

Ti(III), VO(IV), Cr(III), Fe(III), MoO₂(VI) AND WO₂(VI) COMPLEXES OF NEW TRIDENTATE SCHIFF BASE LIGAND: SYNTHESIS, SPECTRAL CHARACTERIZATION, THERMAL AND BIOLOGICAL STUDIES

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ABSTRACT

A new Schiff base ligand derived from the condensation of pyrazine-2-carbohydrazide with 2-hydroxy-4-methoxybenzophenone and its Complexes of Ti(III), VO(IV), Cr(III), Fe(III), MoO₂(VI) and WO₂(VI) have been prepared and characterized by elemental analysis, molar conductance, spectral, magnetic moment measurement, PXRDs, SEM and thermogravimetric analysis. The elemental analyses suggest 1:1 metal to ligand stoichiometry for all the complexes. The hydrazone ligand acted as bi-negative tridentate coordinating through the phenolic oxygen, azomethine nitrogen and enolic oxygen atom forming a five/six membered chelating rings. On the basis of various physicochemical studies, octahedral geometry was proposed for Fe(III), Cr(III), Ti(III), MoO₂(VI) and WO₂(VI) complexes and square pyramidal geometry to VO(IV) complex. The Schiff base and metal complexes have been evaluated for antimicrobial activities which shows that all the complexes were found more active than the ligand. Furthermore, kinetic parameters were determined from the thermal data by using both Freeman-Carroll and Sharp-Wentworth methods and comparable values are obtained.

Keywords: Pyrazine-2-carbohydrazone, Spectral Data, XRDs, SEM, TGA, Biological Activity.

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INTRODUCTION

Due to the strong chelating ability through the electron delocalization and wide range of applications, hydrazones are found interesting ligands in coordination chemistry.¹⁻³ Hydrazone Schiff bases are capable of forming coordinate bonds with many metal ions via azomethine, phenolic, enolic, or thiolic groups, and so they have been used for the synthesis of metal complexes due to their easy formation and strong metal-binding ability.^{4,5} Over the past several years a large number of transition metal complexes of aroylhydrazones have been tested for their antibacterial activities and they have been found antibacterial⁶ antifungal⁷ anticancer⁸ and herbicidal⁹ activities. Furthermore, the pyrazine acid hydrazone derivatives containing hetero atoms or heterocyclic nucleus within moiety were found to exhibit remarkable biological activity.¹⁰⁻¹³ However studies of pyrazine-2-carbohydrazone of 2-hydroxy-4-methoxy benzophenone with higher valent metal ions are not reported in the literature. We were thus motivated to undertake a systematic study of preparation and characterization of Ti(III), VO(IV), Cr(III), Fe(III), MoO₂(VI) and WO₂(VI) complexes formed with pyrazine-2-carbohydrazone derived from 2-hydroxy-4-methoxy benzophenone and pyrazine-2-carbohydrazide to see the electronic effect on properties. Furthermore, we have also evaluated the biological screening of these compounds.

EXPERIMENTAL

AR Grade chemicals and solvents were utilized and commercially purchased. All the solvents were purified by standard method and used.¹⁴ Pyrazine-2 carboxylic acid and 2-hydroxy-4-methoxy benzophenone (Aldrich Chemical Company, USA), acetyl acetone, hydrazine hydrate, anhydrous titanium chloride, chromium chloride hexahydrate, anhydrous ferric chloride and Vanadyl sulphate pentahydrate were of

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A Carlo Erba 1108 elemental analyser was used to analyse carbon, hydrogen and nitrogen elements. The IR spectra of ligand and its complexes were recorded on KBr pellets using a Shimadzu 8201 spectrophotometer in the range of 400-4000 cm⁻¹. Magnetic moment measurements should be carried out by using the Sherwood magnetic susceptibility balance MK1 at room temperature. NMR spectrophotometer On Bruker Advance II, 400 MHz, in d₆-DMSO with TMS, ¹H and ¹³C NMR spectra were recorded at SAIF, Punjab University, Chandigarh, India. A Cary 60 UV-Vis spectrophotometer in the range of 200-1000 nm (as MgO) disc was applied to record the diffuse reflectance spectra of the complexes. With the use of a Bruker AXS-D₈ Advance equipped with Si(Li)PDS instrument, Powder X-ray diffraction patterns were determined. On a Waters Q-TOF micro-mass (LC-MS) spectrometer, mass spectra of ligand and complexes were recorded. Thermal study of complexes usually done on a Perkin Elmer, Diamond TG thermal analyzer in the temperature range 40-750 °C with a heating rate of 10 °C min⁻¹. The electrical conductance measurements were carried out using Elico conductivity bridge and dip type cell calibrated with KCl solution. SEM images and EDX graphs of complexes were recorded at SAIF, KBC North Maharashtra University, Jalgaon, India.

^{13}C -NMR (DMSO- d_6 , 400MHz) : 160.76 (C=N), 158.96 (C12), 157.68 (C10), 150.27 (C=O), 148.27 (C6), 143.71 (C2), 142.86 (C3), 142.88 (C5), 131.74 (C8), 112.03 (C11), 106.23 (C7), 101.62 (C9), 127.88-131.74 (Ar-H), 55.28 (CH_3) (Fig.-2).

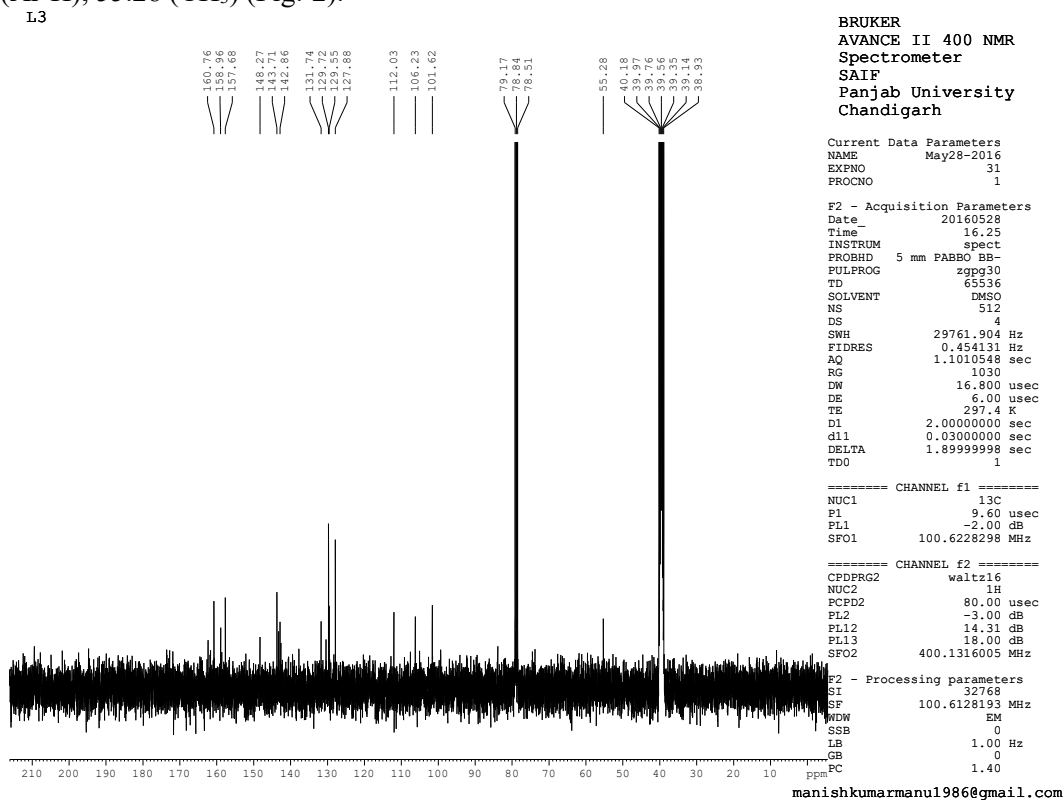


Fig.-2: ^{13}C NMR Spectrum of Ligand (H_2L)

Mass Spectrum (ESI) $[\text{M}]+1 = 349.0900$ (Fig.-3).

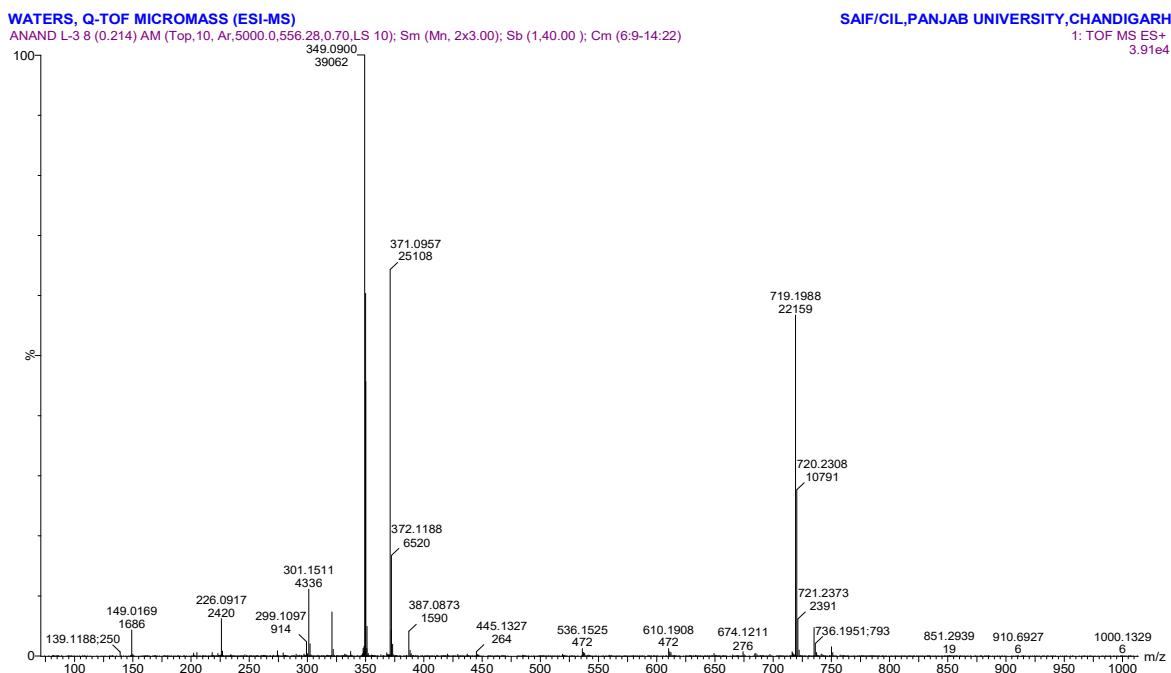
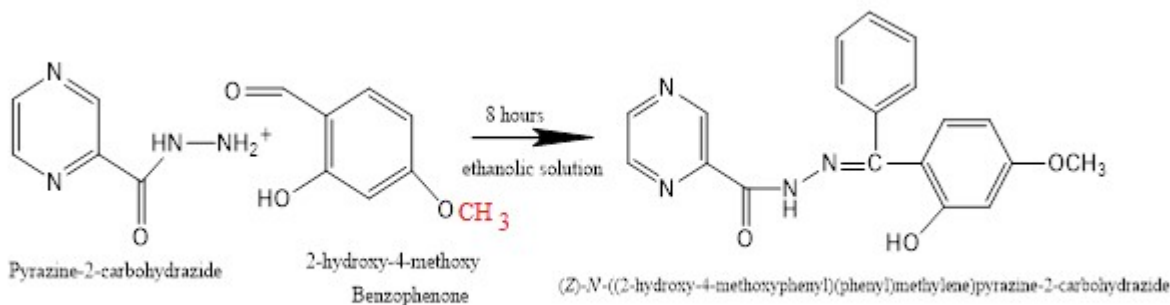


Fig.-3: Mass Spectrum of Ligand (H_2L)

The general scheme for the synthesis of Ligand shown in Scheme-1.



Scheme-1: Synthesis of Ligand (H_2L)

Synthesis of the Complexes

For the synthesis of Ti(III), VO(IV), Cr(III), and Fe(III) complexes, An equimolar amount of ligand (0.01 mol) and respective metal salt (0.01 mol) were dissolved separately in DMF and Ethanol (50:50 v/v) (25 mL). Both the solutions were filtered and mixed them in warm conditions with continuous stirring. The reacting mixture was refluxed for 5 h on an oil bath and its pH was maintained 7.0 by adding ethanolic solution of sodium acetate (0.5 g) and again refluxing for another 1 h. On cooling to room temperature, the solid product separated out was filtered, washed with cold DMF, ethanol and finally petroleum ether to remove excess of metal salts and ligand and finally dried under vacuum over $CaCl_2$. Yield: 55-68 %.

Synthesis of $[MoO_2(L)(H_2O)]$ and $[WO_2(L)(H_2O)]$ Complexes

A hot methanolic solution (25 mL) of $[MoO_2(acac)_2]$ (0.44 g, 1 mmol) was mixed dropwise with a hot ethanolic solution of ligand (H_2L) (0.1 mmol) with vigorous shaking. The resulting turbid solution was filtered and then refluxed on a water bath with continuous stirring for 4 h. After reducing the volume of the solution to 10 mL and cooling at $10^\circ C$ overnight, the separated colored product obtained was filtered, washed with ethanol followed by petroleum ether and finally dried in a desiccator over anhydrous $CaCl_2$. Yield: 65 %. The $[WO_2(L)(H_2O)]$ complex was prepared under the similar condition as above using $[WO_2(acac)_2]$ and H_2L with 63% yield. All the complexes were found to be insoluble in water and in most of the common organic solvents except sparingly soluble in DMF and DMSO.

Antimicrobial Activity

The antimicrobial activities of the ligand (H_2L) and its complexes were carried out at the Department of Microbiology, Bhartiya Mahavidyalaya, Amravati by disc diffusion method against *S. aureus* and *E. coli* and fungi *A. Niger* and *C. albicans* at a concentration of $10 \mu g/ml$ in DMSO. The standard drugs like Streptomycin and Clotrimazole were used for antibacterial and antifungal activity. All these tests were performed triplicates under identical conditions and DMSO was used as a negative control and model values were selected.

RESULTS AND DISCUSSION

The reaction between pyrazine-2-carbohydrazide with 2-hydroxy-4-methoxy benzophenone in methanol yields a hydrazone ligand. The chemical equations concerning the formation of the hydrazone are represented in scheme 1. The formation of the ligand was confirmed by its spectral and elemental data. Reaction of ligand with metal salts under reflux condition gave the products presented in table 1. All complexes are colored solids, stable at room temperature and insoluble in common solvents such as ethanol, methanol, chloroform, benzene, cyclohexane, acetone, diethyl ether and but sparingly soluble in DMF and DMSO. The analytical and physical data of the metal complexes are summarized in Table-1. The elemental analyses indicate 1:1 (metal: ligand) stoichiometry and good agreement with the proposed structures and geometry of complexes. The mass spectrum of ligand showed a molecular ion peak at $m/z = 349$ which is consistent with its formula weight. Most of the complexes are decomposes at higher temperature without

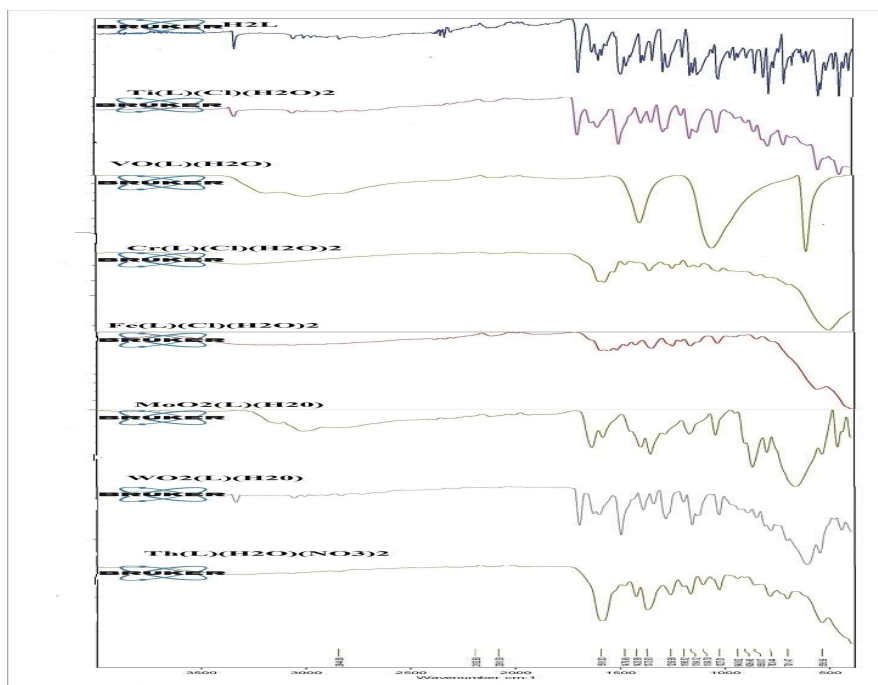
melting. The observed low value of molar conductivity of complexes in DMSO indicating non-electrolytic nature.¹⁸⁻¹⁹

Table-1: Elemental Analysis and Physical Data of Ligand and Its Metal Complexes

Compound	Colour	Molecular Formula	Molecular wt.	Elemental Analysis % Found (Calculated)						Molar Conductance ($\Omega^{-1}\text{cm}^2 \text{mol}^{-1}$)
				C	H	N	O	M	Cl	
H ₂ L	Crème white	C ₁₉ H ₁₆ N ₄ O ₃	348.36	64.81 (65.51)	4.11 (4.63)	14.08 (16.08)	12.14 (13.78)			3.9
[Ti(L)(Cl)(H ₂ O) ₂]	Yellowish white	C ₁₉ H ₁₈ ClN ₄ O ₅ Ti	465.69	46.99 (48.79)	3.89 (4.31)	11.66 (11.98)	16.51 (17.1)	9..83 (10.23)	5.58 (7.58)	3.9
[VO(L)(H ₂ O)]	Yellowish white	C ₁₉ H ₁₆ N ₄ O ₅ V	431.30	51.77 (52.91)	3.61 (3.74)	11.73 (12.99)	17.66 (18.55)	12.34 (11.81)		6.8
[Cr(L)(Cl)(H ₂ O) ₂]	Greenish yellow	C ₁₉ H ₁₈ ClCrN ₄ O ₅	469.82	48.21 (49.00)	3.65 (3.19)	11.69 (12.03)	16.99 (17.18)	12.22 (11.07)	6.91 (7.61)	4.5
[Fe(L)(Cl)(H ₂ O) ₂]	Brown	C ₁₉ H ₁₈ ClFeN ₄ O ₅	473.67	46.18 (48.18)	3.03 (3.83)	12.33 (11.83)	15.39 (16.89)	10.58 (11.79)	6.38 (7.48)	4.6
[MoO ₂ (L)(H ₂ O)]	Yellowish white	C ₁₉ H ₁₆ MoN ₄ O ₆	492.32	46.61 (46.35)	3.9 (3.28)	10.89 (11.38)	18.85 (19.50)	19.99 (19.49)		6.4
[WO ₂ (L)(H ₂ O)]	Greenish white	C ₁₉ H ₁₆ N ₄ O ₆ W	584.20	39.12 (39.33)	2.94 (2.78)	8.44 (9.66)	14.77 (16.55)	29..78 (31.69)		8.3

IR Spectra

To study the binding mode of hydrazone to metal ion, the IR spectrum of free ligand was compared with that of metal complexes. The most relevant bands and proposed assignments for all complexes along with hydrazone ligand are given in Table-2 and shown in Fig.-4.

Fig.-4: IR Spectra of Ligand (H₂L) and its Metal Complexes

The ligand (H_2L) shows a medium band at 3334cm^{-1} assignable to intramolecular hydrogen bonded ($O-H\cdots N$) phenolic OH stretching vibrations. In the spectra of the complexes, this band was found to be absent due to coordination that occurs through the phenolic oxygen atom to the metal ion. This is further supported by the upward shift of $\nu(C-O)$ phenolic band (~ 25 to 35 cm^{-1}) in the spectra complexes as compared to free ligand²⁰. The bands due to $\nu(C=N)$ and $\nu(N-N)$ were shifted to a lower frequency i.e. $1579-1541\text{ cm}^{-1}$ and $1057-1041\text{ cm}^{-1}$ on complexation. IR spectrum of ligand shows a characteristic absorption band of $\nu(C=O)$ and $\nu(N-H)$ were observed respectively at 1692 cm^{-1} and 3051 cm^{-1} . These bands showed that ligand exists in keto-form in the solid state. The absence of these bands in the spectra of complexes indicates the destruction of carbonyl moiety due to the enolization and subsequent coordination of the enolate oxygen to metal. The appearance of another new medium intensity band at $\sim 1249-1284\text{ cm}^{-1}$ in the spectra of complexes due to coordination of enolic oxygen after de-protonation²¹. Bonding was further substantiated by the appearance of new stretching vibrations at $534-693\text{ cm}^{-1}$ and $499-430\text{ cm}^{-1}$ due to $\nu(M-O)$ and $\nu(M-N)$ modes respectively. The $MoO_2(VI)$, $WO_2(VI)$ and $VO(IV)$ complexes display medium bands at $746-792$, $841-891$ and 965 cm^{-1} due to $(O=Mo=O)$, $(O=W=O)$ and $(V=O)$ modes, respectively. In $MoO_2(VI)$ complexes, medium and strong band are observed in region $3421-3457\text{ cm}^{-1}$ due to $\nu(OH)$ and shoulder band at $1541-1548\text{ cm}^{-1}$ due to $\nu(H_2O)$ indicating the presence of water molecules. In the spectra of $WO_2(VI)$ complexes, three bands are observed at 455 , 714 and 541 cm^{-1} suggest thiocyanate group, which is N-bonded²². Therefore, the IR data of the ligand and metal complexes indicate coordination of the ligand through the phenolic oxygen, azomethine nitrogen and enolic oxygen atom.

Table-2: Important IR Spectral Bands (cm^{-1}) of the Ligand and its Metal Complexes

Compound	V(O-H)	V(NH)	V(C=O)	V(C=N)	V(C-O) Phenolic	V(C-O)	V(N-N)	V(M-O)	V(M-N)
						Enolic			
H_2L	3334	3051	1692	1596	1336		1021		
[Ti (L)(Cl)(H ₂ O) ₂]	-	-	-	1554	1386	1280	1025	542	439
[Vo(L) (H ₂ O)]	-	-	-	1541	1378	1264	1057	607	447
[Cr(L)(Cl)(H ₂ O) ₂]	-	-	-	1571	1357	1277	1026	693	499
[Fe(L)(Cl)(H ₂ O) ₂]	-	-	-	1554	1348	1249	1036	561	430
[MoO ₂ (L)(H ₂ O)]	-	-	-	1560	1353	1284	1043	534	450
[WO ₂ (L)(H ₂ O)]	-	-	-	1559	1388	1282	1028	545	442

Electronic Spectra and Magnetic Moments

The diffuse reflectance spectrum of the Fe(III) complex shows three bands at 13887 , 18452 and 25412 cm^{-1} , which can be assigned to ${}^6A_{1g} \rightarrow {}^4T_{1g}(G)$, ${}^6A_{1g} \rightarrow {}^4T_{2g}(G)$ and ${}^6A_{1g} \rightarrow {}^4E_g(G)$ transitions, respectively, for an octahedral complex. The magnetic moment of Fe(III) complex is 5.86 B.M. , corresponding to five unpaired electrons.²³ The Cr(III) complex exhibited three characteristic bands at 18555 , 26411 and 40125 cm^{-1} which may be assigned to the ${}^4A_{2g} \rightarrow {}^4T_{2g}(F)$, ${}^4A_{2g} \rightarrow {}^4T_{1g}(F)$ and ${}^4A_{2g} \rightarrow {}^4T_{1g}(P)$ transitions, respectively in an octahedral environment around the Cr(III) ion. The ligand field Parameters (Dq), Racah interelectronic repulsion parameter (B), covalency factor (nephelauxetic ratio) (β) and % covalency (β_0) of the metal-ligand bond have been calculated for the Cr(III) complex and the values for Dq , B , ν_2/ν_1 , β and % covalency (β_0) and values are given in Table-3. For Cr(III) complex, due to delocalization of electron from metal into molecular orbital, the value of B (Racah inter electronic repulsion parameter) was found to be lower than the free ion values (918 cm^{-1}) covering both the metal and the ligand corresponding to an appreciable covalent character of the metal-ligand bond (% covalency (β_0) = 23). The ratio ν_2/ν_1 is found to be 1.39 , which is very close to the value of 1.42 obtained for pure octahedral Cr(III) complexes. The magnetic moment for Cr(III) complex was 3.99 B.M. indicating three unpaired electrons in an octahedral environment.²⁴ The Ti(III) complex shows one broadband around at $\sim 18168\text{ cm}^{-1}$ due to the ${}^2T_{2g} \rightarrow {}^2E_g$, transition for octahedral symmetry in the Ti(III) complex. The Ti(III) complex has a magnetic moment 1.76 B.M. corresponding to one unpaired electron in an octahedral environment. The broad and double hump nature of the spectrum of the complex indicates the presence of Jahn-Teller distortion.²⁵ The VO(IV) complex shows three bands at 14570 , 17846 and 25664 cm^{-1} due to ${}^2B_2 \rightarrow {}^2E_0$, ${}^2B_2 \rightarrow {}^2B_1$ and ${}^2B_2 \rightarrow {}^2A_1$, transitions, respectively, towards square pyramidal geometry around VO(IV) ion. The magnetic moment

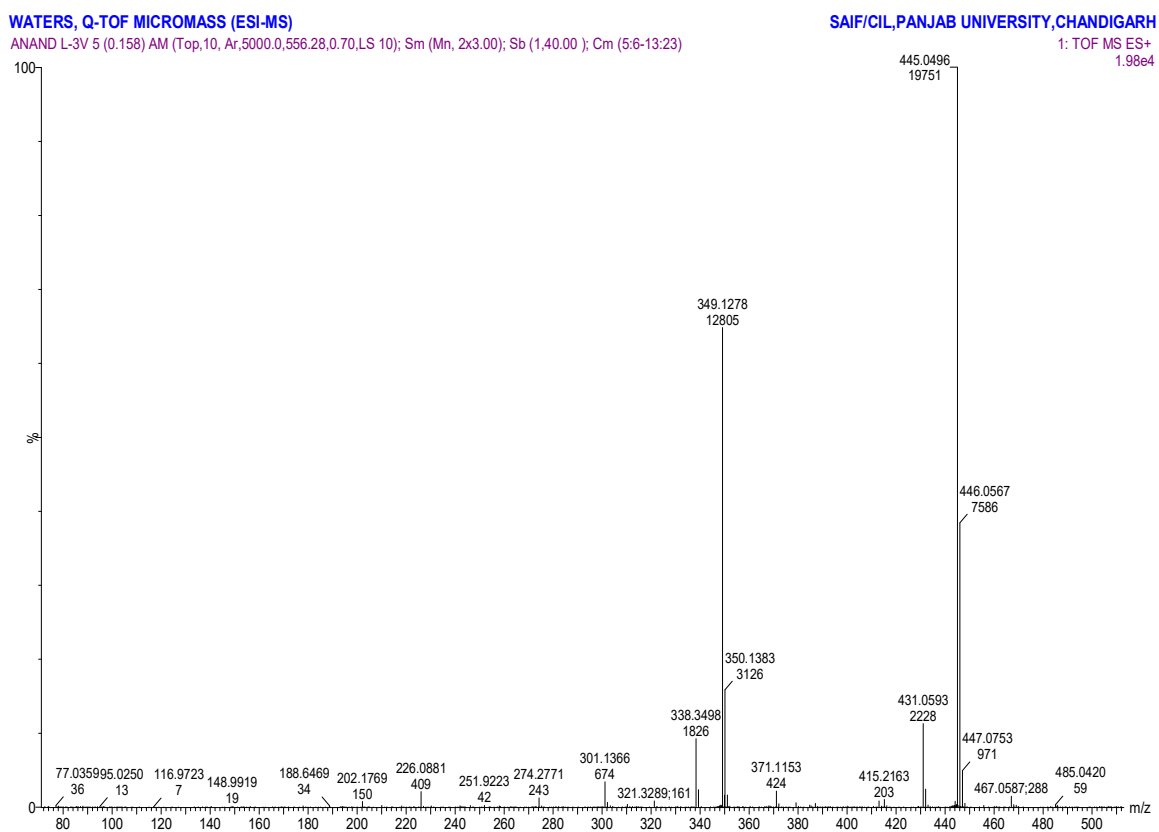
for VO(IV) complex at room temperature was found to be 1.75 B.M, corresponding to one unpaired electron. The dimagnetic behaviour shown by MoO₂(VI) and WO₂(VI) complexes from their configurations which indicates that there is no any d-d transitions possible in their reflectance spectra and exhibits octahedral geometry towards MoO₂(VI) and WO₂(VI) ions.²⁶

Table-3: Magnetic Moments and Electronic Spectral Data of Metal Complexes

Compound	μ_{eff} (BM)	Band Position (cm ⁻¹)	Assignments	ν_2/ν_1	Dq (cm ⁻¹)	B (cm ⁻¹)	β	B ₀
[Ti(L)(Cl)(H ₂ O) ₂]	1.76	$\nu_1=18168$	${}^2T_{2g} \rightarrow {}^2E_g$	--	--	--	--	--
[VO(L) (H ₂ O)]	1.75	$\nu_1=14570$ $\nu_2=17846$ $\nu_3=25664$	${}^2B_2 \rightarrow {}^2E_0$ ${}^2B_2 \rightarrow {}^2B_1$ ${}^2B_2 \rightarrow {}^2A_1$	--	--	--	--	--
[Cr(L)(Cl)(H ₂ O) ₂]	3.99	$\nu_1=18555$ $\nu_2=26411$ $\nu_3=40125$	${}^4A_{2g} \rightarrow {}^4T_{2g}(F)$ ${}^4A_{2g} \rightarrow {}^4T_{1g}(F)$ ${}^4A_{2g} \rightarrow {}^4T_{1g}(P)$	1.39	1776	708	0.77	23
[Fe(L)(Cl)(H ₂ O) ₂]	5.26	$\nu_1=13887$ $\nu_2=18452$ $\nu_3=25412$	${}^6A_{1g} \rightarrow {}^4T_{1g}(G)$ ${}^6A_{1g} \rightarrow {}^4T_{2g}(G)$ ${}^6A_{1g} \rightarrow {}^4E_g(G)$	--	--	--	--	--

Mass Spectra

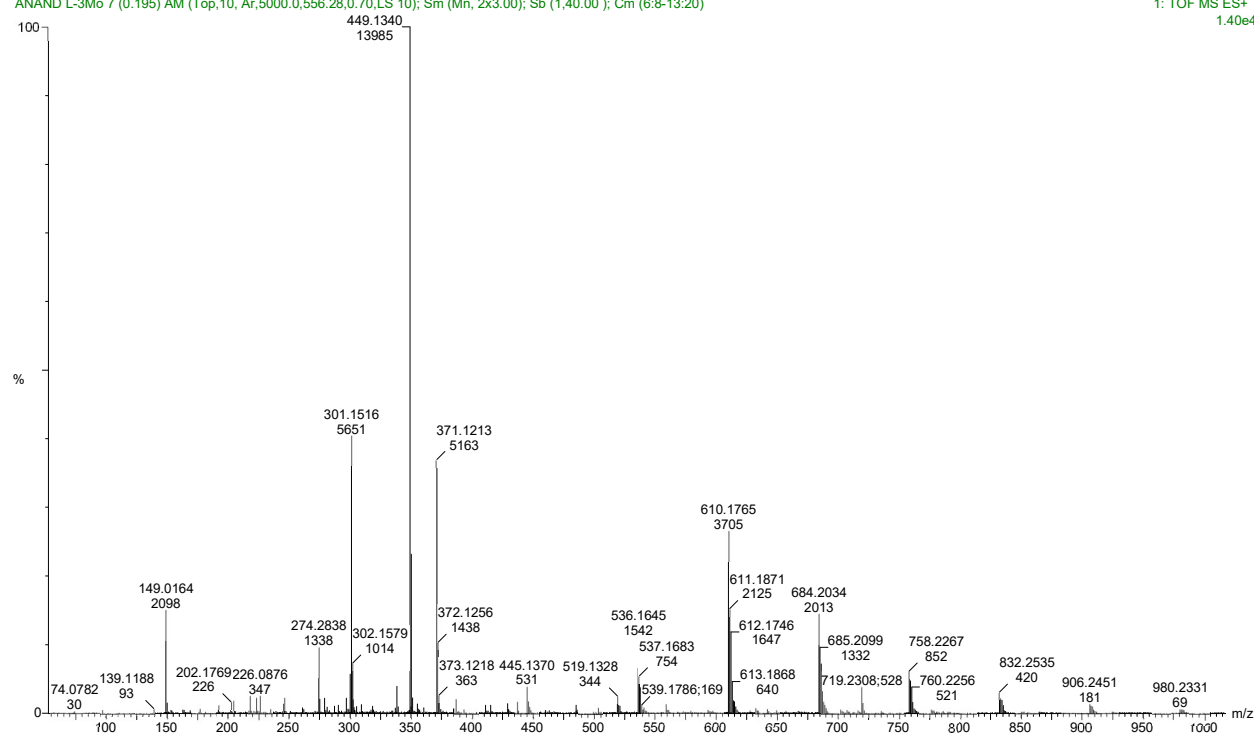
To compare their stoichiometric composition, the ESI mass spectra of ligand and its VO(IV) and MoO₂(VI) complexes have been recorded as representative case . The mass spectra of VO(IV) and MoO₂(VI) complexes showed m/z peaks at 445 and 449 ,respectively, corresponding to the molecular weight of the parent ion and depicted in Figs.-5 and 6.The spectra of complexes show molecular ion peaks in good agreement with the structure suggested by elemental analysis, spectral and magnetic studies.²⁷

Fig.-5: Mass Spectrum of [VO(L) (H₂O)] Complex

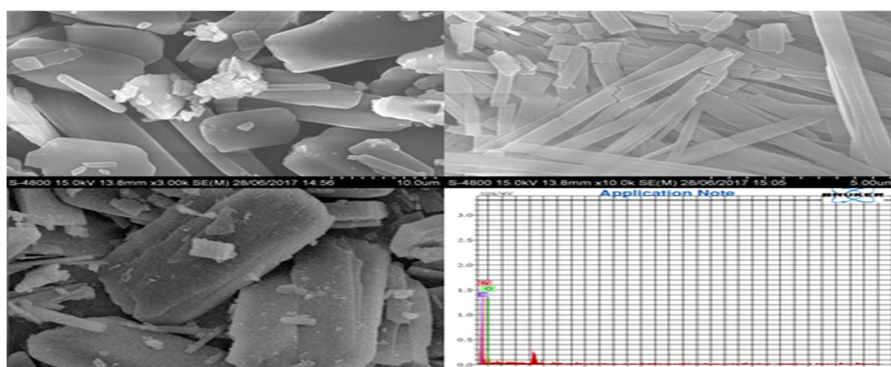
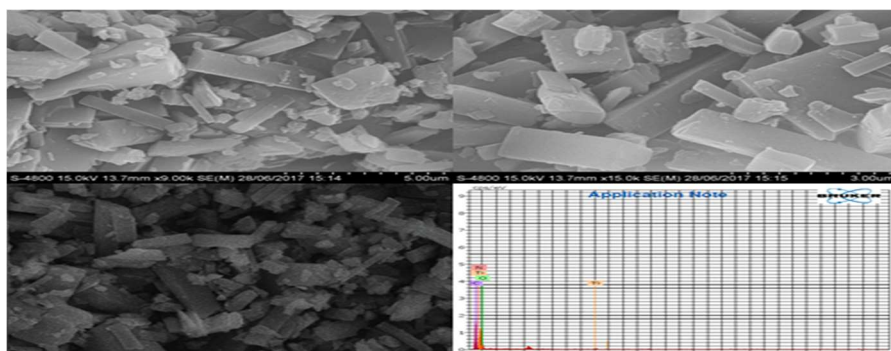
WATERS, Q-TOF MICROMASS (ESI-MS)

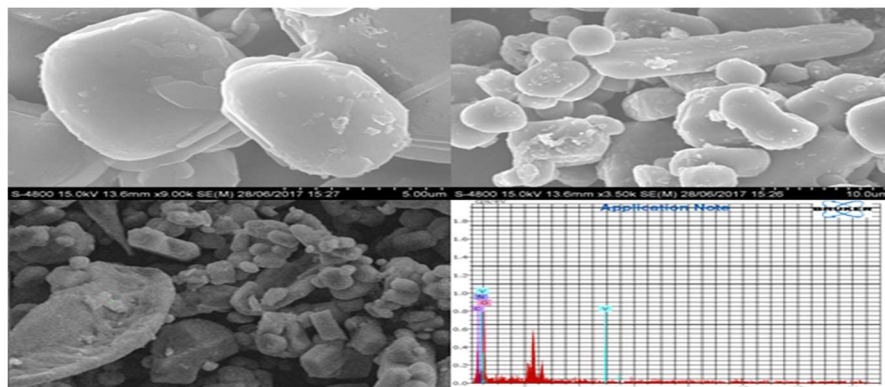
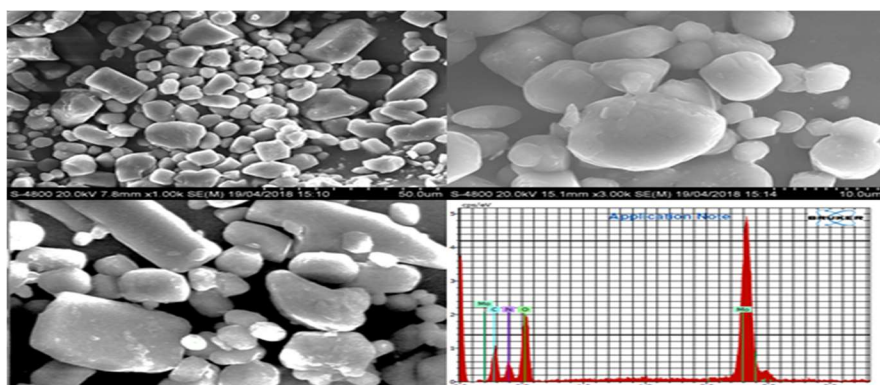
ANAND L-3Mo 7 (0.195) AM (Top,10, Ar,5000.0,556.28,0.70,LS 10); Sm (Mn, 2x3.00); Sb (1,40.00); Cm (6:8-13:20)

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1: TOF MS ES+
1.40e4Fig.-6: Mass Spectrum of $[\text{MoO}_2(\text{L})(\text{H}_2\text{O})]$ Complex**SEM Analysis**

The morphology and the distribution of particle sizes of the ligand (H_2L), Ti(III) , VO(IV) and $\text{MoO}_2(\text{VI})$ complexes are shown in Figs.-7(a-d).

Fig.-7a: Scanning Electron Microscope Image of Ligand (H_2L)Fig.-7b: Scanning Electron Microscope Image of $[\text{Ti}(\text{L})(\text{Cl})(\text{H}_2\text{O})_2]$ Complex

Fig.-7c: Scanning Electron Microscope Image of $[\text{VO}(\text{L})(\text{H}_2\text{O})]$ ComplexFig.-7d: Scanning Electron Microscope Image of $[\text{MoO}_2(\text{L})(\text{H}_2\text{O})]$ Complex

The complexes show smooth and irregular surface morphology with particle sizes of greater than $10\ \mu\text{m}$. The average crystalline size shows that the particles were agglomerated that these complexes were polycrystalline with nano sized grains, and results obtained from SEM are in good agreement with the powder XRD results. The rock needle-like appearance was exhibited by the H_2L ligand, spherical granular-like structure observed for $\text{MoO}_2(\text{VI})$ and $\text{VO}(\text{IV})$ complexes while cauli flower-like structure found for $\text{Ti}(\text{III})$ complex.

Powder XRD

X-ray diffraction patterns of H_2L ligand and $[\text{Ti}(\text{L})(\text{Cl})(\text{H}_2\text{O})_2]$, $[\text{MoO}_2(\text{L})(\text{H}_2\text{O})]$ and $[\text{WO}_2(\text{L})(\text{H}_2\text{O})]$ complexes are shown in Figs.-8 to 11. Ligand shows well defined crystal peaks indicating formation of crystalline phase. The appearance of crystalline ligand is due to inherent crystalline nature of the ligand. The unit cell data and crystal lattice parameters of ligand H_2L are $a=11.6595\text{\AA}$, $b=7.2927\text{\AA}$, $c=12.0835\text{\AA}$, $\alpha=90^\circ$, $\beta=113.928^\circ$, $\gamma=90^\circ$, $V=935.293\text{\AA}^3$ belongs to orthorhombic system. Indexed X-ray diffraction data and crystal lattice parameters of $[\text{WO}_2(\text{L})(\text{H}_2\text{O})]$ complexes are $a=29.0676\text{\AA}$, $b=8.8013\text{\AA}$, $c=18.4470\text{\AA}$, $\alpha=90^\circ$, $\beta=125.978^\circ$, $\gamma=90^\circ$, $V=3819.096\text{\AA}^3$, therefore system is orthorhombic. The unit cell data and crystal lattice parameters of $[\text{MoO}_2(\text{L})(\text{H}_2\text{O})]$ complexes are $a=8.8745\text{\AA}$, $b=10.4444\text{\AA}$, $c=9.7268\text{\AA}$, $\alpha=90^\circ$, $\beta=93.79^\circ$, $\gamma=90^\circ$, $V=899.593\text{\AA}^3$, therefore system is monoclinic. $[\text{Ti}(\text{L})(\text{Cl})(\text{H}_2\text{O})_2]$ complex are $a=13.3540\text{\AA}$, $b=9.2100\text{\AA}$, $c=8.3500\text{\AA}$, $\alpha=90^\circ$, $\beta=108.360^\circ$, $\gamma=90^\circ$, $V=998.03\text{\AA}^3$, therefore system is monoclinic. $[\text{Cr}(\text{L})(\text{Cl})(\text{H}_2\text{O})_2]$ complex are $a=6.7383\text{\AA}$, $b=10.3948\text{\AA}$, $c=12.8735\text{\AA}$, $\alpha=79.933^\circ$, $\beta=81.754^\circ$, $\gamma=84.103^\circ$, $V=875.845\text{\AA}^3$, therefore system is triclinic.

The average crystallite particle size of the ligand and its complexes such as $[\text{Ti}(\text{L})(\text{Cl})(\text{H}_2\text{O})_2]$, $[\text{MoO}_2(\text{L})(\text{H}_2\text{O})]$ and $[\text{WO}_2(\text{L})(\text{H}_2\text{O})]$ were calculated from Scherer's formula. Using the full width at half maximum (FWHM) intensity of the patterns, the average particle sizes of the ligand and its complexes are

around 27.55, 30.39, 24.51, 65.79 and 15.07 nm, respectively, indicating that they were in nanocrystalline phase.³²⁻³⁵

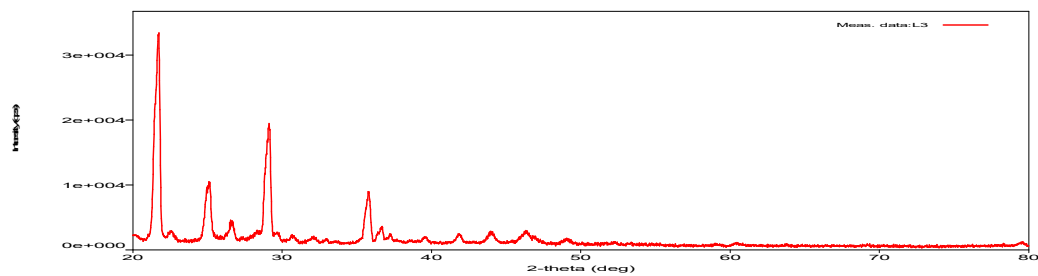


Fig.-8. XRD Pattern of the Ligand (H₂L)

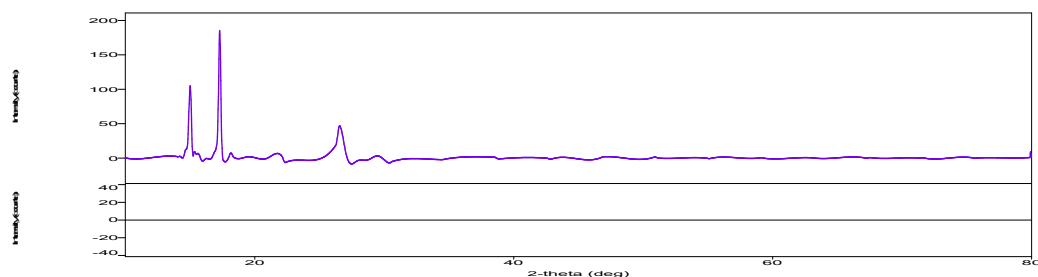


Fig.-9: XRD Pattern of [Ti(L)(Cl)(H₂O)₂] Complex

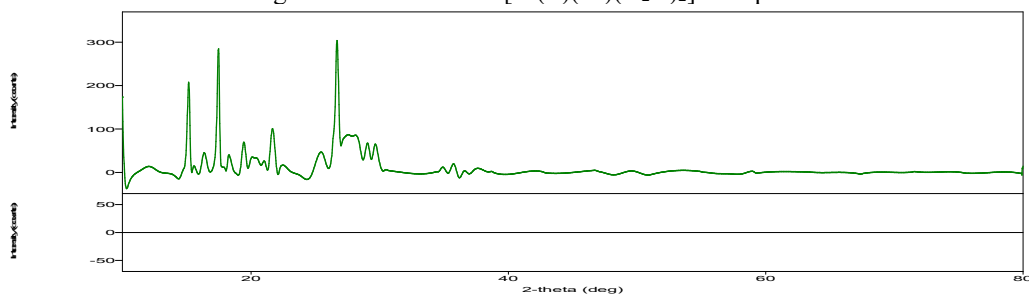


Fig.-10. XRD Pattern of [Cr(L)(Cl)(H₂O)₂] Complex

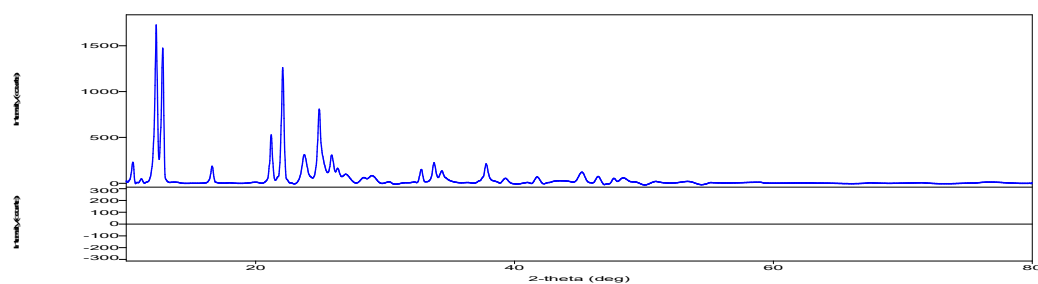


Fig.-11: XRD Pattern of [MoO₂(L)(H₂O)]Complex

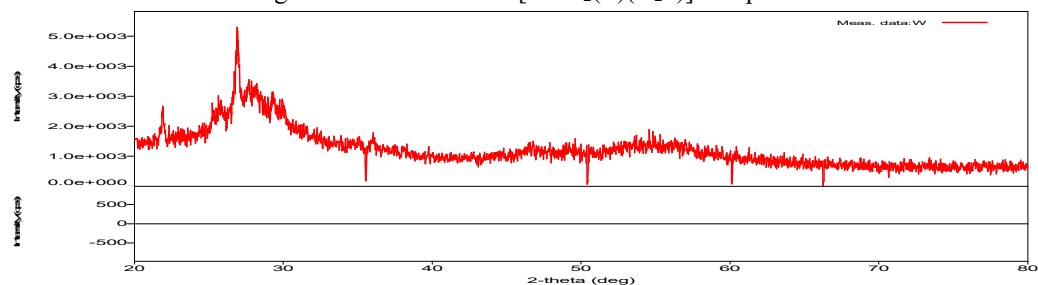


Fig.-12: XRD Pattern of [WO₂(L)(H₂O)] Complex

Thermo-gravimetric Analysis

Thermo-gravimetry is one of the most commonly used thermal analysis techniques for the characterization of both inorganic and organic materials. TG measurements provide important information about structural features of compounds and the preferential ligation of the different groups direct-attached to and /or associated with metal ions. Thermal analyses of ligand and its metal complexes were carried out in the temperature range from 40 to 800 °C with a heating rate of 10 °C min⁻¹ in a nitrogen atmosphere to examine their thermal stability and to investigate the percentage mass loss of compounds. The proposed stepwise thermal degradation pattern of all the complexes with respect to temperature is listed in Table-4 and shown in Fig.-13. The pattern of decomposition in thermograms of the complexes was found to be similar, which suggests their isostructural characteristics. As temperature increases, a regular weight loss was observed in the TGA curves of complexes indicates decomposition occurs by fragmentation. On heating, the ligand shows one step decomposition pattern, whereas complexes of VO(IV), MoO₂(VI) and WO₂(VI) ions are found to decompose in two steps while Ti(III), Cr(III) and Fe(III) complexes exhibits three step decomposition after dehydration while ligand undergoes only one-step decomposition. In case of Fe (III), Cr(III) and Ti(III) complexes mass loss observed up to ~239°C was [% wt. loss obs./calcd. : VO(IV) : 5.87/5.07, Cr(III) : 9.30/9.5, MoO₂(VI) : 5.65/5.33, Fe(III) : 9.25/9.06, Ti(III) : 9.65/9.25; WO₂(VI) and 3.85/3.57 indicating the presence of two coordinated water molecules while one coordinated water was observed in [VO(L)(H₂O)] and [WO₂(L)(H₂O)] complexes. Thermogram of Fe(III) complex shows mass loss up to 300°C corresponds to two coordinated water molecules and one coordinated chloride ion. In all the complexes speedy weight loss has been observed above 300°C, indicative of decomposition of the free parts of the coordinated ligand. Finally, beyond 563°C temperature, a horizontal line observed which corresponds to metal oxides as the final decomposition products.

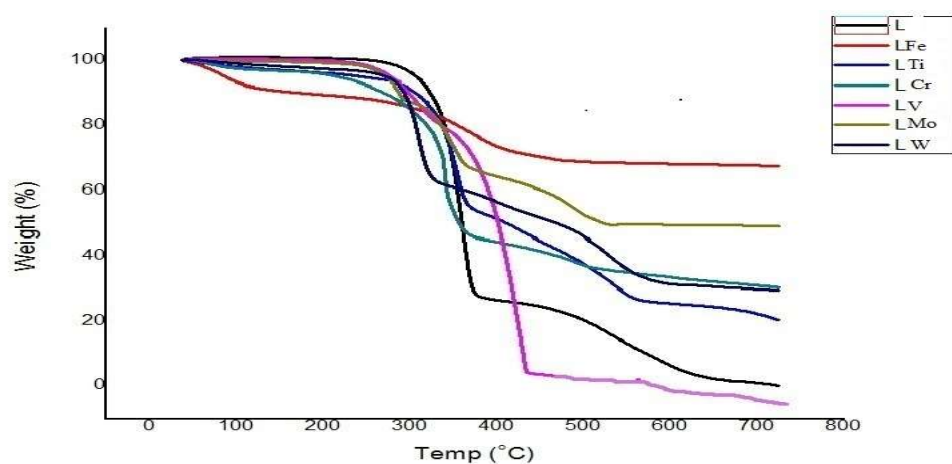


Fig.-13: TGA Curves of Ligand (H₂L) and its Metal Complexes

Table-4: Stepwise Thermal Degradation Data Obtained for Metal Complexes

Compound	Temp. Range (°C)	% Mass Loss		Assignments/Observation
		Found	Calcd.	
[Ti(L)(Cl)(H ₂ O) ₂]	85-195	7.87	7.70	Loss of 2 mol of coordinated water molecules
	195-275	7.44	7.59	Loss of 1 coordinated chloride ion.
	275-750	--	--	Deligation
[VO(L)(H ₂ O)]	90-150	4.55	4.15	Loss of 1 mol of coordinated water molecule.
	150-750	--	--	Deligation
[Cr(L)(Cl)(H ₂ O) ₂]	85-150	7.22	7.63	Loss of 2 moles of coordinated water molecules
	150-270	7.85	7.52	Loss of 1 coordinated chloride ion.
	270-750	--	--	Deligation
[Fe(L)(Cl)(H ₂ O) ₂]	75-155	7.80	7.60	Loss of 2 moles of coordinated water molecules
	155-260	7.88	7.49	Loss of 1 coordinated chloride ion.

	260-750	--	--	Deligation
[MoO ₂ (L)(H ₂ O)]	90-225	3.78	3.75	Loss of 1 mol of a coordinated water molecule.
	225-750	--	--	Deligation
[WO ₂ (L)(H ₂ O)]	90-225	3.98	3.02	Loss of 1 mol of a coordinated water molecule.
	225-750	--	--	Deligation

The thermodynamic activation parameters of decomposition process of ligand and its complexes, namely energy of activation (E_a), frequency factor (Z), free energy change (ΔF) and entropy of activation (ΔS^{*}) were calculated by employing Freeman-Carroll²⁷ and Sharp-Wentworth methods²⁸ and values are summarized in Table-5. According to kinetic data obtained from curves, the complexes have entropy which indicates that activated complexes have more ordered systems than the reactants. The entropy change, for the formation of most activated complexes from starting reactants is negative. This suggests slow rate for decomposition reactions.²⁹ The values of activation energy obtained for the decomposition of the compounds (100-650°C) by both the methods are comparable. The values obtained for E_a and frequency factor (z) suggests the smoothness in the feasibility of the reaction reaction rate of the initial reactants and intermediate stage compounds.

Table-5: The Kinetic Parameters for Ligand and its Metal Complexes

Compound	Decomposition Temp. (°C)	Activation Energy (kJ mole ⁻¹)		Entropy Change	Free Energy Change	Frequency Factor	Order of Reaction
		FC	SW	ΔS (J)	ΔF (kJ)	Z (s ⁻¹)	n
H ₂ L	643	23.28	24.81	-88.80	57.95	7.091x10 ⁻⁴	0.86
[Ti(L)(Cl)(H ₂ O) ₂]	643	12.64	11.64	-88.71	58.18	2.511x10 ⁻³	1.14
[VO(L)(H ₂ O)]	643	24.58	27.61	-88.59	57.67	5.743x10 ⁻⁴	0.71
[Cr(L)(Cl)(H ₂ O) ₂]	633	27.41	24.81	-79.65	51.14	4.947x10 ⁻⁴	0.72
[Fe(L)(Cl)(H ₂ O) ₂]	623	22.70	19.54	-87.92	55.67	7.767x10 ⁻⁴	0.90
[MoO ₂ (L)(H ₂ O)]	623	22.34	22.63	-77.38	49.13	6.444x10 ⁻⁴	0.92
[WO ₂ (L)(H ₂ O)]	603	33.30	28.49	-87.42	53.21	4.197x10 ⁻⁴	0.50

Antimicrobial Activity

The synthesized ligand and its complexes were screened for their biological activity against Gram-positive bacteria (*S. aureus*) and Gram-negative bacteria (*E. coli*) and two fungal species (*A. Niger* and *C. albicans*) by disc diffusion technique and results are presented in Table-6.

Table-6: Biological Activity of the Ligand and its Metal Complexes

Compound	Bacteria		Fungi	
	Gram Positive	Gram Negative		
	<i>Escherichia Coli</i>	<i>Staphylococcus Aureus</i>	<i>C. Albicans</i>	<i>A. Niger</i>
H ₂ L	-	-	-	11
[Ti(L)(Cl)(H ₂ O) ₂]	10	10	10	12
[VO(L)(H ₂ O)]	11	12	11	12
[Cr(L)(Cl)(H ₂ O) ₂]	10	12	11	14
[Fe(L)(Cl)(H ₂ O) ₂]	10	10	11	11
[MoO ₂ (L)(H ₂ O)]	11	11	10	10
[WO ₂ (L)(H ₂ O)]	10	11	15	10
Streptomycin (standard)	18	20	-	-
Clotrimazole (standard)	-	-	16	16

On comparing the results of antimicrobial activity for ligands and their metal complexes, it was found that the metal complexes show higher activity than the ligands.

This enhancement in biological activity on the complexation of ligand with metal ion was explained by overtone's concept and Tweedy chelation theory.^{30,31} According to this theory, the chelation lowers down the polarity of the metal ion considerably, due to the partial sharing of its positive charge with donor groups

and possible π -electron delocalization over the whole chelate ring. This increases its lipophilic character, which favors interaction with lipids and polysaccharides, which are important components of cell walls and cell membranes. This interaction leads to the breakdown of the permeability barrier of the cell, resulting in an interface with the normal cell processes i.e. toxicity.

This process, in turn, increases the lipophilic nature of the central metal atom, which favors its permeation more and efficiently through the lipid layer of the cell membrane, thus destroying them more aggressively. Streptomycin was used as a standard drug for antibacterial activity and Clotrimazole is an antifungal drug.

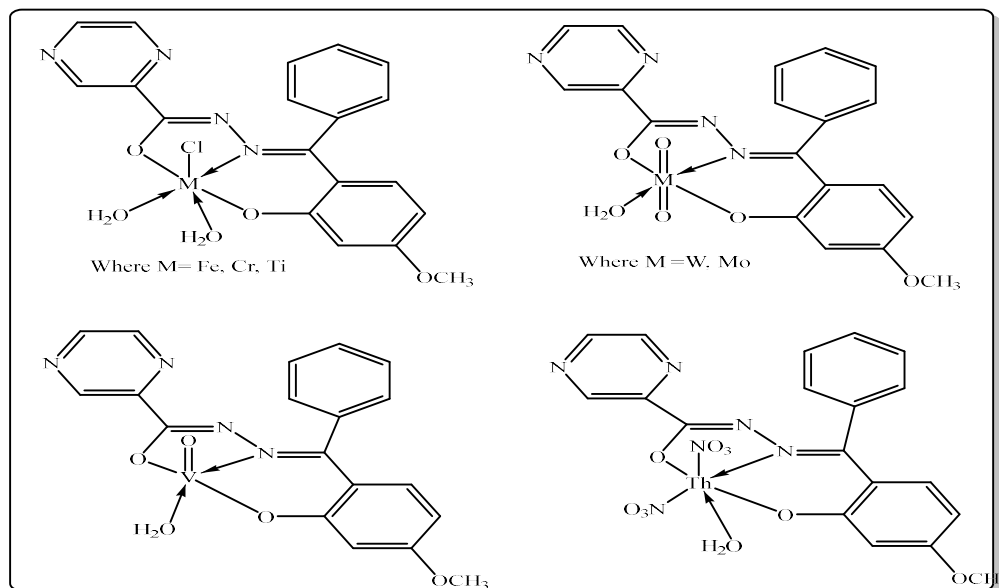


Fig.-14: The proposed Structure of Metal Complexes

CONCLUSION

In the present study, we have attempted to synthesis heterocyclic hydrazone ligand derived from the condensation of pyrazine-2-carbohydrazide with 2-hydroxy-4-methoxybenzophenone and its metal complexes have been synthesized and characterized by physico-chemical methods. An octahedral geometry has been inferred for Ti(III), Cr(III), Fe(III), MoO₂(VI) and WO₂(VI) complexes and square pyramidal geometry to VO(IV) complex, ligand behaves dibasic tridentate coordinating through phenolate oxygen, azomethine nitrogen and enolate oxygen atoms. The TG analysis indicated that the complexes decompose in two or three overlapping steps where organic part of the complexes losses as intermediates; finally leaving metal oxide. The results of antimicrobial activity show that the metal complexes show enhanced inhibitory activity compared to the free ligand under identical experimental conditions.

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