



Some Transitional Metal Ion Complexes With 2,2'-{1,1'-Bi(Ferrocene-2,4-Dien-1-yl) -2,2'-Diylbis[Nitrilo(E)Methylylidene]}Bis(4-Chlorophenol) and Antimicrobial Activity

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ABSTRACT

The synthesis, structure, physico-chemical investigation and antimicrobial biological studies of some Mn(II), Co(II), Ni(II), Cu(II) Rh(II) and Pd(II) complexes of 2,2'-{1,1'-bi(ferrocene-2,4-dien-1-yl)-2,2'-diylbis [nitrilo (E) methylylidene]} bis(4-chlorophenol) compounds are described. Organometallic schiff base compounds, which are defined as metal complexes containing at least one direct, covalent metal-carbon bond. Several types of Organometallic Schiff base compounds have been prepared and characterized by using some physical techniques, in terms; elemental analysis, TGA/DTA, electronic spectra, ESR, Electron spin resonance and SEM. The elemental analysis data exhibit the formation of 1:2 [M: L] complexes. The molar conductance values reveal a non- electrolytic in nature. These complexes were also tested for their in vitro antimicrobial activities against some bacterial strains to assess their inhibiting potential and the activities shown by these complexes were compared with bacteria.

Keywords: Organometallic Schiff bases compounds, antimicrobial activity, IR, TGA/DTA, Electronic Spectra, ESR and SEM.

INTRODUCTION

Organometallic chemistry to basic issues related to sustainability, i.e. energy processing and environmental remediation [1]. The coordination chemistry of simple unfunctionalized ligands is mature and but complexes of functional ligands is filled with opportunities, inspired by supramolecular chemistry, organocatalysis and nanoscience [2-5]. Nature makes good use of organometallic chemistry for transformations of the energy-relevant substrates CO and H₂[6-8]. We would like to 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

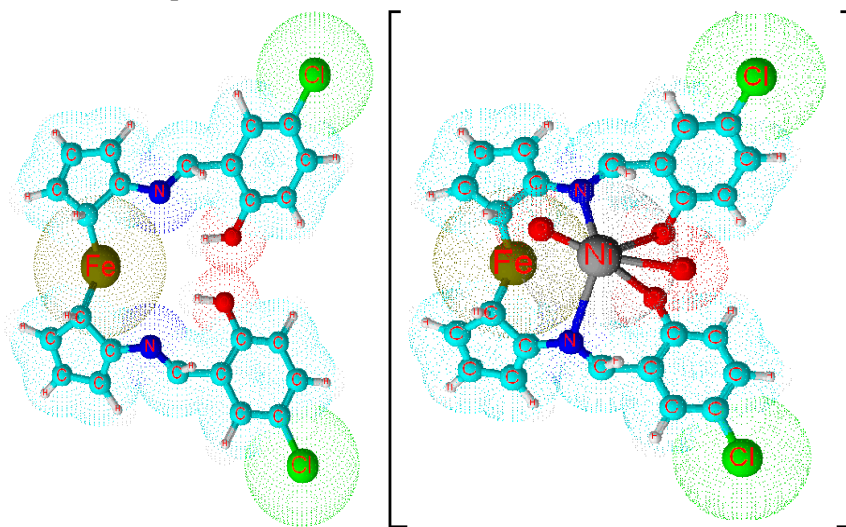
transformations based on the characteristic Numerous methods for the preparation of organometallic compounds are known in the literature [9] and can be mainly divided into four categories. The first and probably the most important one, is the reaction between an organic halide or pseudo halide and a metal such as the classical oxidative metalation or the halogen–metal exchange, have recently been found to be promising anticancer drug. [10]. the second category also very popular and recently reviewed, concerns the exchange reactions between acidic hydrogen's and basic organometallic derivatives, namely the metalation reactions. The third category concerns all the transmetalation reactions, whereas the fourth is related to the hydro- and carbometalation reactions across unsaturated systems. The growth of Schiff base organometallic Chemistry is gathering much interest in the multinuclear metal complexes owing to the oxidation- reduction reactions and photo-reactive metal centers coupling electronically through an unsaturated bridging ligand. The investigators in the area of Schiff base organometallic ligand are concentrating on their biological activity like potent inhibitors and variable bonding [11-15]. The thermal stability and the strong bonding of the ligand to the d- block elements have made the complexes more interesting. The pharmaceutical companies are targeting on the synthesis of the Schiff base organometallic complexes and their heterometallic and heterobimetallic complexes due to their improved potency and wide specificity like antitumor and anticancerous properties [16].

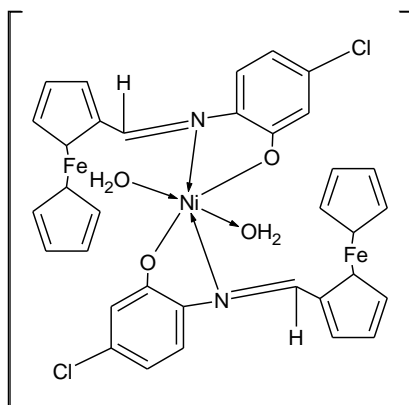
MATERIALS AND METHODS

Diamino Ferrocene (Merck) 1.87g and 1.2g of 5- chloro salicylaldehyde dissolved in butanol separately and mixed with 1:1 ratio in round bottom flask. This solution was reflux for~ 5hrs using water condenser at 80 °C. After refluxing solution was cooled at room temperature, solid separates, washed with butanol and dried at 60°C in oven to overnight. The variety of metal complexes have been prepared with Mn(II), Co(II), Ni(II), Cu(II), Rh (II) & Pd(II)metal. These organometallic Schiff base complexes are characterized by IR, UV-VIS, TGA/DTA, SEM and antimicrobial studies.

Reaction :

Ferrocene +2(5 chloro-2-hydroxybenzaldehyde)→2,2'-{ 1,1'-bi(ferrocene-2,4-dien-1-yl)-2,2'-diylbis[nitrilo (E) methylylidene]} bis(4-chlorophenol)





3D view of the Schiff base Organometallic Ni complex

Instrumental techniques: The C, H, N of Schiff base organometallic compound and its metal complexes were determined by using micro analytical methods. IR spectra of the organometallic Schiff base compounds and their complexes were carried out by using KBr pellets by using Perkin Elmer spectrophotometer. SEM recorded at TIFR Mumbai. The electronic spectra were recorded using DMSO and water as a solvent. TGA/DTA spectra were carried on Mettler Toledo Star system in the temperature range of 20-800 °C. Melting points of the ligand and decomposition temperature of complexes were determined in our laboratory.

RESULTS 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[17a].

Table 1 . Physical and Analytical data

Ligand/ Complexes	% yield	D.P/MP °C	C%	H%	N%	Fe%	M%
$(C_{17}H_{14}FeClNO)$	78	255-257	60.07*	04.12*	04.13*	16.63*	--
			59.72	03.84	03.88	16.21	
$[Mn(C_{34}H_{28}FeCl_2N_2O_2).2H_2O]$	58	232-234	53.11	03.90	03.64	07.35	07.15
			52.85	03.72	03.49	07.22	06.92
$[Co(C_{34}H_{28}FeCl_2N_2O_2).2H_2O]$	67	224-226	52.84	03.62	03.64	07.31	07.63
			52.52	03.15	03.42	07.12	07.47
$[Ni(C_{34}H_{28}FeCl_2N_2O_2).2H_2O]$	52	215-217	52.83	03.61	03.62	07.30	07.60
			52.58	03.14	03.39	07.12	07.42
$[Cu(C_{34}H_{28}FeCl_2N_2O_2).2H_2O]$	55	209-212	52.52	03.60	03.59	07.27	08.18
			52.35	03.32	03.27	07.09	08.92
$[Rh(C_{34}H_{28}FeCl_2N_2O_2).2H_2O]$	59	205-207	49.99	03.43	03.41	06.92	12.60
			49.71	03.22	03.18	06.77	12.39
$[Pd(C_{34}H_{28}FeCl_2N_2O_2).2H_2O]$	57	201-203	49.77	03.41	03.40	06.89	12.98
			49.59	03.12	03.15	06.72	12.77

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 capillary and are uncorrected. The molar conductivity conductivity values of the complexes are observed in dimethyl sulfoxide in 10^{-3} molar solution [17b] and it is non-electrolytic in nature.

Infrared Spectra: The IR spectra provide valuable information regarding the nature of functional group attached to the metal atom. The bonding mode of in the organometallic Schiff base metal ion complexes and their assignments are listed in table 2. The Infra red bands assignments of all organometallic Schiff base metal complexes exhibit broad bands in the range of 3395 to 3480 cm^{-1} indicating the presence of two coordinated water in sphere. [19-20]. A band at 1680 cm^{-1} in organometallic Schiff base is due to $\nu\text{C}=\text{N}$ vibration. The shifting of this group at lower frequency in the range 1625-45 cm^{-1} in the metal complexes, when these values compared to organometallic Schiff base. Hence it suggests that the bonding through metal ion with nitrogen atom of azomethine group [21]. The coordinate bonding of nitrogen to the central metal atom which reduces the electron density in the azomethine link and thus lower the $\text{HC}=\text{N}$ absorption.

Table 2. The Infrared spectra of organometallic Schiff base and its complexes.

Ligand/complexes	$\nu(\text{OH})\text{cm}^{-1}$	$\nu(\text{C}=\text{N})\text{cm}^{-1}$	$\nu(\text{M}-\text{O})\text{cm}^{-1}$	$\nu(\text{M}-\text{N})\text{cm}^{-1}$	$(\text{H}_2\text{O}) \text{cm}^{-1}$
($\text{C}_{17}\text{H}_{14}\text{FeClNO}$)	3340	1680	---	--	--
$[\text{Mn}(\text{C}_{34}\text{H}_{28}\text{FeCl}_2\text{N}_2\text{O}_2) \cdot 2\text{H}_2\text{O}]$	-	1645	595	470	3395,3480
$[\text{Co}(\text{C}_{34}\text{H}_{28}\text{FeCl}_2\text{N}_2\text{O}_2) \cdot 2\text{H}_2\text{O}]$	-	1625	572	457	3384,3472
$[\text{Ni}(\text{C}_{34}\text{H}_{28}\text{FeCl}_2\text{N}_2\text{O}_2) \cdot 2\text{H}_2\text{O}]$	-	1638	558	442	3380,3455
$[\text{Cu}(\text{C}_{34}\text{H}_{28}\text{FeCl}_2\text{N}_2\text{O}_2) \cdot 2\text{H}_2\text{O}]$	-	1655	584	435	3375,3448
$[\text{Rh}(\text{C}_{34}\text{H}_{28}\text{FeCl}_2\text{N}_2\text{O}_2) \cdot 2\text{H}_2\text{O}]$	-	1642	578	459	3388,3458
$[\text{Pd}(\text{C}_{34}\text{H}_{28}\text{FeCl}_2\text{N}_2\text{O}_2) \cdot 2\text{H}_2\text{O}]$	-	1647	552	428	3390,3455

A band at 3340 cm^{-1} is assigned to Ar-OH frequency in the spectrum of organometallic Schiff base, but in the complexes this bands does not appears means it indicates that involvement of oxygen atom of hydroxyl group of Ar-OH group in bonding with metal ions [22]. New bands are observed in the metal ion complexes, but bands are not present in the spectrum of organometallic Schiff base. The spectra of complexes in the range of 552-595 cm^{-1} , corresponding to metal- nitrogen bonding and 428-470 cm^{-1} corresponding to metal-oxygen vibrations respectively. The appearances of $\nu\text{M}-\text{N}$ and $\nu\text{M}-\text{O}$ vibrations support the involvement of N and O atoms in complexation with metal ions under investigation [23-25]. The $\nu\text{C}-\text{O}$ (Phenol) stretching frequency of organometallic Schiff base has seen at 1355 cm^{-1} gets shifted to a lower frequency region in the complexes in the range of 1318-1335, it indicates that bonding through phenol –Oxygen. Therefore the infrared spectral data indicates that the coordination sites of the metal ions are $\text{C}=\text{N}$ and Ar-OH.

Mass spectra: Mass spectroscopic techniques have been successfully used to check the molecular ion peaks of free organometallic Schiff base compound. The pattern of mass spectrum gives an impression of the successive fragmentations of the organometallic Schiff base compound with the series of various peaks corresponding to the different patterns and their intensities. Their intensity gives an idea about stability of fragments. The mass spectrums of organometallic Schiff base compound have a prominent base peak at 336(99% m/z). In Ni (II) complex of organometallic Schiff base compound base peak at 768(99% m/z) indicates $[\text{M}^{+2}]$ respectively. The mass spectra of organometallic Schiff base (ligand) and complex are assigned in figure 1.

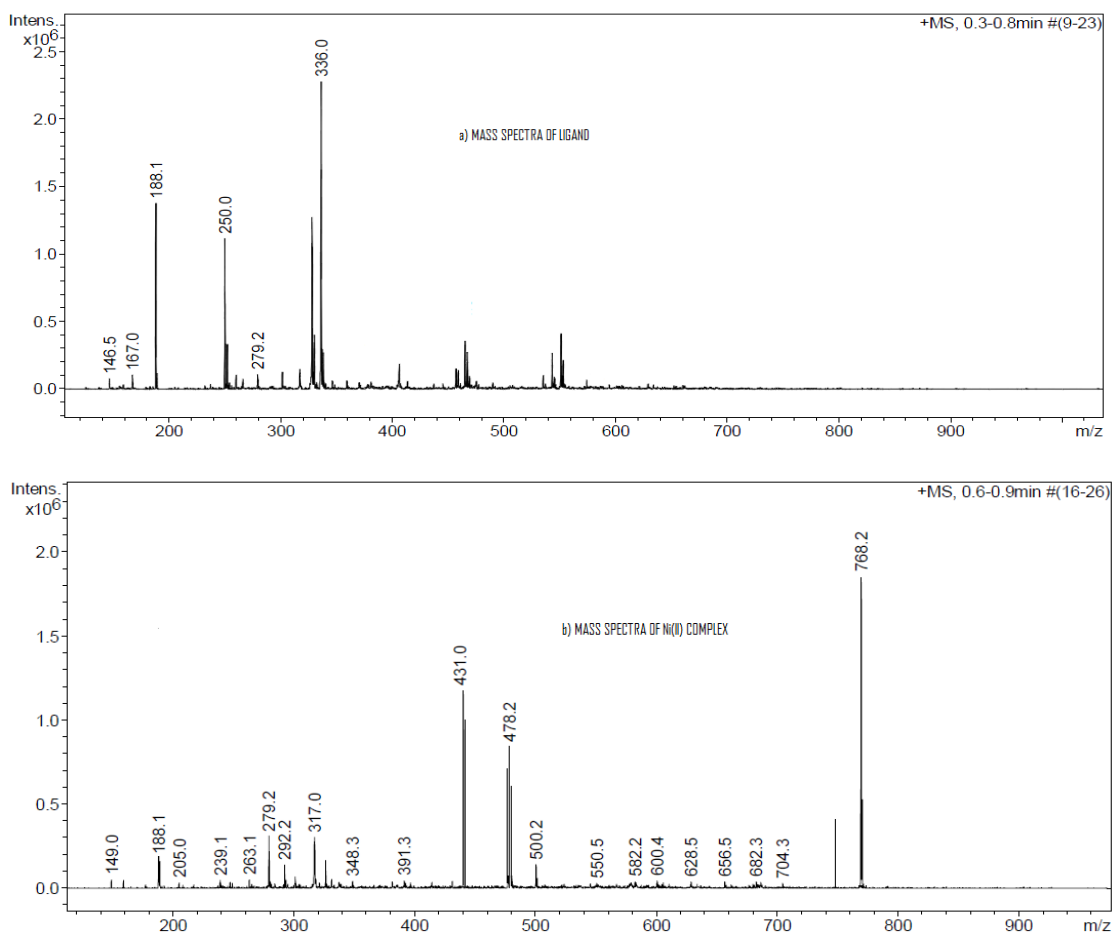


Figure 1. Mass spectra of (a) ligand($C_{17}H_{14}FeClNO$) & (b) complex $[Ni(C_{34}H_{28}FeCl_2N_2O_2) \cdot 2H_2O]$

Electronic spectra: The electronic spectral data of the Schiff base organometallic compounds and its complexes were recorded in DMSO and Ethanol. ($0.002 \text{ Mole L}^{-1}$) the nature of electronic spectra of all the complexes indicates an octahedral geometry around the central metal ions in the complexes. The Ni (II) & Co (II) complexes. This indicates that the all complexes of 6-coordinate and probably octahedral. Bonding parameter ($b^{1/2}$), Nephelauxetic parameter (β) Angular covalency (η) and Sinha's covalency parameter ($\delta \%$) [26-29] have been calculated % are given in table 3.

Table 3. Electronic spectral assignments and parameters

Complexes	Bands(cm^{-1})	Assignments	Parameters
$[Co(C_{34}H_{28}FeCl_2N_2O_2) \cdot 2H_2O]$	8723	${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$	$\beta = 0.9711$
	13450	${}^3A_{1g}(F) \rightarrow {}^2T_{2g}$	$b^{1/2} = 0.0851$
	21750	${}^3A_{2g}(P) \rightarrow {}^3T_{2g}(P)$	$\delta \% = 1.5035$ $\eta = 0.01482$
$[Ni(C_{34}H_{28}FeCl_2N_2O_2) \cdot 2H_2O]$	6290	${}^4A_2 \rightarrow {}^4T_2(F)$,	$\beta = 0.9648$
	8820	${}^4A_2 \rightarrow {}^4A_2(F)$	$b^{1/2} = 0.0938$
	20570	${}^4A_2 \rightarrow {}^4T_1(P)$.	$\delta \% = 1.8449$ $\eta = 0.01822$

Electron Spin resonance :The ESR spectra of Co (II) and Ni (II) complex recorded in atmospheric nitrogen , when they compared with samples of room temperature exhibiting all the hyperfine lines. The calculated Values and parameters [30-33] of are shown in table 4 and spectrum is shown in figure 2.

Table 4. Electron spin resonance spectra parameters

	g_{II}	g_I	g_{av}	A_o	A_{II}	A_I	K
Ni(II)	2.12	1.97	2.07	131	179	100	0.98
Cu(II)	2.02	1.94	1.99	128	192	88	0.90

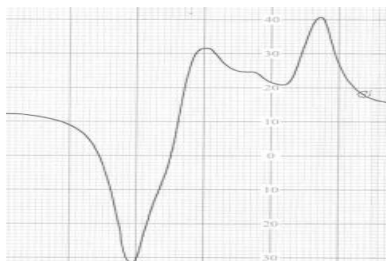


Figure 2. Electron spin resonance spectra of Cu(II) complex

SEM: The morphological characterization of nanoparticles synthesized from the organometallic Schiff base complexes were done by SEM (figure 3). SEM image shows size, shape and distribution of nanoparticle. It illustrates that nanoparticle as well as number of aggregates and it illustrates the particles are predominantly spherical in shape with uniformly distribution. Similarly monodispersed nanoparticle was reported by using the crystal of $[Rh(C_{34}H_{28}FeCl_2N_2O_2) \cdot 2H_2O]$ and $[Pd(C_{34}H_{28}FeCl_2N_2O_2) \cdot 2H_2O]$. The crystal size will be 100nm.

Thermal analysis: The thermal analysis $[Rh(C_{34}H_{28}FeCl_2N_2O_2) \cdot 2H_2O]$ complex is given in table.5 It is found that from the figure 4 heating rates were suitably controlled at $20\text{ }^\circ\text{C min}^{-1}$ under nitrogen atmosphere. The weight loss was measured from the ambient temperature upto $800\text{ }^\circ\text{C}$. Thermogram of Rh-complex indicated a total weight loss of 79% up to $800\text{ }^\circ\text{C}$, which is observed in four steps, in first stage, the weight loss in the range of $30\text{ }^\circ\text{C} - 130\text{ }^\circ\text{C}$ which is assigned to loss of water molecule which is present in the co-ordination sphere. In second stage, the weight loss in the range between $130\text{ }^\circ\text{C} - 280\text{ }^\circ\text{C}$ is attributable to the loss of both coordinated water molecules with some part of the ligand. In third state, most of the part of ligand will losses in the range of $300\text{ }^\circ\text{C} - 450\text{ }^\circ\text{C}$.

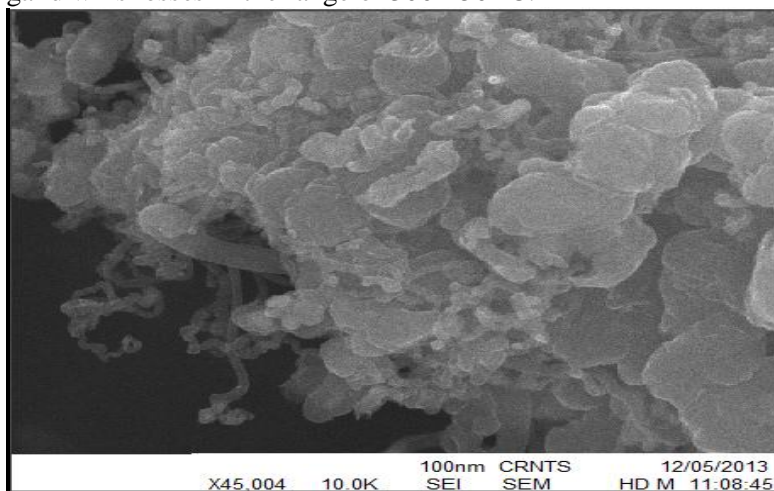


Figure 3. SEM image

In the fourth stage, it can be assigned to complete decomposition of ligand moiety around the metal ion [34] respectively. Finally the complex is converted into its metal oxide i.e rhodium oxide [35]. The presence of water molecules is further confirmed by the endothermic bands observed in respective DTA curve in the temperature region where TGA curves indicate loss in weight.

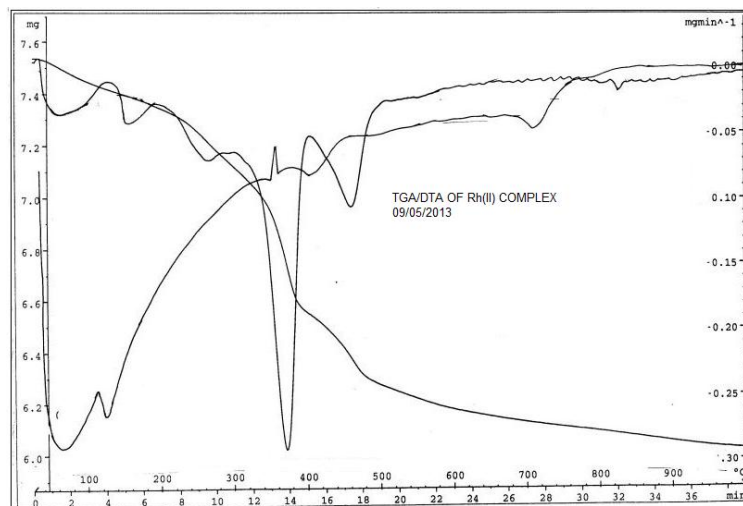


Figure 4. TGA /DTA of Rh(II) complex

Table 5. Thermo gravimetric analysis data of the complex

Complex	Temp. Range (°C)	Calculated value (%)	Experimental value (%)	Possible leaving groups
[Rh(C ₃₄ H ₂₈ FeCl ₂ N ₂ O ₂) .2H ₂ O]	30-130	4.89	4.94	H ₂ O, C ₄ N
	130-280	15.88	15.03	C ₁₀ H ₈ NCl, H ₂ O,
	300-450	12.78	11.25*	C ₈ H ₁₀ N
	450-800	52.12	53.12	Rh oxide

APPLICATIONS

Antimicrobial activity: The invitro anti bacterial activity [36] of the ligand and its complexes have been carried out against the gram negative Escherischia Coli and gram positive staphylococcus aureus using disc diffusion method by taking DMSO as solvent. A comparative study of the growth inhibition zone values of organometallic Schiff base and its complexes indicate that metal complexes exhibits higher antibacterial activity than the free ligand and the same is indicated from the results given in the below . This is probably due the greater lipophilic nature of the complexes. Such increased activity of the metal chelates can be explained on the basis of over tone's concept and Tweed's chealation theory [37-38]. According to over tones concept of shell permeability the lipid membrane that's around the cell favors the passage of only lipid soluble materials due to which liposolubility is considered to be an important factor that controls the antimicrobial activity. On chealation, the polarity of the metal ion will be reduced to a greater extent due to the overlap of the ligand orbital and partial sharing of positive charge of metal ion with donor groups[39-41] . Future it increases the delocalization of the Π electrons over the whole chalate ring and enhances the lipohilicity of the complex. This increase lipohilicity enhances the penetration of the complexes into lipid membrane and thus blocks the metal binding sights on enzymes of microorganisms [42]. These metal complexes also disturbed the respiration process of the cell and thus block the synthesis

of proteins, which restricts future growth of the organism [43-45]. The variation in the activity of different complexes against different organisms depend either on the impermeability of the cells of the microbes or difference in ribosomes of microbial cells. The detail values are given in table 6.

Table no.6: Antimicrobial activity of ligand and complexes.

Complexes/ ligand	Micro organism				
	S. Aureus	P.aeruginosa	Salmonella Sp.	Pathogenic fungi	E. Coli
[Mn(C ₃₄ H ₂₈ FeCl ₂ N ₂ O ₂) .2H ₂ O]	+++	++	++	+	+++
[Co(C ₃₄ H ₂₈ FeCl ₂ N ₂ O ₂) .2H ₂ O]	++	++	++	+	+++
[Ni(C ₃₄ H ₂₈ FeCl ₂ N ₂ O ₂) .2H ₂ O]	+++	+	++	+	+++
[Cu(C ₃₄ H ₂₈ FeCl ₂ N ₂ O ₂) .2H ₂ O]	+++	++	++	+	+++
[Rh(C ₃₄ H ₂₈ FeCl ₂ N ₂ O ₂) .2H ₂ O]	++	+	++	+	+++
[Pd(C ₃₄ H ₂₈ FeCl ₂ N ₂ O ₂) .2H ₂ O]	+++	++	++	+	+++
(C ₁₇ H ₁₄ FeClNO)	+	+	-	-	-

(Highly active = +++ (inhibition zone > 20 mm); moderately active = ++ (inhibition zone > 15 mm); slightly active = + (inhibition zone > 10 mm))

CONCLUSIONS

Organometallic schiff base compounds and their metal ions complexes are prepared, on the basis of elemental analysis and mass spectra confirm that they having 1:2 metal-ligand ratio. From Infrared spectra of the complexes indicates that, the bonding between metal-nitrogen and metal-oxygen. the size of the crystal will be 100nm.

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