



Synthesis, Structural Characterization, Thermal and Biological Studies of Some Metal Complexes with Aroyl Hydrazone Based Ligand

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The metal complexes of Ti(III), Cr(III), Fe(III), VO(IV), MoO₂(VI), WO₂(VI), Th(IV) have been synthesized with hydrazone ligand. The mononucleating hydrazone ligand has been synthesized *via* condensation reaction between pyrazine-2-carbohydrazide and 2,4-dihydroxy benzophenone in 1:1 ratio. The ligand and its complexes were studied on the basis of elemental analysis, magnetic susceptibility measurements, IR and electronic spectra, TGA, XRD, ¹H NMR, mass spectroscopy and SEM analysis. Spectroscopic and magnetic studies suggest coordination of most of the metal complexes in a regular octahedral around the central metal ions except vanadium which is square pyramidal. Free ligand as well as its metal complexes were screened against the growth of pathogenic bacteria. The inhibition data revealed that metal complexes exhibit higher inhibition potential against growth of bacteria and fungi than free ligand.

Keywords: Metal complexes, Aroyl hydrazone, Pyrazine-2-carbohydrazide, 2,4-dihydroxy benzophenone, Biological activities.

INTRODUCTION

In the last few decades, inorganic chemistry is most widely developed mainly due to coordination chemistry and applies very particularly to the coordination compounds of transition and inner transition metals [1,2]. Due to their applicability in various fields of current interest, mainly in medicine, agriculture and chemical industries, Schiff base ligands are considered as "privileged ligands". This is because they are easily prepared by the condensation between aldehydes/ketones and imines. Schiff bases have been extensively studied because of their chemical permutation and it is reported that the rapidly developing field of bioinorganic chemistry is centered on the presence of coordination compounds in living systems. Schiff bases constitute a special class of compounds; these compounds have played a central role as chelating ligands for a large number of metal ions and are further associated with a variety of applications [3-6].

Schiff base ligands particularly molecules possessing nitrogen, oxygen and sulphur donor sites are important in the development of coordination as well as in the biomimetic chemistry of a number of metal ions, particularly the transition metals. With increasing knowledge of properties of functional

groups, as well as the nature of donor atoms and central metal ion, ligands with more selective chelating groups, *i.e.* imine and azomethines are used for complex and several azomethines and their metal complexes were reported to possess antifungal, antibacterial, antitumour, anti-inflammatory, analgesic, anti-HIV, antidibetic and diuretic activities [7-12]. Thus Schiff base ligands are useful chelating ligands and have biological importance. The presence of additional amino group in the these compounds causes delocalization of electrons with subsequent changes in energy level associated with the carbonyl oxygen, which acts as doner atoms. In the recent past, there has been a growing interest in the study of aroylhydrazones derived from the condensation between aldehydes/ketones and imines [13-15].

There are a number of hydrazide-hydrazone derivatives have been claimed to posses as an antibacterial, antifungal, anti-convulsant, antiinflammetary as well as ability to form chelate complexes with transition metals [16-18]. In view of the importance associated with hydrazones on account of the structural, analytical and biological importance of their metal complexes, the synthesis of acid hydrazone derived from the condensation of 2,4-dihydroxy benzophenone with pyrazonic acid hydrazide and its metal complexes with Ti(III), VO(IV), Cr(III), Fe(III), MoO₂(VI), WO₂(VI) and Th(IV) have been carried out.

EXPERIMENTAL

Pyrazonic acid and 2,4-dihydroxy benzophenone were procured from Sigma-Aldrich. All other chemicals used were of A.R. grade. All metal salts such as titanium trichloride, vanadium sulphate pentahydrate, anhydrous ferric chloride, chromium trichloride, thorium nitrate pentahydrate, sodium tungstate dehydrate were procured from S.D. Fine Chemicals, India. Molybdenum acetate was prepared by reported method.

Microanalysis of elements C, H, N and metal ions of the complexes were carried on Carlo Erba 1108 Elemental analyzer. The IR spectra of ligand and its complexes were recorded on KBr pellets using a Shimadzu 8201 spectrophotometer in the range of 4000-200 cm^{-1} . ^1H & ^{13}C NMR spectra were recorded on Bruker Advance II, 400 MHz, NMR spectrophotometer in DMSO- d_6 with TMS as an internal standard at SAIF, Punjab University, Chandigarh, India. Magnetic measurements were carried out by the Sherwood magnetic susceptibility balance MK1 at room temperature. The solid state reflectance spectra of the complexes were recorded in the 200-1000 nm range (as MgO) disc on a Cary 60 UV-Vis spectrophotometer. X-ray diffraction patterns were obtained with a Bruker AXS, D₈ Advance equipped with Si(Li)PDS. Mass spectra of ligand and complexes were recorded on a waters, Q-TOFmicro-mass (LC-MS) spectrometer. Thermogravimetric analysis were performed on a Perkin Elmer, Diamond TG thermal analyser in the temperature range 40-750 °C with a heating rate of 10 °C/min⁻¹. SEM images and EDS graphs of complexes were recorded at SAIF, Kavayitri Bahinabai Chaudhari North Maharashtra University, Jalgaon, India. The molar conductance values were recorded using 10 mg/mol solution in DMSO with an Elico conductivity bridge and dip type cell calibrated with KCl solution.

Synthesis of Schiff base ligand (H₂L): Taken exactly 10 g of pyrazine-2-carbohydrazide (10 g, 0.07239 mol) in 100 mL of ethanol till it forms clear solution. To this added 15.50 g of 2,4-dihydroxy benzophenone (15.50 g, 0.07239 mol) and few drops of conc. H₂SO₄ as a catalyst and reflux this reaction mixture on a water bath for 6 to 8 h. The progress of the reaction was monitored by TLC. The solution was cooled and the Schiff base ligand was separated out, filtered and washed with ethanol and recrystallized with DMF. ^1H NMR (DMSO- d_6 , 400 MHz): δ 12.60 (d, 1H, N-H), 10.35 (d, 1H, OH), 9.98 (d, 1H, OH), 9.25 (s, 1H, C5-H), 8.83 (d, 1H, C6-H), 8.19 (d, 1H, C3-H), 7.71-7.44 (s, 1H, Ar-H), 6.38 (d, 1H, C9-H), 6.22 (d, 1H, C10-H),

3.39 (d, 1H, CH₃). ^{13}C NMR (DMSO- d_6 , 400 MHz): 161.11 (C=N), 160.82 (C12), 159.27 (C10), 157.96 (C=O), 148.129 (C6), 143.64 (C2), 143.11 (C11), 107.35 (C7), 103.24 (C9), 127.80-131.96 (Ar-H). Mass spectrum (ESI) [M]+1 = 335.1144.

Synthesis of Ti(III), Cr(III), Fe(III), VO(IV), MoO₂(VI) and Th(IV) complexes: The ligand (0.01 mol) was dissolved in DMF (10 mL) by heating at 80 °C. To this refluxed ligand solution, an ethanolic solution of appropriate metal salt solution (0.01 mol) was added dropwise through condenser in a sand bath for 6 to 8 h. On cooling at room temperature, solid coloured products are obtained which were filtered, washed with DMF, ethanol and petroleum ether to remove unreacted ligand and metal salts and finally dried under vacuum at room temperature over CaCl₂ (Yield = 63%).

Synthesis of WO₂(VI) complex: Sodium tungstate dihydrate (1.2 g, 0.00363 mol) and ammonium thiocyanate (2.3 g, 0.00363 mol) were dissolved in water (30 mL) at room temperature and added HCl (7.5 mL) to it. The resulting yellow solution was cooled in an ice bath and DMF solution of ligand (10 mL, 0.00363 mol) was added to it. The precipitate formed was filtered under suction, washed with water and HCl and dried under vacuum at room temperature over CaCl₂ (yield = 83%).

RESULTS AND DISCUSSION

All the metal complexes obtained by the condensation reaction of pyrazine-2-carbohydrazide with 2,4-dihydroxy benzophenone in ethanol are coloured solids, stable towards air and moisture at room temperature and insoluble in common organic solvents such as ethanol, acetone, methanol, chloroform, benzene, cyclohexane, diethyl ether but mostly soluble in DMF and DMSO. The elemental analysis proposed 1:1 metal ligand stoichiometry for all the synthesized complexes (Table-1). The structures and geometries of the ligand and complexes were in good agreement with the structural characterisation done in this present work. The electrical conductivity measurements implies the non-electrolyte nature, due to low values of molar conductance of all the complexes were measured in DMSO using 10⁻³ M solutions at room temperature are non electrolytes [19,20].

Infrared spectra: During complexation, the coordination sites of the ligands are studied on the basis of the IR spectra of the ligand and its comparison with the metal complexes. The IR spectrum of the ligand shows medium intensity band at

TABLE-1
ANALYTICAL AND MOLAR CONDUCTANCE DATA OF THE LIGAND AND METAL COMPLEXES

Compound	Colour	m.f.	m.w.	Elemental analysis (%): Found (calculated)				Λ^*
				C	H	N	M	
H ₂ L	Yellow	C ₁₈ H ₁₄ N ₄ O ₃	334.11	64.67 (60.45)	4.22 (3.84)	16.76 (15.8)	–	–
[Fe(Cl)(H ₂ O) ₂ HL]	Dark chocolate	C ₁₈ H ₁₆ FeN ₄ O ₅ Cl	459.02	47.04 (38.56)	3.51 (3.45)	12.19 (12.5)	12.15 (13.95)	9.50
[Ti(Cl)(H ₂ O) ₂ HL]	Dark crimson	C ₁₈ H ₁₆ N ₄ O ₅ TiCl	451.03	47.87 (46.95)	3.57 (3.02)	12.40 (12.8)	10.60 (9.06)	7.35
[Cr(Cl)(H ₂ O) ₂ HL]	Brown red	C ₁₈ H ₁₆ CrN ₄ O ₅ Cl	455.02	47.43 (46.06)	3.54 (3.47)	12.29 (12.8)	11.41 (12.98)	8.25
[VO(L)(H ₂ O)]	Dark yellow	C ₁₈ H ₁₄ N ₄ O ₅ V	417.04	51.81 (50.28)	3.38 (3.98)	13.43 (12.3)	12.21 (12.81)	3.30
[WO ₂ (L)(H ₂ O)]	Smoke white	C ₁₈ H ₁₄ N ₄ O ₆ W	566.04	38.90 (37.18)	2.49 (2.45)	9.90 (9.19)	32.47 (32.34)	12.15
[MoO ₂ (L)(H ₂ O)]	Canary yellow	C ₁₈ H ₁₄ N ₄ O ₆ Mo	480.00	45.20 (47.18)	2.95 (2.85)	11.71 (11.28)	20.06 (20.71)	11.30
[Th(L)(H ₂ O)(NO ₃) ₂]	Greenish yellow	C ₁₈ H ₁₆ N ₆ O ₁₁ Th	724.13	29.85 (28.98)	2.23 (2.35)	11.60 (12.5)	32.03 (31.13)	15.00

* Λ = Conductance ($\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$)

3318 cm^{-1} due to intramolecular hydrogen bonding $\nu(\text{O-H})$ group [21]. This band was disappeared in the spectra of the complexes indicating the coordination of phenolic oxygen to the metal ion *via* deprotonation. This was further supported by upward shifting of $\nu(\text{C-O})$ phenolic band by 20-25 cm^{-1} from 1322 cm^{-1} suggesting the coordination of phenolic oxygen to the metal ion [22].

The strong band at 1571 cm^{-1} is due to azomethine group $\nu(\text{C=N})$ exhibits by the ligand. This bond is shifted to lower frequency in all the complexes (20-25 cm^{-1}) due to the azomethine nitrogen coordinates to metal ion by the donation of the electrons from nitrogen to empty *d*-orbital of the metal ions [23]. This is again supported by the region 453-403 cm^{-1} in the complexes attributable to $\nu(\text{M-N})$ vibrations.

A ligand spectrum exhibits band at 966 cm^{-1} due to the $\nu(\text{N-N})$ stretching. This band is shifted to higher wave number by 25-60 cm^{-1} in the complexes also supports the coordination of the azomethine nitrogen atom. The IR spectrum of the ligand shows a strong band at 3056 and 1603 cm^{-1} due to $\nu(\text{N-H})$ and $\nu(\text{C=O})$ stretching, respectively. The absence of these bands in the spectra of all complexes indicating the destruction of carbonyl moiety as a result of the enolization and subsequent coordination of the enol to oxygen with metal ions. The important IR spectral bands of the ligand and its metal complexes are depicted in Table-2.

Magnetic moment and electronic spectra: The electronic spectrum of Fe(III) complex shows three bands at 13560, 17887 and 24345 cm^{-1} , which can be assigned to ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{1g}(\text{G})$, ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{2g}(\text{G})$ and ${}^6\text{A}_{1g} \rightarrow {}^4\text{E}_g(\text{G})$ spin allowed transitions in octahedral geometry. The magnetic moment of 5.92 B.M. at room temper-

ature for this complex lies in the range accepted for octahedral species with five unpaired electrons. The Cr(III) complex in the present study exhibited three characteristic bands at 17125, 25255 and 39984 cm^{-1} , which may be assigned to the ${}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{2g}(\text{F})$, ${}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{1g}(\text{F})$ and ${}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{1g}(\text{P})$ 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 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) are 786 cm^{-1} , 725 cm^{-1} , 1.42, 0.78 and 22, respectively (Table-3).

The Racah inter electronic repulsion parameter B is 725 cm^{-1} for the Cr(III) complex and is found to be lower than the free ion values (918 cm^{-1}) suggesting delocalization of electron on metal into molecular orbital covering both the metal and the ligand corresponding to an appreciable covalent character of the metal ligand bond (% covalency (β_0) = 22). The ratio ν_2/ν_1 is found to be 1.42, which is exactly equal to the value of 1.42 obtained for pure octahedral Cr(III) complexes. The observed magnetic moment of 4.06 B.M. is an additional evidence for towards octahedral geometry around the Cr(III) ion. The Ti(III) complex shows a broad band around at 18168 cm^{-1} due to the ${}^2\text{T}_{2g} \rightarrow {}^2\text{E}_g$ transition in an octahedral geometry around the Ti(III) ion. The magnetic moment of Ti(III) complex is found to be 1.61 B.M. corresponding to one unpaired electron in an octahedral environment. The VO(IV) complex shows three bands at 14570, 17846 and 25664 cm^{-1} due to ${}^2\text{B}_2 \rightarrow {}^2\text{E}_0$, ${}^2\text{B}_2 \rightarrow {}^2\text{B}_1$ and ${}^2\text{B}_2 \rightarrow {}^2\text{A}_1$ transitions, respectively towards square pyramidal geometry around VO(IV) ion. The magnetic moment

TABLE-2
INFRARED SPECTRAL DATA (cm^{-1}) OF THE LIGAND AND ITS COMPLEXES

Compound	$\nu(\text{OH-N})$	$\nu(\text{N-H})$	$\nu(\text{C=O})$	$\nu(\text{C=N})$	$\nu(\text{C-O})$ phenolic	$\nu(\text{C-O})$ enolic	$\nu(\text{N-N})$	$\nu(\text{M-O})$	$\nu(\text{M-N})$
H ₂ L	3318	3056	1603	1571	1322	–	–	–	–
[Fe(Cl)(H ₂ O) ₂ HL]	–	–	–	1514	1345	1243	1043	788	547
[Ti(Cl)(H ₂ O) ₂ HL]	–	–	–	1589	1334	1267	1047	739	450
[Cr(Cl)(H ₂ O) ₂ HL]	–	–	–	1520	1366	1243	1060	458	403
[VO(L)(H ₂ O)]	–	–	–	1408	–	–	1082	521	425
[WO ₂ (L)(H ₂ O)]	3458	–	–	1591	1325	1266	1022	577	446
[MoO ₂ (L)(H ₂ O)]	3314	–	–	1594	1388	1264	1048	508	453
[Th(L)(H ₂ O)(NO ₃) ₂]	–	–	–	1484	1345	1248	1053	546	439

TABLE-3
MAGNETIC MOMENTS, ELECTRONIC SPECTRAL DATA AND LIGAND FIELD PARAMETERS OF METAL COMPLEXES

Compound	μ_{eff} (BM)	Band position (cm^{-1})	Assignments	ν_2/ν_1	Dq (cm^{-1})	B (cm^{-1})	β	β_0
[Cr(Cl)(H ₂ O) ₂ L]	3.99	$\nu_1 = 18555$ $\nu_2 = 26411$ $\nu_3 = 40125$	${}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{2g}(\text{F})$ ${}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{1g}(\text{F})$ ${}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{1g}(\text{P})$	1.42	786	725	0.78	22
[Fe(Cl)(H ₂ O) ₂ L]	5.26	$\nu_1 = 13887$ $\nu_2 = 18452$ $\nu_3 = 25412$	${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{1g}(\text{G})$ ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{2g}(\text{G})$ ${}^6\text{A}_{1g} \rightarrow {}^4\text{E}_g(\text{G})$	–	–	–	–	–
[VO(L)(H ₂ O)]	1.15	$\nu_1 = 14570$ $\nu_2 = 17846$ $\nu_3 = 25664$	${}^2\text{B}_2 \rightarrow {}^2\text{E}_0$ ${}^2\text{B}_2 \rightarrow {}^2\text{B}_1$ ${}^2\text{B}_2 \rightarrow {}^2\text{A}_1$	–	–	–	–	–
[Ti(Cl)(H ₂ O) ₂ L]	1.76	$\nu_1 = 18168$	${}^2\text{T}_{2g} \rightarrow {}^2\text{E}_g$	–	–	–	–	–

obtained for VO(IV) complex at room temperature is observed to be 1.15 B.M. (Table-3). MoO₂(VI) and WO₂(VI) complexes are found to be diamagnetic as expected for their configurations and do not show any *d-d* transitions in their reflectance spectra and may have octahedral geometry towards MoO₂(VI) and WO₂(VI) ions. The electronic spectrum of Th(IV) complex shows band at 22220 cm⁻¹ due to the ligand to metal charge transfer transition. The Th(IV) complex was found to be diamagnetic nature [24].

¹H NMR spectra of the ligand shows a signal at 12.30 ppm due to -OH proton, which is absent in the spectrum of the representative case of MoO₂(VI) complex indicating the deprotonation of -OH group and gets coordinated to the metal ion. The signal for N-H proton of the ligand was observed at δ 10.31 ppm, which gets disappeared in case of complex supports the coordination through enolic form of the ligand to the metal ion. ¹H NMR of MoO₂(L)(H₂O)], (DMSO-*d*₆, 400 MHz): 9.26(s, 1H, C3-H), 8.82(s, 1H, C5-H), 8.48(d, 1H, C6-H), 7.69(d, 1H, C11-H), 6.61 (dd, 1H, C9-H), 6.29 (d, 1H, C8-H), 2.53(s, 3H, Ar- methyl), 7.66 (m, 3H, phenyl)

Mass spectral analysis: The mass spectrum of the ligand shows the molecular ion peak at *m/z* = 335, which corresponds to the molecular mass of the ligand. The mass spectra of Ti(III), Th(IV) and WO₂(VI), complexes show molecular ion peak at *m/z* = 457, 697 and 566, respectively is indicative of monomeric nature of the complex.

Powder XRD analysis: The X-ray diffraction study of ligand H₂L and its complexes with Ti(III), VO(IV), Cr(III), Fe(III), MoO₂(VI), WO₂(VI) and Th(IV) was carried out using CuKα radiation with λ = 1.5406 Å. The XRD analysis of these compounds were recorded at 2θ values between 5° and 55° and shows the crystalline nature of the complexes. A X-ray crystal system has been worked out by trial and error method for finding the best fit between observed and calculated values. The unit cell parameters of ligand H₂L and its representative complex of MoO₂(VI) are as follows:

H₂L: triclinic, crystalline, a = 7.6022 Å, b = 4.4343 Å, c = 5.2969 Å, α = 102.760°, β = 107.325°, γ = 96.305°, V = 163.270 Å³.

[MoO₂(L)(H₂O)] complex: Monoclinic, crystalline, a = 16.1770 Å, b = 7.5746 Å, c = 19.6980 Å, α = 90°, β = 107.485°, γ = 90°, V = 2302.158 Å³.

SEM-EDS: The SEM-EDS micrographs of H₂L ligand, Ti(III), Fe(III) and VO(IV) complexes (Figs. 1-3) indicate that Fe(III) and VO(IV) complexes have spherical granular like structure, while Ti(III) complex exhibits crystal cluster-like structure. The H₂L ligand can be seen that it gave a rock needle like appearance. The surface morphology of the complexes shows that the particles are agglomerated.

Thermogravimetric analysis: Thermal analysis of ligand (H₂L) and its metal complexes indicates that the complexes of Fe(III), Cr(III), Ti(III) and Th(IV) decomposes in three steps while complexes of Mo(VI) and WO₂(VI) and Th(VI) in two steps. This suggests that coordinated water molecules are present in the former complexes, which get decomposed at 80 to 120 °C. This is also confirmed from IR spectra. The decomposition of complexes up to 220 °C corresponding to two coordinated water molecules for Fe(III), Cr(III) and Ti(III) complexes while one coordinated water molecule for VO(IV), MoO₂(VI), WO₂(VI) and Th(VI) complexes.

The thermograms of H₂L and its complexes are shown in Fig. 4. All the metal complexes show a regular weight loss indicating decomposition by fragmentation as the temperature was increased. The thermograms of the complexes show nearly the same pattern of decomposition reflecting their isostructural characteristics. A careful analysis of the thermograms of Fe(III), Cr(III), Ti(III), VO(IV), WO₂(VI), MoO₂(VI) and Th(IV) indicates that these complexes undergo two step and three step decomposition after dehydration and ligand undergoes one step decomposition. VO(II): 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): 3.85/3.57 and Th(IV): 2.89/2.79]. In these complexes, there is further

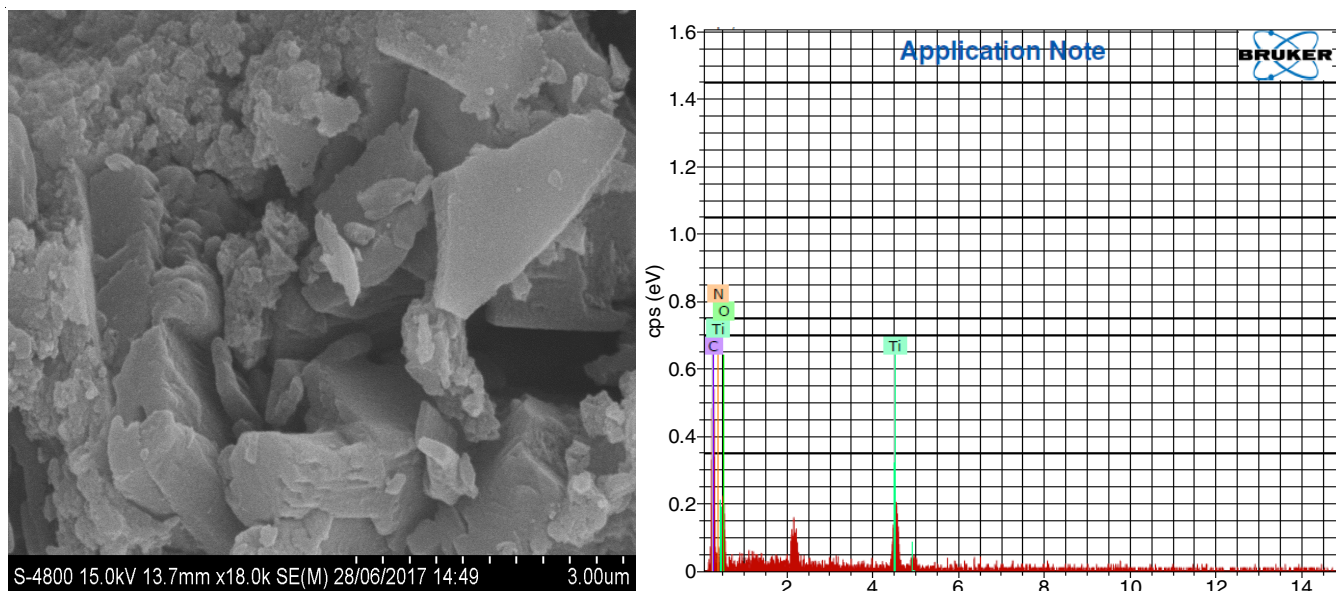


Fig. 1. SEM-EDS graph of [Ti(Cl)(H₂O)₂HL]

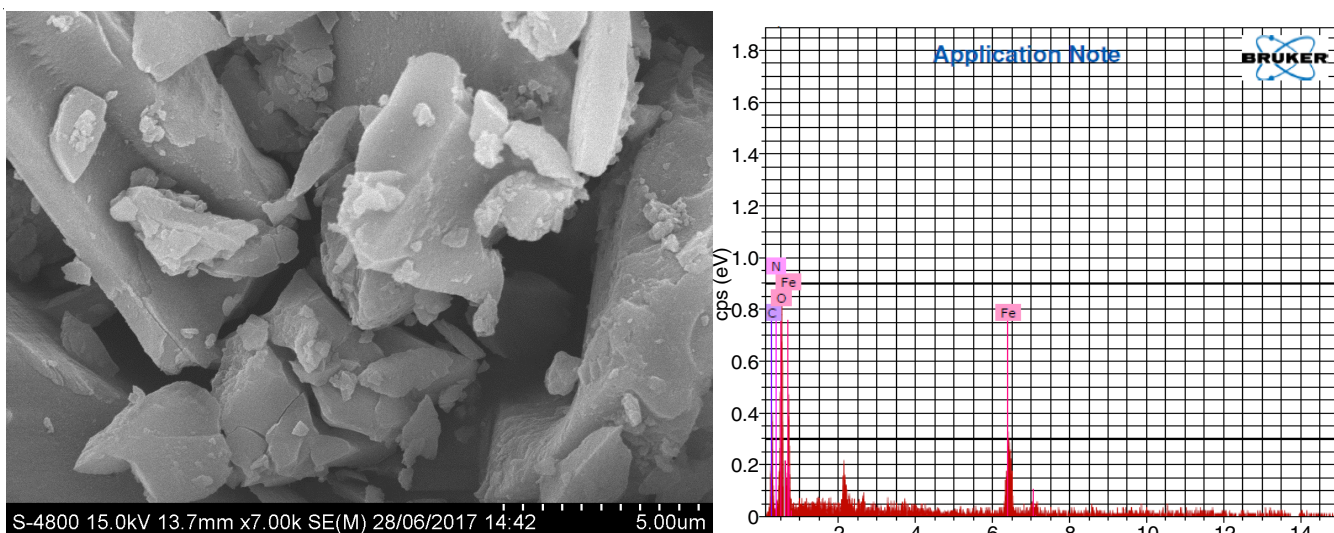


Fig. 2. SEM-EDS graph of $[Fe(Cl)(H_2O)_2HL^2]$

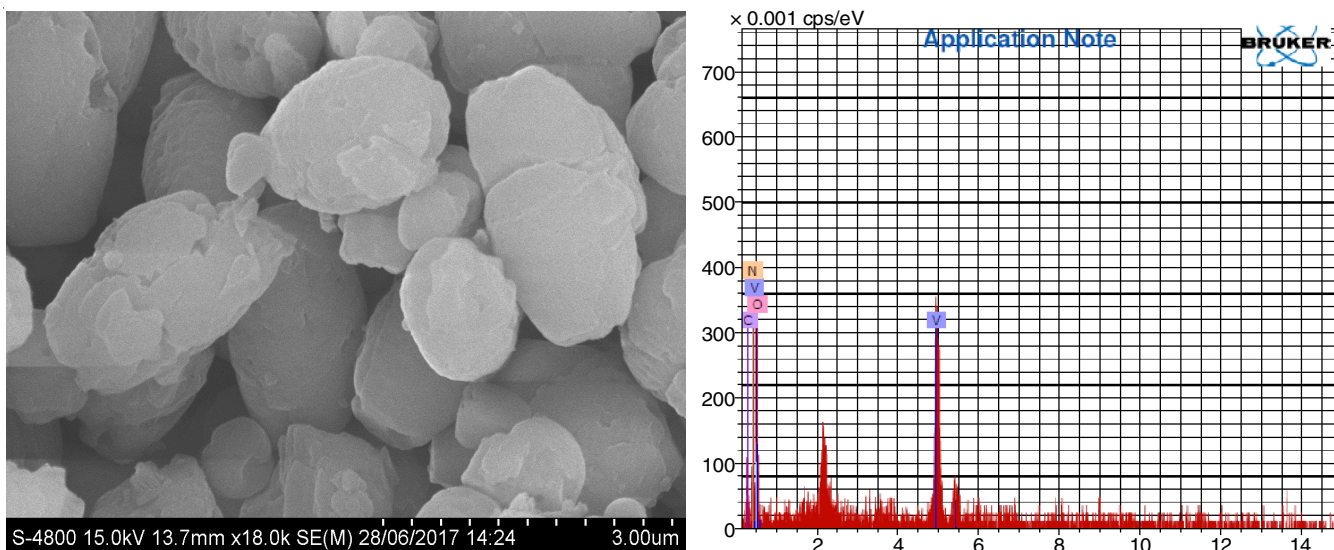


Fig. 3. SEM-EDS graph of $[VO(L)(H_2O)]$

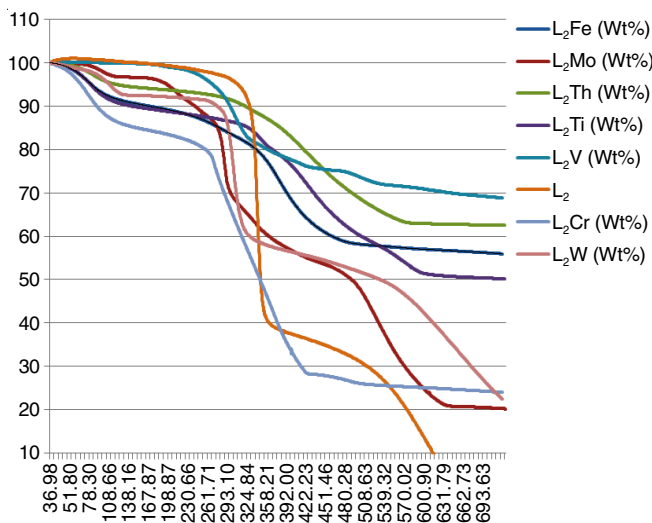


Fig. 4. TGA curves of synthesized metal complexes

loss in weight up to $\sim 239^\circ C$ indicating the presence of two coordinated water in $[Cr(L_2)(Cl)(H_2O)_2]$, $[Fe(L_2)(Cl)(H_2O)_2]$ and $[Ti(L_2)(Cl)(H_2O)_2]$ complexes while one coordinated water in $[VO(L_2)(H_2O)]$, $[WO_2(L_2)(H_2O)]$ and $[Th(L_2)(H_2O)(NO_3)_2]$ complexes. Thermogram of Fe(III) complex shows a weight loss upto $300^\circ C$ correspond to one coordinated water [3.37/3.07], it loss two molecules of coordinated water molecules and one coordinated chloride ion. Thorium(IV) complex is stable upto $75^\circ C$ and loss of one coordinated water molecule and it loses two molecules of nitrate (wt. loss 5.89/5.79). In all the complexes, a speedy weight loss has been observed around $300^\circ C$, indicative of decomposition of the free parts of the coordinated ligand, a gradual weight loss above $\sim 150^\circ C$ corresponding to the degradation of actual coordination part of the ligand. Finally, the horizontal level beyond $563^\circ C$ (except for Mo complex suggests the formation of final decomposition products corresponding oxides).

TABLE-4
THERMAL DECOMPOSITION OF AROYL HYDRAZONE BASED LIGAND AND ITS METAL COMPLEXES

Compounds	Order of reaction (n)	Activation energy, ΔE (KJ mol ⁻¹)	Entropy change, ΔS (KJ mol ⁻¹)	Free energy change, ΔG (KJ mol ⁻¹)	Frequency factor, Z (s ⁻¹)	Apparent entropy change S*
[VO(L)H ₂ O]	1.21	17.9900	-0.09507	75.31721	1.722×10^{-3}	-36.53
[Fe(Cl)(H ₂ O) ₂ HL]	0.90	17.8834	-0.08600	73.18140	1.570×10^{-3}	-36.68
[Ti(Cl)(H ₂ O) ₂ HL]	0.90	18.3429	-0.05589	55.39797	1.321×10^{-3}	-36.89
[Cr(Cl)(H ₂ O) ₂ HL]	0.29	37.2603	-0.08499	88.50927	3.707×10^{-3}	-38.06
[MoO ₂ (L)H ₂ O]	0.61	24.9678	-0.09592	84.72596	2.037×10^{-3}	-36.39
[WO ₂ (L)H ₂ O]	1.05	19.7024	-0.09076	74.43068	1.663×10^{-3}	-36.56
Th(L)(H ₂ O)(NO ₃) ₂	1.30	12.6562	-0.09287	79.80121	5.678×10^{-4}	-37.82

TABLE-5
ANTIMICROBIAL ACTIVITY OF AROYL HYDRAZONE BASED LIGAND AND ITS METAL COMPLEXES

Sample	Inhibition zone (mm/mg sample) MIC (mg mL ⁻¹)			
	Gram-negative	Gram-positive	Fungi	
	<i>Escherichia coli</i>	<i>Staphylococcus aureus</i>	<i>Candida albicans</i>	<i>Aspergillus niger</i>
H ₂ L	10	10	12	12
[Fe(Cl)(H ₂ O) ₂ HL]	11	10	10	12
[Ti(Cl)(H ₂ O) ₂ HL]	–	11	11	11
[Cr(Cl)(H ₂ O) ₂ HL]	–	10	–	11
[VO(L)H ₂ O]	10	11	14	11
[WO ₂ (L)H ₂ O]	10	11	10	12
[MoO ₂ (L)H ₂ O]	10	11	–	11
Th(L)(H ₂ O)(NO ₃) ₂	–	10	11	12
Standard	22	25	15	15

From the thermal decomposition data, various kinetic parameters have been evaluated. The negative values of ΔS suggest a more ordered activated state than the individual reactants and may be possible through the chemisorption of oxygen and other decomposition products. No definite trend in the values of E_a is observed. The activation energies of decomposition are found to be in the range 12.65-37.26 kJ mol⁻¹. Thermal decomposition data of the complexes is given in Table-4.

Biological activity: The ligand and its metal complexes were tested for biological activity against the Gram-positive bacteria (*S. aureus*) and Gram-negative bacteria (*E. coli*) and fungi (*A. niger* and *C. albicans*) at the concentration of 2 mg/mL by disc diffusion technique. It is observed that complexes exhibits significant activity against all bacterial and fungal strains (Table-5). This suggest that the metal complexes show higher antimicrobial properties than the free ligand. Due to coordination, the polarity of the metal ion [16-18] reduces mainly because of partial sharing of its positive charge with the donor groups within the chelate ring system.

Conclusion

In this work, metal complexes of Ti(III), Cr(III), Fe(III), VO(IV), MoO₂(VI), WO₂(VI), Th(IV) have been synthesized with hydrazone ligand and characterized. The newly synthesized complexes and ligand were confirmed by analytical and physico-chemical methods. The spectral analysis led to the conclusion that the metal complexes have different geometries. All the complexes except VO(IV) complexes shows octahedral geometry while VO(IV) metal ion shows square pyramidal geometry. The antimicrobial screening of free ligand and its metal complexes

showed a high activity for complexes in comparison to its ligand.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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