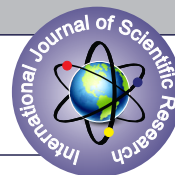


SYNTHESIS, STRUCTURAL CHARACTERIZATION AND ANTIMICROBIAL ACTIVITY OF TRANSITION METAL COMPLEXES WITH TRIDENTATE HYDRAZONE SCHIFFS BASE LIGAND



Chemistry

Kanchan Thakare Research Student At S.G.B.A.U., Amravati

Anand Aswar* Head of the Department, S.G.B.A.U, Amravati *Corresponding Author

ABSTRACT

The transition metal complexes of Ti(III), Cr(III), Fe(III), VO (IV), MoO₂ (VI), WO₂(VI), Th(IV) have been synthesized with tridentate N'-(1-(2,4-dihydroxyphenyl)ethylidene)pyrazine-2-carbohydrazone ligand synthesized from condensation pyrazine-2- carbohydrazone and 2,4 dihydroxyacetophenone. The synthesized and purified metal complexes were characterized by IR, ¹H-NMR, UV- diffuse reflectance, Mass spectra, XRD, TGA, SEM-EDS analysis, magnetic moment. The IR spectral data suggest that the ligand behaves as tridentate moiety with ONO donor atoms sequence towards central metal ion. Free ligand as well as its all metal complexes has been 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

Hydrazone ligand, Transition metal Complexes, TGA, Antimicrobial activity

INTRODUCTION

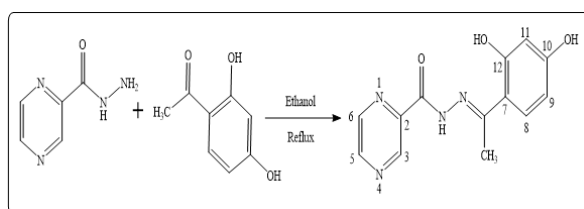
In Schiff's base family, hydrazones constitute an important class of compounds in which the presence of two interlinked nitrogen atoms which was separated from imines, oximes, etc. Hydrazone Schiff bases of heteroaryl compounds have an additional donor sites which makes them more versatile and flexible [1,2]. Due to this versatility, made such hydrazones more effective multidentate chelating agent which forms a variety of complexes with transition metals [3,4]. Such complexes have wide applications in medicinal field such as in the treatment of cancer, tuberculosis, leprosy and mental disorder [5,6]. As these compounds are known to have wide spectrum of pharmaceutical properties, the study of such hydrazone based complexes was found to be essential in the era of bioinorganic chemistry [7]. Literature survey reveals that most of work on complexes derived from aroyl hydrazones of first transition series of d-block elements, but in our present work we carry out systematic investigation on higher valent elements of transition as well as inner transition elements.

Keeping all above facts in mind, we report the synthesis and characterization of Ti(III), Cr(III), Fe(III), VO(IV), Th(IV), MoO₂(VI) and WO₂(VI) complexes of Schiff base hydrazone derived from the condensation of 2,4-dihydroxy acetophenone with pyrazonic acid hydrazide.

MATERIALS AND METHODS

Pyrazonic acid and 2,4 dihydroxyacetophenone were procured from Sigma Aldrich. All other chemicals used were of AR grade. All metal salts such as titanium trichloride, vanadium sulphate pentahydrate, anhydrous ferric chloride, chromium trichloride, thorium nitrate pentahydrate were used of SD's fine chemicals. Molybdenum acetate and sodium tungstate dehydrate were prepared by reported method [8]

Microanalysis of elements C, H, N and metal ions of the complexes were carried on Carlo Erba 1108 elemental analyser. 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. ¹H and ¹³C NMR spectra were recorded on Bruker Advance II, 400 MHz, NMR spectrophotometer in d₆-DMSO with TMS as an internal standard at SAIF, Punjab University, Chandigarh, India. Magnetic measurements were carried out by the Sherwood magnetic susceptibility balance MK 1 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-TOF micro-mass (LC-MS) spectrometer. Thermogravimetric analysis was performed on a Perkin Elmer, Diamond TG thermal analyzer 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, Jalgaon University, India. The molar conductance values were recorded using 10 mg per mole solution in DMSO with an Elico conductivity bridge and dip type cell calibrated with KCl solution



Scheme 1. Synthesis of N'-(1-(2,4-dihydroxyphenyl) ethylidene) pyrazine-2-carbohydrazone ligand (H,L).

Synthesis of the N'-(1-(2,4-dihydroxyphenyl)ethylidene)pyrazine-2-carbohydrazone ligand (H,L)

An equimolar quantity mixture of pyrazine-2-carbohydrazone (0.07239 moles) and 2,4 dihydroxyacetophenone (0.07239 moles) were taken in RBF with 200 mL of ethanol as solvent. The reaction mixture was refluxed for 5 hrs on oil bath with magnetic stirrer. The progress of reaction was monitored by TLC. The resulting Schiff base that separated out on cooling the reaction mixture was filtered, washed with ethanol, dry and recrystallized with DMF. Yield: 78%

¹H-NMR (DMSO-d₆, 400 MHz): 13.21(s, 1H, NH), 11.32(s, 1H, OH), 9.85(s, 1H, OH), 9.28(d, 1H, C5-H), 8.91(d, 1H, C6-H), 8.78(s, 1H, C3-H), 7.42(d, 1H, C11-H), 6.36(dd, 1H, C9-H), 6.30(d, 1H, C8-H), 2.43(s, 3H, CH₃).

¹³C NMR (DMSO-d₆, 100 MHz): 160.94(C=N), 160.90(C12), 160.76(C10), 159.18(C=O), 147.77(C6), 144.15(C2), 143.91(C3), 143.22(C5), 129.90(C8), 111.17(C7), 107.02(C9), 103.17(C11), 13.59(CH₃).

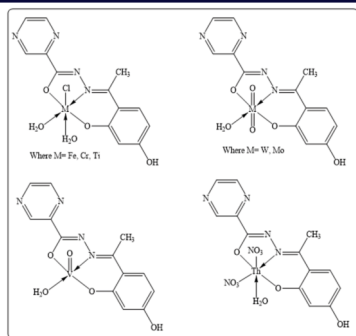
Mass spectrum (ESI) [M]⁺ = 273.1046 (M+1).

Synthesis of the Ti(III), Cr(III), Fe(III), VO (IV), MoO₂ (VI) and Th(IV) complexes

Equimolar quantities of synthesized ligand (H,L) and appropriate metal salt were dissolved separately in DMF (20 mL) and ethanol respectively. The solutions were filtered and mixed them in hot conditions under continuous stirring. The resulting reaction mixture was refluxed for 6-8 h on an oil bath. Further, it was allowed to cool at room temperature to obtain colored complexes. It was filtered washed with DMF, ethanol and chloroform and finally dried under vacuum at room temperature. Yield: 55-68%

Synthesis of WO₂(VI) complex

Sodium tungstate dihydrate (0.00363 mole) and ammonium thiocyanate (0.00363 mole) were dissolved in water (20 mL) at room temperature and 7.5 ml of 11M HCl was added to it. The resulting solution was cooled in an ice bath and DMF + ethanolic solution (10 ml) of ligand (0.00363 mole) was added to it. The precipitate so formed was filtered under suction, wash 3 to 4 times with water containing few drops of HCl, further wash with methanol + chloroform solvent mixture then dried under vacuum at room temperature. Yield: 63%.



Scheme 2. The proposed structure of metal complexes.

Table 1. Analytical and molar conductance data of the ligand and metal complexes

Compound	colour	Molecular formula	Formula weight	Elemental analysis % found (calculated)				Molar conductance ($\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$)
				C	H	N	M	
H ₂ L	Pale yellow	C ₁₃ H ₁₂ N ₂ O ₃	272.26	57.35(56.0)	4.44(7.84)	20.58(79.58)	-	--
[Fe(Cl)(H ₂ O) ₂ L]	Dark chocolate	C ₁₃ H ₁₄ ClFeN ₂ O ₅	397.57	39.27(38.56)	3.55(3.45)	14.09(14.56)	14.05(13.95)	3.8
[Ti(Cl)(H ₂ O) ₂ L]	Dark crimson	C ₁₃ H ₁₄ ClN ₂ O ₅ Ti	389.60	40.08(39.95)	3.62(3.02)	14.38(14.28)	12.29(12.06)	4.3
[Cr(Cl)(H ₂ O) ₂ L]	Olive dark	C ₁₃ H ₁₄ ClCrN ₂ O ₅	393.01	39.66(38.06)	3.58(3.47)	14.23(14.28)	13.21(12.98)	5.7
[VO(L)(H ₂ O)]	Blackish green	C ₁₃ H ₁₄ N ₂ O ₅ V	357.22	43.71(43.28)	3.95(3.98)	15.68(14.63)	14.26(14.81)	1.4
[WO ₂ (L)(H ₂ O)]	Smoke white	C ₁₃ H ₁₂ N ₂ O ₆ W	504.03	30.97(30.18)	2.40(2.45)	11.11(11.19)	36.47(37.34)	1.1
[MoO ₂ (L)(H ₂ O)]	Canary yellow	C ₁₃ H ₁₂ N ₂ O ₆ Mo	417.98	37.51(37.18)	2.91(2.85)	13.46(13.28)	23.06(23.71)	1.9
[Th(L)(H ₂ O)(NO ₃) ₂]	Off white	C ₁₃ H ₁₃ N ₆ O ₉ Th	628.29	24.93(23.98)	2.61(2.35)	13.42(13.85)	37.05(37.13)	8.3

IR SPECTRA

The IR spectra of the metal complexes are compared with the free ligand in order to determine the coordination sites that may be involved

Table 2. Infrared Spectral Data (cm^{-1}) of the Ligand and its Complexes

Compound	ν (C12-OHN)	ν (NH)	ν (C=O)	ν (C=N)	ν (C12-O) Phenolic	ν (C-O) enolic	ν (N-N)	ν (M-O)	ν (M-N)
H ₂ L	3348	3107	1694	1625	1328	-	1021	-	-
[Fe(Cl)(H ₂ O) ₂ L]	-	-	-	1584	1356	1249	1102	567	443
[Ti(Cl)(H ₂ O) ₂ L]	-	-	-	1578	1346	1251	1079	557	433
[Cr(Cl)(H ₂ O) ₂ L]	-	-	-	1598	1352	1279	1055	528	444
[VO(L)(H ₂ O)]	-	-	-	1572	1353	1248	1040	548	404
[WO ₂ (L)(H ₂ O)]	-	-	-	1587	1366	1246	1054	497	414
[MoO ₂ (L)(H ₂ O)]	-	-	-	1566	1339	1266	1038	467	403
[Th(L)(H ₂ O)(NO ₃) ₂]	-	-	-	1590	1342	1264	1059	570	450

The phenolic C12OH bond stretching frequency of the ligand was observed at 3348 cm^{-1} due to the intramolecular hydrogen bonding (O-H...N). This band disappeared in the spectra of the complexes, indicate that phenolic oxygen atom undergo coordination via deprotonation [11]. This is further supported by upward shift of (C12-O) Phenolic band (~ 25 to 35 cm^{-1}) in the spectra complexes as compared to free ligand. The free ligand has a characteristic C=N bond at 1625 cm^{-1} . For the Schiff base complexes C=N was observed in 1566 - 1598 cm^{-1} . The C=N stretching band of the Schiff base complexes is generally shifted to a lower frequency, indicating a decrease in the C=N bond order due to the coordinate bond formation between the metal and the imine nitrogen lone pair. IR spectrum of the free ligand contains a strong C=O absorption band at 1694 cm^{-1} and a N-H absorption medium band at 3107 cm^{-1} . Both of these bands disappear upon complexation and new C-O (enolic) absorption band appears at 1246 - 1279 cm^{-1} for complexes providing strong evidence for ligand coordination to the metal ion in the enol form by losing its N-H hydrogen [12]. A ligand spectrum exhibits band at 1021 cm^{-1} due to the (N-N) stretch. This band is shifted to higher wave number by 17 - 81 cm^{-1} in the complexes also supports the coordination of the azomethine nitrogen atom [13]. The presence of new bands in the spectra of complexes in the range 403 - 567 cm^{-1} are attributed to $\nu(\text{M-N})$ and $\nu(\text{M-O})$ modes respectively. The MoO₂(VI), WO₂(VI) and VO(IV) complexes display strong bands in the range 878 - 892 ($\text{O}=\text{M}=\text{O}$), 862 - 881 ($\text{O}=\text{W}=\text{O}$) and 968 cm^{-1} ($\text{V}=\text{O}$). Th(IV) complexes show spectral bands in the range 1531 - 1530 and 1278 - 1287 cm^{-1} due to the presence of nitrate groups, which suggest bidentate nature of ligands towards Th(IV) complexes. In MoO₂(VI) complexes medium and strong band are observed in region 3468 - 3482 cm^{-1} due to $\nu(\text{OH})$ and shoulder band at 1635 - 1647 cm^{-1} due to $\nu(\text{H}_2\text{O})$ indicate the presence of water molecules. In the spectra of WO₂(VI) complexes three bands are observed at 2055 , 772 and 487 cm^{-1} suggest thiocyanate group which is N-bonded. Therefore, the IR data of the ligand and metal complexes indicate coordination of the ligand through the phenolic oxygen and azomethine nitrogen and enolic oxygen atom.

RESULTS AND DISCUSSION

All the complexes obtained by the condensation reaction of pyrazine-2-carbohydrazone with 2,4-dihydroxyacetophenone in ethanol are coloured solids, stable towards air and moisture at room temperature and insoluble in common organic solvents such as ethanol, methanol, chloroform, benzene, cyclohexane, acetone, diethyl ether but mostly soluble in DMF and DMSO. The elemental analysis proposed 1:1 metal ligand stoichiometry for all the synthesized complexes. The structures and geometries of the ligand and complexes were in good agreement with the structural characterization done in this present work. The electrical conductivity measurements implies that 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 [9,10]. The analytical and molar conductance data of the metal complexes are given in (Table 1)

in coordination complexes (Fig. 2.). The important IR bands with their tentative assignments are depicted in Table 2

Electronic spectra and magnetic moment study of Complexes

The electronic spectrum of the Fe(III) complex shows three bands at 13605 , 17482 and 24390 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 5.93 B.M. at room temperature 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 17762 , 24691 and 39215 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), Convalency 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 , β and % covalency (β_0) are 1776 cm^{-1} , 708 cm^{-1} , 1.39 , 0.77 and 23 respectively. The Racah interelectronic repulsion parameter B is 708 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) = 23). The ratio β is found to be 1.39 which is very close to the value of 1.42 obtained for pure octahedral Cr(III) complexes. The observed magnetic moment of 3.96 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 18348 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 1.54 B.M. corresponding to one unpaired electron in an octahedral environment. The VO(IV) complex shows three bands at 13550 , 16806 and 23529 cm^{-1} due to ${}^2\text{B}_2 \rightarrow {}^2\text{E}_g$, ${}^2\text{B}_2 \rightarrow {}^2\text{B}_1$ and ${}^2\text{B}_2 \rightarrow {}^2\text{A}_1$ transitions, respectively towards square pyramidal geometry around VO(IV) ion. The magnetic moment obtained for VO(IV) complex at room temperature is observed to be 1.74 B.M. 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 $\text{MoO}_2(\text{VI})$ and $\text{WO}_2(\text{VI})$ ions. The electronic spectrum of $\text{Th}(\text{IV})$ complex shows band at 22220 cm^{-1} due to the ligand to metal charge transfer transition. The $\text{Th}(\text{IV})$ complex was found to be diamagnetic nature [14].

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	B_0
$[\text{Cr}(\text{Cl})(\text{H}_2\text{O})_2\text{L}]$	3.96	$\nu_1=17762$ $\nu_2=24691$ $\nu_3=39215$	${}^4A_{2g} \rightarrow {}^4T_{2g}(\text{F})$ ${}^4A_{2g} \rightarrow {}^4T_{1g}(\text{F})$ ${}^4A_{2g} \rightarrow {}^4T_{1g}(\text{P})$	1.39	1776	708	0.77	23
$[\text{Fe}(\text{Cl})(\text{H}_2\text{O})_2\text{L}]$	5.93	$\nu_1=13605$ $\nu_2=17482$ $\nu_3=24390$	${}^6A_{1g} \rightarrow {}^4T_{1g}(\text{G})$ ${}^6A_{1g} \rightarrow {}^4T_{2g}(\text{G})$ ${}^6A_{1g} \rightarrow {}^4E_g(\text{G})$	--	--	--	--	--
$[\text{VO}(\text{L})(\text{H}_2\text{O})]$	1.74	$\nu_1=13550$ $\nu_2=16806$ $\nu_3=23529$	${}^2B_2 \rightarrow {}^2E_g$ ${}^2B_2 \rightarrow {}^2B_1$ ${}^2B_2 \rightarrow {}^2A_1$	--	--	--	--	--
$[\text{Ti}(\text{Cl})(\text{H}_2\text{O})_2\text{L}]$	1.54	$\nu_1=18348$	${}^2T_{2g} \rightarrow {}^2E_g$	--	--	--	--	--

THERMOGRAVIMETRIC ANALYSIS

Table 4. Thermogravimetric data of metal complexes.

Compound	Temp. range ($^{\circ}\text{C}$)	% mass loss		Assignments
		Found	Calcd.	
$[\text{VO}(\text{L})(\text{H}_2\text{O})]$	90-260 260-750	5.87 -	5.07 -	Loss of 1 mole of coordinated water molecule. deligation
$[\text{MoO}_2(\text{L})(\text{H}_2\text{O})]$	90-255 255-750	4.65 -	4.33 -	Loss of 1 mole of coordinated water molecule Deligation
$[\text{WO}_2(\text{L})(\text{H}_2\text{O})]$	90-260 300-750	3.85 -	3.57 -	Loss of 1 mole of coordinated water molecule. deligation
$[\text{Cr}(\text{L})(\text{Cl})(\text{H}_2\text{O})_2]$	90-150 150-275 275-750	9.30 10.85 -	9.15 10.01 -	Loss of 2 moles of coordinated water molecules Loss of 1 coordinated chloride ion Deligation
$[\text{Fe}(\text{L})(\text{Cl})(\text{H}_2\text{O})_2]$	90-150 150-225 225-750	9.25 9.04 -	9.06 8.92 -	Loss of 2 moles of coordinated water molecules Loss of 1 coordinated chloride ion Deligation
$[\text{Ti}(\text{L})(\text{Cl})(\text{H}_2\text{O})_2]$	90-190 190-350 350-750	9.65 9.35 -	9.25 9.11 -	Loss of 2 moles of coordinated water molecules Loss of 1 coordinated chloride ion deligation
$[\text{Th}(\text{L})(\text{H}_2\text{O})(\text{NO}_3)_2]$	90-100 100-325 325-750	2.89 20.25 -	2.79 19.24 -	Loss of 1 mole of coordinated water molecule. Loss of 2 moles of Nitrate ion deligation

Thermogravimetric analysis was used to explore associated water or solvent molecules in the coordination sphere or crystalline form. Table 4 shows TG analysis data of the ligand and its complexes that recorded in the temperature range from 40 up to 750°C .

The results are in good agreement with the proposed formulae. The ligand (H_2L) decompose in a single stage, whereas $\text{VO}(\text{IV})$, $\text{MoO}_2(\text{VI})$ and $\text{WO}_2(\text{VI})$ complexes decomposed in two stages while $\text{Ti}(\text{III})$, $\text{Cr}(\text{III})$, $\text{Fe}(\text{III})$ and $\text{Th}(\text{IV})$ complexes decomposed in three stages. The first stage is due to the loss of coordinated water molecules in the temperature range $90\text{--}260^{\circ}\text{C}$. In case of $\text{Cr}(\text{III})$, $\text{Fe}(\text{III})$ and $\text{Ti}(\text{III})$ complexes second stage is corresponds to the loss of coordinated chloride ions in the temperature range $150\text{--}290^{\circ}\text{C}$. After the loss of coordinated chloride ion, all the complexes shows rapid degradation in the temperature range $350\text{--}750^{\circ}\text{C}$. This may be due to the decomposition of organic part of the complex, indicated by the rapid fall in the percentage mass loss. The decomposition continues above 360°C in each complex as indicated by the consistency in weight in the plateau of the thermogram and formed stable respective metal oxide [15].

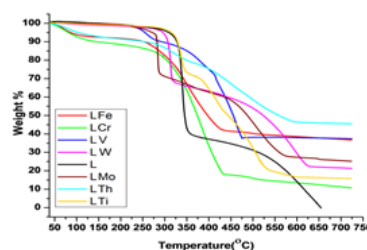


fig. Thermographs of ligand and its metal complexes

POWDER XRD

The X-ray diffraction study of ligand H_2L and its $\text{VO}(\text{IV})$ and $\text{MoO}_2(\text{VI})$ complexes was carried out using $\text{CuK}\alpha$ radiation with $k = 1.5406 \text{ \AA}$. The XRD patterns of the compounds were recorded at 2θ values between 5° and 80° and. The diffraction patterns reveal the crystalline nature of complexes [16]. 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 all complexes are as follows;

H_2L : system= triclinic, Nature= crystalline, $a=11.5161 \text{ \AA}$, $b=15.5318 \text{ \AA}$, $c=10.3697 \text{ \AA}$, $=108.194^{\circ}$, $\beta=142.116^{\circ}$, $=93.382^{\circ}$, $V=1024.64 \text{ \AA}^3$,
 $[\text{VO}(\text{L})(\text{H}_2\text{O})]$: system = triclinic, Nature=Crystalline, $a=9.9999 \text{ \AA}$, $b=11.7533 \text{ \AA}$, $c=11.4367 \text{ \AA}$, $=96.452^{\circ}$, $\beta=93.617^{\circ}$, $=113.638^{\circ}$, $V=1214.87 \text{ \AA}^3$;

$[\text{MoO}_2(\text{L})(\text{H}_2\text{O})]$: system = triclinic, Nature=Crystalline, $a=7.3003 \text{ \AA}$, $b=4.4506 \text{ \AA}$, $c=5.8530 \text{ \AA}$, $=92.558^{\circ}$, $\beta=99.793^{\circ}$, $=105.335^{\circ}$, $V=179.92 \text{ \AA}^3$.

ESR SPECTRA

The X - band ESR Spectra of $\text{VO}(\text{IV})$ complex was recorded at room temperature and g_{\parallel} , g_{\perp} and g_{av} values were found to be 1.98, 1.95 and 1.92 respectively which are deviate from the free ion value 2.0036. This is in agreement with those obtained for Vanadyl complex with square pyramidal geometry [17] given in fig.

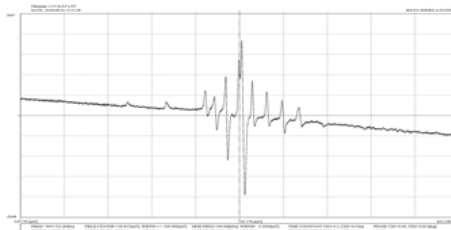


Fig. ESR Spectrum of $[\text{VO}(\text{L})(\text{H}_2\text{O})]$ complex

${}^1\text{H}$ NMR spectra

The essential features of the ${}^1\text{H}$ NMR spectrum of the $\text{MoO}_2(\text{VI})$ complex as a representative case is similar to that of ligand (H_2L). The ${}^1\text{H}$ NMR spectrum of ligand shows a signal at 11.32 ppm due to $-\text{OH}$ proton, which is absent in the spectrum of $\text{MoO}_2(\text{VI})$ complex, indicating the deprotonation of the $-\text{OH}$ group and confirming that the ligand coordinate to metal ion via deprotonation[18]. The signal for NH proton of the ligand was observed at 13.21 ppm which gets disappeared in case of $\text{MoO}_2(\text{VI})$ complex supports the coordination through enolic form of ligand to the $\text{MoO}_2(\text{VI})$ ion. ${}^1\text{H}$ NMR of $\text{MoO}_2(\text{L})(\text{H}_2\text{O})$, (DMSO- d_6 , 400 MHz): 10.44 (s, 1H, OH), 9.27 (d, 1H, C5-H), 8.90 (d, 1H, C6-H), 8.77 (t, 1H, C3-H), 7.44 (d, 1H, C11-H), 6.33 (dd, 1H, C9-H), 6.29 (d, 1H, C8-H), 2.42 (s, 3H, CH_3).

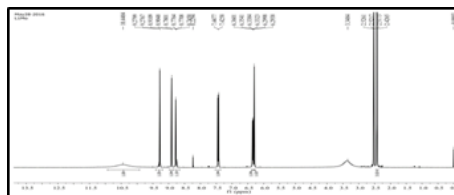


Fig. ${}^1\text{H}$ -NMR of $[\text{MoO}_2(\text{L})(\text{H}_2\text{O})]$ complex.

MASS SPECTRA

Mass spectrum of the ligand shows the molecular ion peak at $m/z =$

273.1046 (M+1), which correspond to the molecular mass of the ligand. The mass spectra of the Fe(III), VO(IV) and MoO₂(VI) complexes show a molecular ion peak (M+) at m/z = 397.190, 355.0367 and 417.2111 respectively is indicative of monomeric nature of the complex.

SEM-EDS

The SEM-EDS micrographs of the H₂L ligand, Ti(III), Cr(III) and Th(IV) complexes (Figs. 2–5) show that the Cr(III) and Th(IV) complexes have spherical granular-like structure, while Ti(III) complex exhibits crystal cluster-like structure. 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.

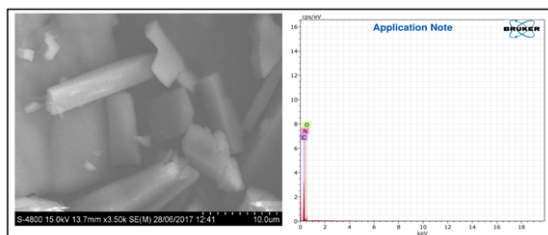


Fig. SEM-EDS graph of H₂L ligand

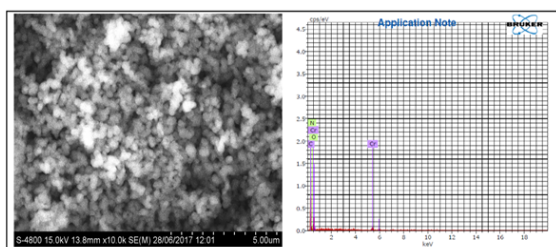


Fig. SEM-EDS graph of [Cr(L)(Cl)(H₂O)₂] complex.

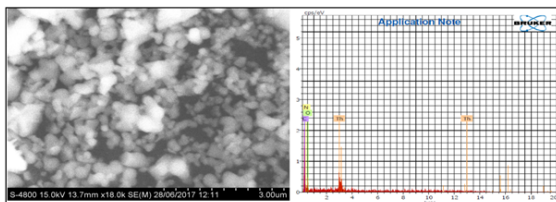


Fig. SEM-EDS graph of [Th(L)(H₂O)(NO₃)₂] complex

ANTIMICROBIALACTIVITY

The synthesized ligand and their complexes were tested for their antimicrobial activity against gram positive bacteria (*S. aureus*) and gram negative bacteria (*E. coli*) and two fungi (*A. Niger* and *C. albicans*) at a concentration of 10 µg/ml by disc diffusion technique. The results of inhibition are then compared with standard antibacterials and antifungal drugs. The antimicrobial results are given in table 5. From the result it is concluded that activity of ligands were appreciably enhanced on complexation with metals. The obtained results reflect against that all the complexes show moderate activity against all bacterial and fungal stains.

Table 5: Antimicrobial activity of ligand and its metal complexes

Sample	Inhibition Zone(mm/mg sample) MIC (mg ML-1)			
	Gram Positive	Gram Negative	Fungi	
	Escherichia Coli	Staphylococcus Aureus	C. Albicans	A. Niger
H2L	-	-	-	11
[Fe(Cl)(H ₂ O) ₂ HL]	10	10	11	-
[Ti (Cl)(H ₂ O) ₂ HL]	10	10	10	-
[Cr (Cl)(H ₂ O) ₂ HL]	10	12	11	-
[VO (L) H ₂ O]	-	12	11	-
[WO ₂ (L) H ₂ O]	-	11	15	10
[MoO ₂ (L) H ₂ O]	-	11	10	10
Th (L) (H ₂ O) (NO ₃) ₂	10	11	10	-
Standard	18	20	16	16

CONCLUSIONS

The physico-chemical and analytical analysis confirmed the composition and structure of the newly synthesized complexes. The IR, electronic spectra and magnetic moment data led to the conclusion that the metal ions take different geometries. An octahedral geometry was assigned to of Ti(III), Cr(III), Fe(III), MoO₂ (VI), WO₂(VI) and Th(IV) complexes while square pyramidal geometry to VO (IV) complex. . Anti microbial screening of the free ligand and its complexes showed high activity for complexes however moderate activity for ligands.

ACKNOWLEDGMENT

The authors are thankful to Director's SAIF Chandigarh for recording ¹H-NMR Spectra and HRMS, SAIF I.I.T. Chennai for recording elemental analysis etc. We acknowledged SGB Amravati University for partial support of this work

REFERENCES :

- Schraufnagel, D. E. ; Int. J. Tuber. Lung. Dis. 1999; 3:651-662
- Patole, J. ; Shingnapurkar, D. ; Padhye S. ; Ratledgebe, C. ; Bioorg. Med. Chem. Lett. 2006; 16:1514-1517
- Maurya, R. C. ; Verma, R. ; Singh, T. ; Synth. React. Inorg. Met. Org. Chem. 2010,33,309
- Jin, N. Y. ; J. Coord. Chem. 2012,65,4013
- Sharaby, C. M. ; Spectrochim. Acta A 66(2007) 1271-1278
- Sang, Y. L. ; Lin X. S. ; J. Coord. Chem. 63(2010) 315-322
- West, D. X. ; Padhye, S. B. ; Sonawane, P. B. ; Chikte, R. C. ; Struct. Bond. 76(1991) 1-50
- Furniss, B. S. ; Hannaford, A. J. ; Smith, P. W. G. ; Tatchell, A. R. ; Vogel's Text book of Practical Organic Chemistry, 5th ed. Longmans, London, 1976
- Silverstein, R. M. ; Bassier, G. C. ; Morrill, T. C. ; Spectroscopic identification of organic compounds, John Wiley and Sons; New York; 1981
- Fouda, A. S. ; Badr, G. E. ; El-Haddad, M. N. ; J. Korean chem. Soc. 2008,2,124
- Narang, K. K. ; Singh, V. P. ; Synth. React. Inorg. Met. Org. Chem. 1997,7,721
- Singh, P. K. ; Kumar, D. L. ; Spectrochim. Acta. Part A 24(2006) 853-858
- Chitrapriya, N. ; Mahalingam, V. ; Zeller, M. ; Natarajan, K. ; Inorg. Chim. Acta 363(2010) 3685-3693
- Tarale, S. S. ; Maurya, M. R. ; Antony D. C. ; Gopinathan, S. ; Furanik, V. G. ; Gopinathan, C. ; 1995, Bull. Chem. Soc. Jpn. 68,2847
- El-Sharif, A. A. ; Inorg. Chim. Acta 362(2009) 4991-5000
- Maurya, M. R. ; Kumar, A. ; J. Mol. Catal A; Chem 250(2006) 190-198
- Chohan, Z. H. ; Soczafava, A. ; Supran, C. T. ; J. Enzyme Inhib. Med.Chem. 18(2003) 259-263
- Chohan, Z. H. ; Pervez, H. ; Khan, M. K. ; Supran, C. T. ; J. Enzyme Inhib. Med.Chem. 19(2004) 417-423