Garland W (1990) *Experiments in Physical Chemistry*, 5th edition McGraw-Hill International Edition, New York., pp.214-222. | 22. Deshmukh M, Dhongale S, Chavan S (2005) *Indian J.Chem.*, Vol. 44, pp.1659. | 23. Lokhande M V (2015) *J. Applicable Chem.*, Vol. 4, No.5, pp. 1477-1485. | 24. Khaydarov R, Khaydarov R, Gapurova O, Scheper T (2009) *J. Nanopartitculars research.*, Vol.11,pp. 1193-200. | 25. Sivakumar P, Nethradevi C, Renganathan S (2012) *Asian J. Pharmaceutical & Clinical Research.*, Vol. 5, pp.48-55.