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SOME TRANSITIONAL METAL IONS COMPLEXES WITH 3-[[*(E)*-(4-FLUOROPHENYL) METHYLIDENE] AMINO] BENZOIC ACID AND ITS MICROBIAL ACTIVITY

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ABSTRACT: Some transitional metal ions complexes with 3-[[*(Z)*-(4-hydroxyphenyl) methylidene] amino] benzoic acid with general formula [M(L₂)_xH₂O], [where M = Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Pd(II) and Pt(II) metal ions and L=3-[[*(E)*-(4-fluorophenyl) methylidene] amino] benzoic acid] have been synthesized and characterized on the basis of elemental analysis, conductance, magnetic susceptibility, IR, UV-Visible, ESR, X-RD and TGA/DTA. The complexes are covalent in nature with octahedral geometry. The covalency factor (β), bonding parameter were calculated. The dentistry of the complexes was in the range between 1.5 to 1.90 m/dm³ in toluene and the spectral line indicates low crystallinity of the complexes. All the complexes are non-electrolytic in nature. All the complexes are paramagnetic in nature expect Zn(II) complexes indicates slight participation of the 3d electron in bond formation. The ligand and its complexes have been screened for their antimicrobial activity with some bacteria it shows that antibacterial and antifungal activity complexes are more active towards these bacteria than Schiff base.

INTRODUCTION: The fields of Schiff base complexes have been fast growing on account of the wide variety of possible structures for the ligands depending upon the ketones, aldehydes & amines.

Schiff bases are very important class of medicinal chemistry have wide applications in many biological systems¹. The transition metal complexes of some Schiff bases containing sulphur are reported to show anticancer and antitumor activity².

The medicinal properties have been reported for the Schiff bases prepared from semicarbazones and thiocarbazones³⁻⁵. The Schiff bases have been effectively used as analytical reagents⁶ in analytical chemistry as they possess excellent ligational property. In biological applications the metal complexes of Schiff bases have been studied mainly for their fungicidal and insecticidal activity⁷.

The Schiff base metal complexes play an important role in biological systems⁸. Transition metal ion complexes of Schiff bases have more important & thoroughly studied in biological and medicinal systems. These complexes have applications wide applications in organic, inorganic, pharmaceutical, analytical and industrial, in addition to their important roles in catalysis and organometallic synthesis⁹⁻¹⁰.

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The chemotherapeutic properties of Schiff bases are now attracting the attention of biochemists¹¹⁻¹³. Earlier work reported that some drugs showed increased activity when administered as metal complexes rather than as organic compounds¹⁴⁻¹⁵.

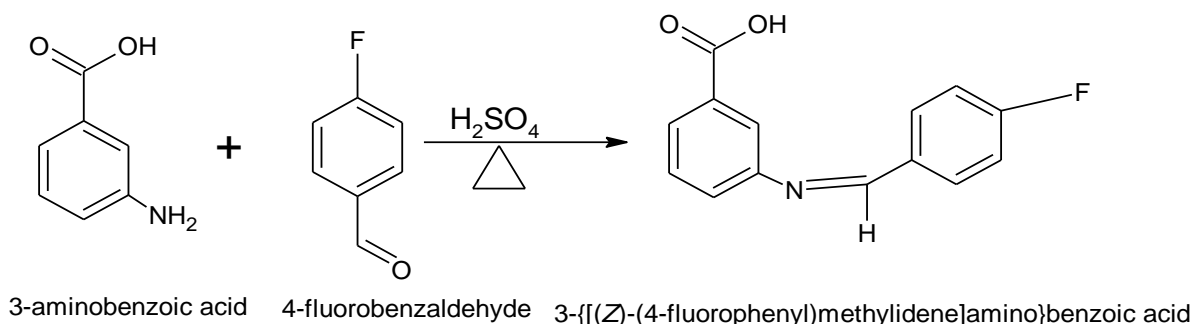
The present aim of the work is to synthesized 3-[[*(E)*-(4-fluorophenyl) methylidene] amino] benzoic acid Schiff base and to prepare its some transition metal ioncomplexes, characterize them and study their antibacterial and anti-fungal activities.

EXPERIMENTAL:

Instrumentation, Materials and methods: All reagents, chemicals were used an analytical grade without any further purification. The drugs were obtained from various pharmaceutical companies. All solvents were purified & distilled by distillation before use. Infra-red spectra recorded Perkin-Elmer paragon-500 Spectrophotometer using KBr Pallets. Electronic spectra recorded on Cintra-5 GBC UV-Visible Spectrophotometer.

Magnetic Susceptibility measurement were carried out using [HgCO (CNS)₄] as a calibrate, X-ray powder diffraction was recorded on Joel- 8030 double Goniometer X-ray powder Diffractometer . The densities of the complexes were calculated using specific density bottle in toluene solvent. TGA, DTA were recorded on mettlor Toledo star^e system, in the range 25⁰ to 1000 °C in atmospheric Nitrogen. The conductivity measurements were made on an Elico conductivity bridge. Elemental analysis, electron spin resonances were carried out at IIT Mumbai.

Preparation of Schiff base: 3-Aminobenzoic acid (1.37g) and 4-fluorobenzaldehyde (1.06 g) of each mentioned quantity was separately dissolved in 100 cm³ of alcohol and then these solutions were mixed. This solution was reflux for ≈4 hrs at 70-80° C by using few drops of acetic acid. After complete refluxing the reaction mixture was cooled to room temperature, solid separates out. The precipitate is filtered through Whatmann 41 filter paper, washed with water and dried at 60 °C for 12 hrs in hot oven. The % yield of the product will be in between 75 – 80%.



Elemental Analysis of the Schiff base:

Molecular formula of Schiff base	Molecular Weight	Elemental data % calculated		
		C	H	N
C ₁₄ H ₁₀ FNO ₂	242.06	69.42	4.54	11.57
[*are experimental values.]		70.01*	4.58*	11.65*

Preparation of Metal complexes: The solutions of Schiff base (0.1M) were prepared in double distilled alcohol and metal chloride solution prepared in double distilled water. The equimolar solutions of Schiff base (L) and of metal chlorides solution (0.1M) were refluxed for ≈3 hrs with constant magnetic stirring on hot plate. After complete refluxation 2-3 drops of alcoholic ammonia were added. Solid reappears, this solid was filtered, washed with alcohol and dried at 70

°C in dry oven for 12 hrs. The resulting complex gives the 60 – 75 % yield. The Physical properties of all prepared complexes are stable at room temperature, are non-hygroscopic and on heating they decompose at high temperature.

The complexes are insoluble in water but soluble in DMF/DMSO. The analytical data and physical properties are given in **table 1**.

RESULT AND DISCUSSION: The physical properties and analytical data of both the Schiff bases and its newly prepared metal ions complexes are listed in Table 1. All these complexes are colored and stable at room temperature. The complexes are insoluble in organic solvents like toluene, methanol, ethanol, acetonitrile & chloroform but they are soluble in dimethyl sulfoxide and dimethyl formamide. They are

decomposed in the range 210-350°C. The melting point and decomposition point reported in open capillary and are uncorrected. The molar conductivity values are in agreement with electrolytic behavior of the complexes. The conductivity values of the complexes are observed in dimethyl sulfoxide in 10^{-3} molar solution¹⁶. It is non-electrolytic in nature.

TABLE 1: ANALYTICAL DATA AND PHYSICAL PROPERTIES OF LIGAND AND ITS COMPLEX

Complex	Colour	%yield	MP/DP °C	N	M
Ligand (C ₁₄ H ₁₀ FNO ₂)	Yellow	82	245-248	5.92(5.77)	09.39(09.15)
[Mn(C ₂₈ H ₂₀ F ₂ N ₂ O ₄).2H ₂ O]	Reddish	73	212-214	4.86(4.72)	10.17(09.98)
[Co(C ₂₈ H ₂₀ F ₂ N ₂ O ₄).2H ₂ O]	Light Blue	65	217-219	4.83(4.69)	10.13(09.92)
[Ni(C ₂₈ H ₂₀ F ₂ N ₂ O ₄).2H ₂ O]	Light Pink	68	209-211	4.87(4.62)	10.88(10.42)
Cu(C ₂₈ H ₂₀ F ₂ N ₂ O ₄).2H ₂ O]	light Green	54	204-207	4.77(4.60)	11.16(10.82)
[Zn(C ₂₈ H ₂₀ F ₂ N ₂ O ₄).2H ₂ O]	colorless	59	200-202	4.75(4.58)	11.93(11.47)
[Pd(C ₂₈ H ₂₀ F ₂ N ₂ O ₄).2H ₂ O]	brownish	57	191-193	4.46(4.30)	16.97(16.17)
[Pt(C ₂₈ H ₂₀ F ₂ N ₂ O ₄).2H ₂ O]	reddish brown	52	187-189	3.91(3.75)	27.25(26.94)

Infrared spectra of Schiff bases: The IR spectrum of the Schiff base shows band at 1620 cm⁻¹ which is assigned to ν (C=N) stretching vibration, a fundamental feature of azomethine group. The broad band in the region 3360-3570 cm⁻¹ is assigned to ν (O—H) stretching vibrations, a feature indicating the presence of water¹⁷⁻¹⁸. The peaks lie in the range 1700-1750cm⁻¹ and 2695cm⁻¹ in the ligand confirms the presence of ν (C—O) and ν (C—H) group respectively. The IR spectra of Schiff base shows the bands 1600 – 1700 cm⁻¹ which attributes towards the presence of ν (C=O) and ν (C=N). In general, the (C-N) bands occur as a sharp peak in the range 1430cm⁻¹ respectively.

Infrared spectra of the Metal ion complexes: The IR spectrum provides valuable information regarding the nature of functional group attached to the metal atom. In order to study the bonding mode of Schiff bases to words metal ion complexes. Relevant IR bands that provide considerable structural evidence for the formation of ligand and complexes are reported in Table No 2. The infrared spectra of complexes were compared with ligand and their substituted moieties.

The IR band assignments of all metal complexes exhibit broad bands in the range of 3350 to 3525 cm⁻¹ indicating the presence of coordinated water molecules¹⁷. A band at 1620 cm⁻¹ in free Schiff base is due to ν C = N vibration. The shifting of this group to lower frequency (1520-1570 cm⁻¹) in the

metal complexes when compared to free ligand, suggests the coordination of metal ion through nitrogen atom of azomethine group¹⁹⁻²⁰. The atom of azomethine would reduce the electron density in the azomethine link and thus lower the –HC=N absorption. A band at 1690 cm⁻¹ is assigned to ν C=O stretching frequency in the spectrum of free Schiff base which is also shifted to lower frequency range in cm⁻¹ in all the metal complexes. This indicates the involvement of oxygen atom of hydroxy group of COOH group in bonding with metal ions²¹.

New bands, which are not present in the spectrum of ligand appeared in the spectra of complexes in the range of 505 - 570cm⁻¹, corresponding to ν M-N²²⁻²³ and 415-440 cm⁻¹ to ν M-O vibrations support the involvement of N and O atoms in complexion with metal ions²⁴⁻²⁵. The ν C-O (Phenolic) stretching frequency of ligand is seen at 1380 cm⁻¹ and shifted to a lower frequency region in the complexes in the range of 1320-1370cm⁻¹ and this is indicate by the bonding through phenolic oxygen. Therefore, the IR spectral data indicate that the coordination sites of the metal ion are - C=N, -C-O and Ar-O. The bands observed at 3490-3550 cm⁻¹ and 3350-3470 cm⁻¹ are due to two coordinated water molecules. The central metal ions have eight co-coordinated numbers and ligand behaves as bidentate ligand. The IR bands & their assignments are listed in **table 2**.

TABLE 2: RELEVANT IR SPECTRAL DATA OF THE SCHIFF BASE AND ITS COMPLEXES IN CM⁻¹

Compound	$\nu\text{C-O}$	$\nu\text{C=O}$	$\nu\text{C=N}$	$\nu\text{M-N}$	$\nu\text{M-O}$
Ligand	-	1690	1630	-	-
Mn(II)	1370	-	1540	545	430
Co(II)	1355	-	1525	555	440
Ni(II)	1340	-	1555	520	425
Cu(II)	1348	-	1528	542	415
Zn(II)	1320	-	1570	505	432
Pd(II)	1358	-	1552	570	422
Pt(II)	1328	-	1520	545	438

Electronic spectra: The electronic spectra of the Co(II), Ni(II) & Cu(II) metal ion complexes have been recorded as DMF solutions in the wavelength range 380-900 nm. The spectral parameters and their assignment are listed as in table no .3. The electronic d-d transition bands normally show weak perturbation due to complexation and increase in the intensity, shift to the red region and also splitting of some bands are observed on complex formation.

The position shapes and of Co(II), Ni(II) & Cu(II) are observed in solution phase using ethanol and dimethyl sulfoxide. The Co(II), Ni(II) & Cu(II)

complexes have lower energies as compared to those of aqua complex. The magnitude of the bathochromic shift of the bands in each case is meager nephelauxetic effect (β)²⁶, the bonding parameter ($b^{1/2}$)²⁷ and Sinha's parameter ($\delta\%$)²⁸ have been calculated. The bonding parameter reflects the participation of 3d orbital. The $b^{1/2}$ value obtained for the present complexes indicates a decreasing order of 3d- orbital participation in the Co(II), Ni(II) & Cu(II) complexes. The average value of Sinha's parameter ($\delta\%$) & η obtained in each case is positive and smaller, indicating the presence of covalent bonding character in the complexes.

TABLE 3: ELECTRONIC SPECTRA OF THE COMPLEXES AND PARAMETERS

Complexes	Absorption bands cm^{-1}	Assignments	Spectral Parameter
[Co(C ₂₈ H ₂₀ F ₂ N ₂ O ₄).2H ₂ O]	22145,	${}^4\text{A}_2 \rightarrow {}^4\text{T}_2$ (F),	$\beta = 0.9780$
	16595,	${}^4\text{A}_2 \rightarrow {}^4\text{A}_2$ (F)	$\delta = 1.13$
	11245	${}^4\text{A}_2 \rightarrow {}^4\text{T}_1$ (P)	$b^{1/2} = 0.0894$ $\eta = 0.01122$
[Ni(C ₂₈ H ₂₀ F ₂ N ₂ O ₄).2H ₂ O]	22770,	${}^3\text{A}_{2g}$ (F) \rightarrow ${}^3\text{T}_{2g}$ (F)	$\beta = 0.9685$
	15830,	${}^3\text{A}_{1g}$ (F) \rightarrow ${}^2\text{T}_{2g}$	$\delta = 1.6417$
	13021	${}^3\text{A}_{2g}$ (P) \rightarrow ${}^3\text{T}_{2g}$ (P)	$b^{1/2} = 0.0887$ $\eta = 0.0161$
[Cu(C ₂₈ H ₂₀ F ₂ N ₂ O ₄).2H ₂ O]	22012,	${}^2\text{B}_{1g} \rightarrow {}^2\text{E}_g$	$\beta = 0.9712$
	17145,	${}^2\text{B}_{1g} \rightarrow {}^2\text{B}_{2g}$	$\delta = 1.503$
	12832	${}^2\text{B}_{1g} \rightarrow {}^2\text{A}_{1g}$	$b^{1/2} = 0.0848$ $\eta = 0.0148$

Electron Spin resonance : The ESR spectra of Cu(II) and Ni(II) complex recorded in nitrogen atmospheric, below room temperature when

compared to that of room temperature in exhibiting all the hyperfine lines. The calculated Values²⁹⁻³⁰ of various parameters are given in table No.4.

TABLE 4: ESR PARAMETERS

Complexes	g_{\parallel}	g_{\perp}	g_{av}	A_0	A_{\parallel}	A_{\perp}	K	β_2	B.M
[Ni(C ₂₈ H ₂₀ F ₂ N ₂ O ₄).2H ₂ O]	2.05	1.89	2.03	122	168	95	0.88	0.97	3.52
[Cu(C ₂₈ H ₂₀ F ₂ N ₂ O ₄).2H ₂ O]	1.98	1.94	2.07	125	165	83	0.84	0.94	1.78

Magnetic properties: The corrected magnetic moment (μ_{eff}) in Bohr magneton units of the Schiff bases complexes are given in table 4. The magnetic moments of the complexes room temperature except that of Zinc(II) complex, which is diamagnetic and other complexes are

paramagnetic in nature³¹⁻³². This indicates slight participation of the 3d electron in bond formation.

X-ray Powder diffraction: The complexes were examined for their powder diffraction data. The nature of spectra indicates low crystallinity³³ of the complexes. The major reflexes were used to

calculate crystal lattice parameters using Back-cal program on computer by Ito's method. The observed values are reported in **table 5 and figure 1**. The diffractogram was indexed using POWD In and OUT software³⁴. The cell parameters of pure crystals were obtained by selecting 20 intense peaks. Calculations of cell parameters reveals that the pure crystal belongs to monoclinic crystal system³⁵, with unit cell parameters $a = 8.5548 \text{ \AA}$, $b = 8.6176 \text{ \AA}$, $c = 9.7084 \text{ \AA}$, $A=90.01$, $B=79.89$, C

$=69.89$ and unit cell volume is 679.25 . The experimental 'D' values are in good agreement with the calculated ones for the above cell parameters of the $[\text{Co}(\text{C}_{28}\text{H}_{20}\text{F}_2\text{N}_2\text{O}_4)\cdot 2\text{H}_2\text{O}]$ complex. The observed value of density of the complex is 1.1061 gm/cm^3 . To the best of author's knowledge, X-ray diffraction data on these crystals is limited only to the 2θ values and intensity. Cell parameters, (hkl) values and d-spacing are reported for the first time.

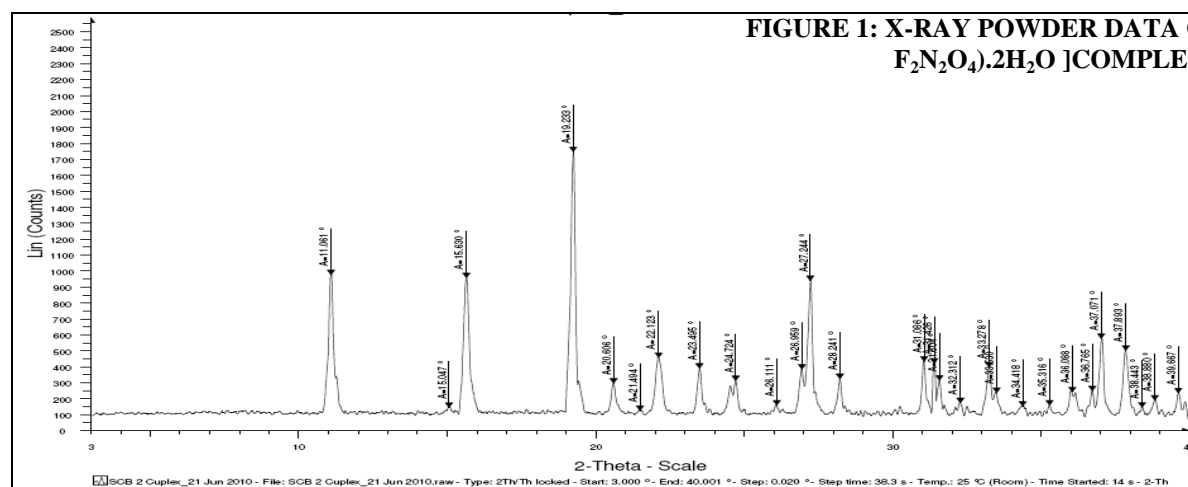


FIGURE 1: X-RAY POWDER DATA OF $[\text{Co}(\text{C}_{28}\text{H}_{20}\text{F}_2\text{N}_2\text{O}_4)\cdot 2\text{H}_2\text{O}]$ COMPLEX

TABLE 5: X-RAY POWDER DATA OF $[\text{Co}(\text{C}_{28}\text{H}_{20}\text{F}_2\text{N}_2\text{O}_4)\cdot 2\text{H}_2\text{O}]$

Parameters:

$A = 90.01$ $a = 8.5548 \text{ \AA}$
 $B = 79.89$ $b = 8.6176 \text{ \AA}$
 $C = 69.89$ $c = 9.7084 \text{ \AA}$
 $\text{Beta} = 108.373\text{D}$ $V = 679.25$

Line No.	d-spacing A°		%intensity	indices			2theta degree		Difference
	Obs.	Calc		h	k	l	Obs.	calc	
1	7.9922	8.1187	55.8	1	0	0	11.06	10.09	0.173
2	5.8828	5.9090	38.0	2	0	0	15.05	14.98	0.068
3	4.6109	4.6068	100	1	0	1	15.63	15.84	-0.207
4	4.3066	4.3088	10.6	2	0	0	19.23	19.25	-0.017
5	4.1307	4.1204	8.9	2	1	0	20.61	20.60	0.011
6	4.0146	4.0594	26.0	2	0	1	21.49	21.55	0.054
7	3.7832	3.8049	22.2	3	1	1	22.12	21.88	0.247
8	3.5979	3.5545	17.7	4	0	0	23.50	23.36	0.136
9	3.4098	3.3794	21.8	1	1	1	24.72	25.03	0.306
10	3.3044	3.3460	53.6	0	1	1	26.11	26.35	0.239
11	3.2705	3.2860	18.4	4	1	0	26.96	26.62	0.154
12	3.1573	3.1469	24.6	0	2	0	27.24	27.11	0.131
13	2.9677	2.9547	24.0	4	0	0	28.24	28.34	0.095
14	2.8442	2.8509	9.7	3	0	2	30.09	30.22	-0.136
15	2.7682	2.7777	22.5	2	0	2	31.43	31.35	0.076
16	2.6900	2.7062	13.3	0	2	1	32.31	32.20	0.114
17	2.6704	2.6754	8.5	2	1	2	33.28	33.07	0.188
18	2.6035	2.6121	8.8	4	2	0	33.53	33.47	0.064
19	2.5393	2.5402	10.5	5	1	0	34.42	34.30	0.117

Thermal analysis: Thermogravimetric and differential thermal analysis results of $[\text{Cu}(\text{C}_{28}\text{H}_{20}\text{F}_2\text{N}_2\text{O}_4)\cdot 2\text{H}_2\text{O}]$ are reported in **table 6 and figure 2**. Complexes lose weight due to exothermic and endothermic process³⁶⁻³⁷. These complexes are thermally stable at room temperature and decompose in four steps.

$[\text{Cu}(\text{C}_{28}\text{H}_{20}\text{F}_2\text{N}_2\text{O}_4)\cdot 2\text{H}_2\text{O}]$: A representative thermogram of $[\text{Cu}(\text{C}_{28}\text{H}_{20}\text{F}_2\text{N}_2\text{O}_4)\cdot 2\text{H}_2\text{O}]$ complex is given in **Fig. 2**. It is found that from the figure, the heating rates have controlled at $20^\circ\text{C min}^{-1}$ under nitrogen atmosphere and the weight loss was measured from the ambient temperature up to 800°C . Thermogram of Cu- complex indicated a total weight loss of 83 % up to 800°C , which is observed in four steps,

- (i) A small weight loss in the range of $100^\circ\text{C} - 180^\circ\text{C}$ which is assigned to loss of lattice water $[-2\text{H}_2\text{O}, \text{CO}_2]$
- (ii) Maximum weight loss in the range of $190-250^\circ\text{C}$ is attributed to the loss of coordinated

water $[-\text{OH}, (\text{C}_6\text{H}_5\text{F})_2]$. The experimental percentage loss is 33.41, which is obtained from Thermogravimetric analysis curve. The experimental percentage loss value is comparable with theoretical percentage loss value i.e. 35.40. The differential thermal analysis peak is exothermic.

(iii) Gradual weight loss in the range of $260 - 380^\circ\text{C}$ $[-\text{C}_4\text{HN}_2]$ and

(iv) Can be assigned to complete decomposition in the range of $400- 800^\circ\text{C}$ of ligand moiety around the metal ion³⁸ respectively.

Finally the complex is converted into its metal oxide. 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. The DTA curve of the complex showed endothermic peak at $190^\circ\text{C}-250^\circ\text{C}$.

TABLE 6: DECOMPOSITION OF $[\text{Cu}(\text{C}_{28}\text{H}_{20}\text{F}_2\text{N}_2\text{O}_4)\cdot 2\text{H}_2\text{O}]$ COMPLEX

complex	Temp. Range($^\circ\text{C}$)	Calculated value (%)	Expt. value (%)	Possible leaving groups
$[\text{Cu}(\text{C}_{28}\text{H}_{20}\text{F}_2\text{N}_2\text{O}_4)\cdot 2\text{H}_2\text{O}]$	100-180	16.75	17.272	$\text{H}_2\text{O}, \text{CO}_2,$
	180-200	35.40	33.41	$(\text{C}_6\text{H}_5\text{F})_2 \text{H}_2\text{O}$
	210-400	13.12	11.91	C_{11}H_4
	410-800	23.32	25.51	CuO

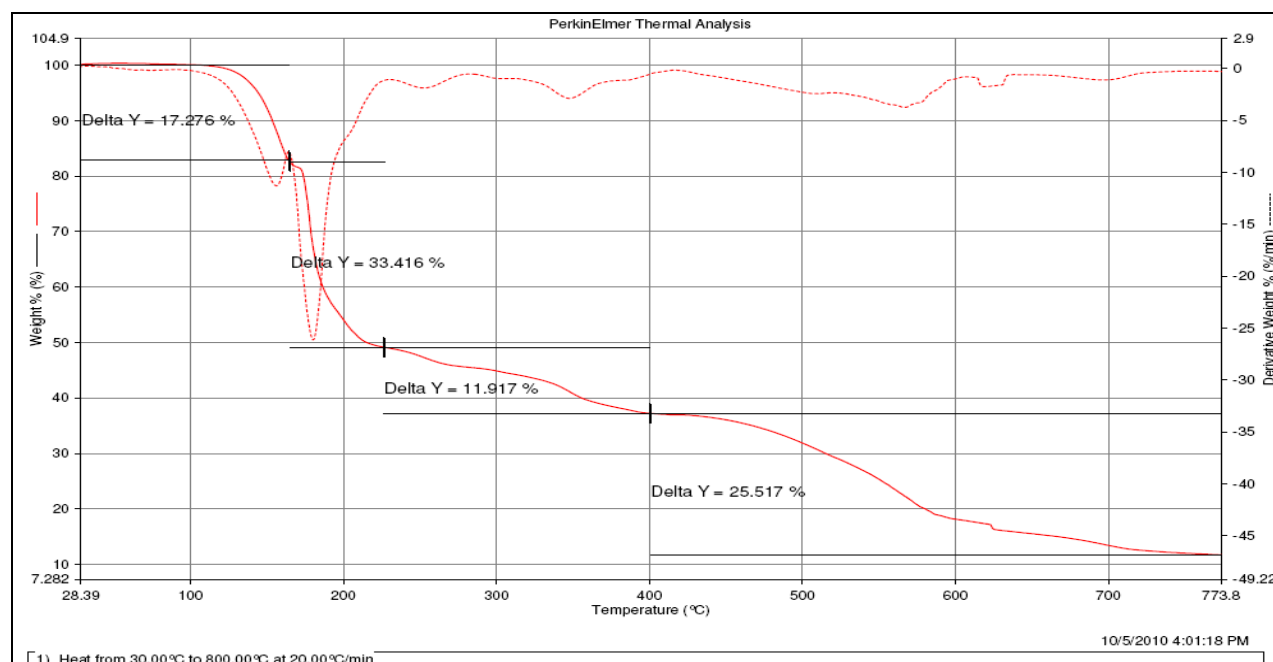


FIGURE 2: THERMOGRAM OF $[\text{Cu}(\text{C}_{28}\text{H}_{20}\text{F}_2\text{N}_2\text{O}_4)\cdot 2\text{H}_2\text{O}]$

Mass Spectral analysis of Schiff bases and their Complexes: The ESI mass spectra of the metal complexes recorded at room temperature are used to compare their composition and are listed in **table 7 and figure 3 A & B**. The Ligand [L] shows a molecular ion peak at m/z 243, which corresponds to [L+H] peak as the calculated m/z being 242. The mass spectra of Cu(II) complex shows a molecular ion peak at $m/z = 543.6$ and Co(II) complex shows a peak at $m/z = 584.4$, which corresponds to molecular weight of the respective compounds while that of Ni(II) complex shows $m/z=579.1[M+1]$ and Zn (II) complex at $m/z=589$, which corresponds to [M+1] and [M+2] respectively. The molecular ion peak at m/z 338 corresponds to the carbon ions present in the metal complex. These peaks support to the structure of the complexes and confirm the stoichiometric of metal chelates as ML type. These peaks support to the structure of the complexes.

The different molecular ion peaks appeared in the mass spectra of complexes (abundance range 2-100%) are attributed to the fragmentation of the metal complex molecule obtained from the rupture of different bonds inside the molecule by successive degradation leading to many more important peaks due to formation of various radicals. The spectra of complexes show molecular ion peaks in good agreement with the structure suggested by elemental analysis, spectral and magnetic studies. The spectra of complexes show molecular ion peaks in good agreement with the structure suggested by elemental analysis, spectral and magnetic studies. The spectra of the Schiff base and complexes shows characteristic molecular ion peaks at their m/z values confirming their monomeric forms. Here the molecular weight of metal complex is shown without water molecule, which may be corrected.

TABLE 7: MASS SPECTRAL DATA OF THE NEWLY SYNTHESIZED COMPLEXES

Compound	Expected m/z	Found m/z	Peak assigned
[Mn(C ₂₈ H ₂₀ F ₂ N ₂ O ₄).2H ₂ O]	575.4	574.0	[M +1]
[Ni(C ₂₈ H ₂₀ F ₂ N ₂ O ₄).2H ₂ O]	579.1	577.1	[M +2]
[Co(C ₂₈ H ₂₀ F ₂ N ₂ O ₄).2H ₂ O]	579.4	579	[M]
[Cu(C ₂₈ H ₂₀ F ₂ N ₂ O ₄).2H ₂ O]	584	584.9	[M]
[Zn(C ₂₈ H ₂₀ F ₂ N ₂ O ₄).2H ₂ O]	589.0	587.0	[M +2]
Schiff base	242.06	242	

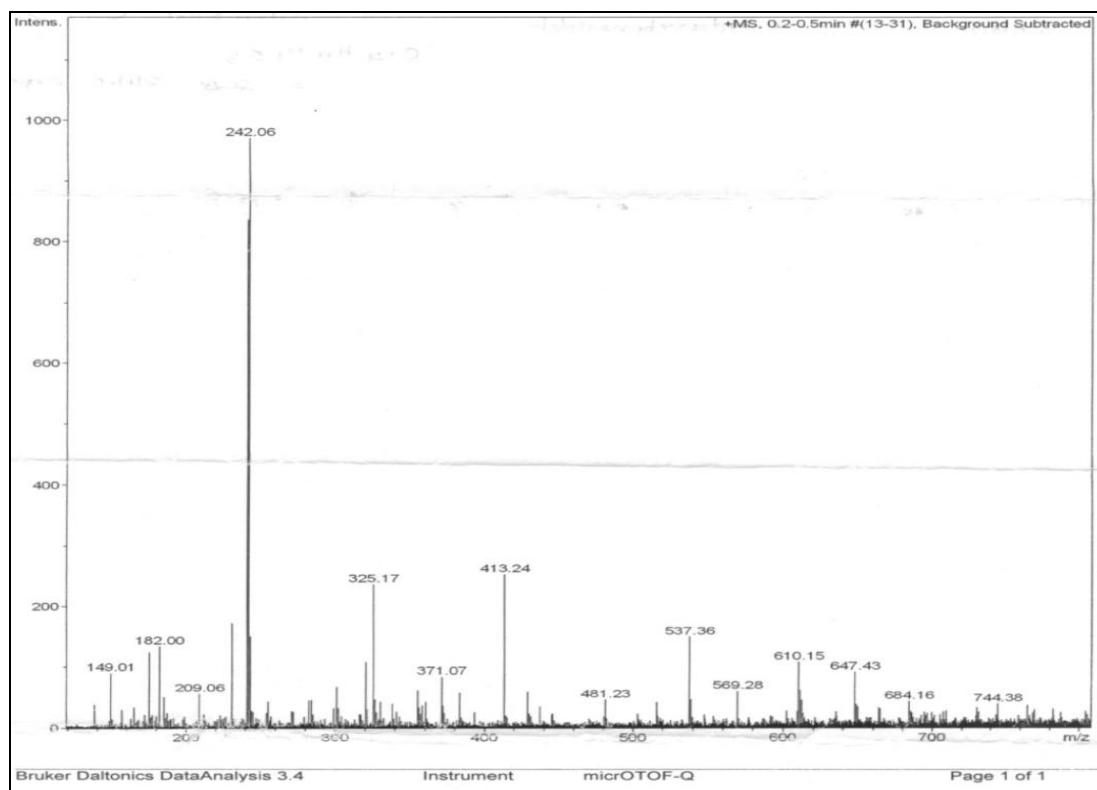


FIGURE 3A: MASS SPECTRA OF THE SCHIFF BASE

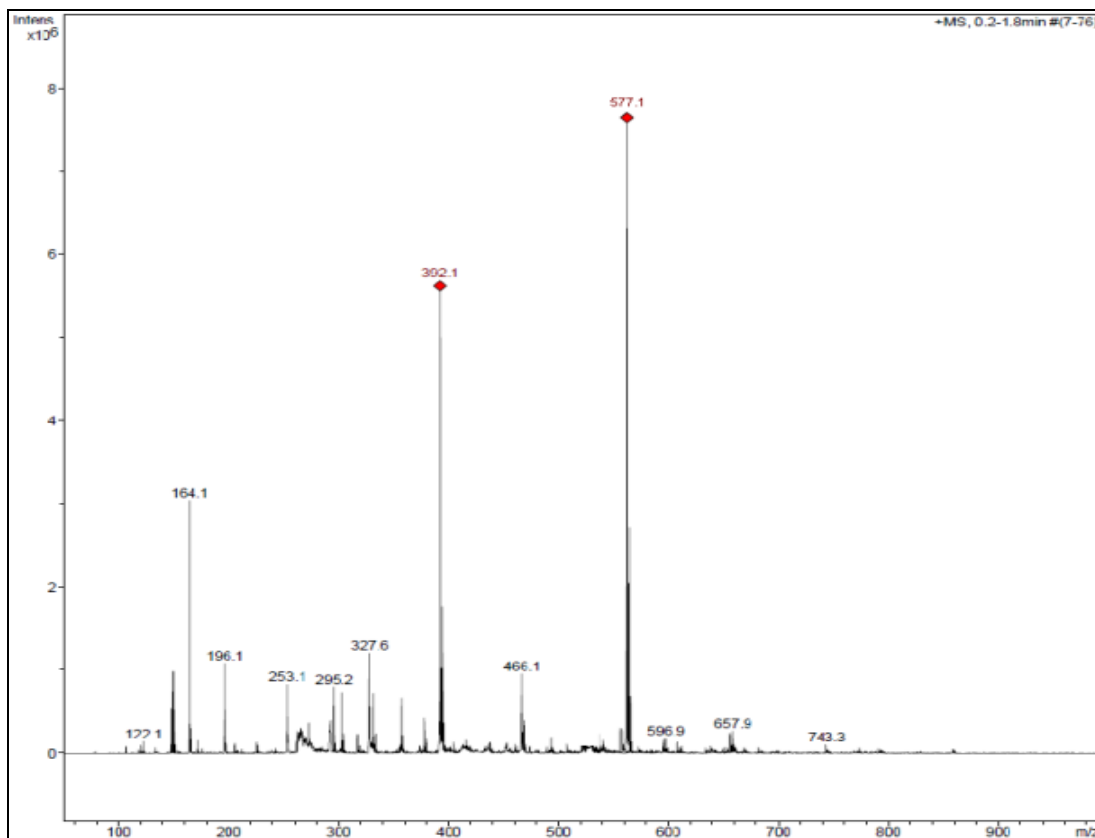


FIGURE 3B: MASS SPECTRA OF THE Ni(II) COMPLEX

Antibacterial activity: The anti-bacterial activity³⁹ of the ligand and their complexes have been carried out with gram positive *E. coli* and gram negative *S. aureus* using disc diffusion method by using DMSO as solvent. A comparative study of the growth inhibition zone values of Schiff base and its complexes shows that the metal complexes exhibit higher than the anti-bacterial activity of the Schiff base; the results are shown below table. This is probably due the greater lipophilic nature of the complexes. Such increased activity of the metal chelates can be explained⁴⁰. Formation of chelates with metal ions, 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 groups⁴¹.

Further, it increases the delocalization of the π electrons over the whole chelates ring and enhances the lipophilicity of the complex. This increased lipophilicity enhances the penetration of the complexes into lipid membrane and thus blocks the metal binding sites on enzymes of microorganisms⁴²⁻⁴³. These metal complexes also disturb the respiration process of the cell and thus block the synthesis of proteins, which restricts further growth of the organism. The variation in the activity of different complexes against different organisms depend either on the impermeability of the cell of the microbes. The inhibition zones of antibacterial activity are given below table. The Cu(II) shows highest microbial activity with gram-negative bacteria. Whereas Co(II) complex shows maximum inhibition zone against *S. aureus* at 1 mg/ml conc.

TABLE 8: ANTI MICROBIAL ACTIVITY OF SCHIFF BASE AND COMPLEXES

Complexes	<i>E. Coli</i>	<i>S. aureus</i>	<i>A. Niger</i>	<i>F. oxysporum</i>
Schiff base	9	7	12	17
[Co(C ₂₈ H ₂₀ F ₂ N ₂ O ₄).2H ₂ O]	12	14	15	21
[Ni(C ₂₈ H ₂₀ F ₂ N ₂ O ₄).2H ₂ O]	11	17	16	22
[Cu(C ₂₈ H ₂₀ F ₂ N ₂ O ₄).2H ₂ O]	14	15	17	26
[Pd(C ₂₈ H ₂₀ F ₂ N ₂ O ₄).2H ₂ O]	13	14	19	25
[Pt(C ₂₈ H ₂₀ F ₂ N ₂ O ₄).2H ₂ O]	14	17	18	23

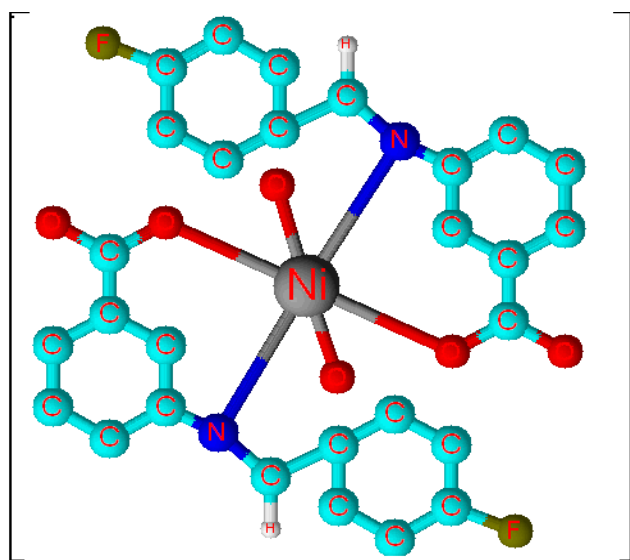
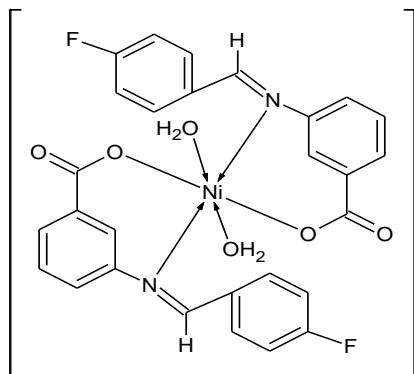


FIGURE 4: STRUCTURE OF COMPLEX

Antifungal activity: The antifungal activities of the Schiff base and their metal complexes were tested against one week old cultures of *Aspergillus niger* and *Fusarium oxysporum* using disc diffusion method. The results show that the metal complexes were more active than the free Schiff base. The azomethine group with of the Schiff base complexes is more active centers of cell constituents, resulting in an interference with normal cell process⁴⁴. The Cu(II) complexes shows highest growth in *A. niger* and *F. Oxysporum* bacteria. All the samples are submitted for clinical test on antifungal activity and antitumour activity in IPCA laboratories.

CONCLUSION: The ligand and its metal complexes of Mn (II), Co(II), Ni(II),Cu(II) and Zn(II) have been characterized. The analytical data show that the metal ligand stoichiometry in all these complexes is 1:2. All the complexes are non-electrolytes in nature due to chloride ion are absent. The spectral data show that the ligand act as neutral and bidentate coordinating through nitrogen and oxygen atom of carboxylic acid of the

Schiff base i.e. 3(2-hydroxybenzylideneamino) benzoic acid. Based on analytical, magnetic and spectral data all these complexes are octahedral geometry. We are proposing the following probable structure of the complex $[M(C_{28}H_{20}F_2N_2O_4).2H_2O]$. In antibacterial and antifungal activity complexes are more active towards these bacteria than Schiff base.

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