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Synthesis, spectral and thermal study: Transition metal complexes of hydrazone ligand

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Abstract

A hydrazone Schiff base ligand 1-(2, 5-dihydroxyphenyl) propylidene) pyrazine-2-carbohydrazide prepared by the condensation of equimolar amounts of 2-5-dihydroxy propiophenone with pyrazine-2-carbohydrazide in ethanol reacts with metal chloride precursor to give complexes of Fe (III), Cr (III), Ti (III), VO (IV), Th (IV), MoO₂ (VI) and WO₂ (VI) respectively. Structure of ligand was confirmed by elemental analysis, IR, ¹H and ¹³C NMR while complexes were additionally characterized by magnetic susceptibility, molar conductance and thermogravimetric analysis. Spectroscopic studies confirmed a tridentate ONO donor behavior of the ligand towards the central metal ion. The kinetic parameters were evaluated from the thermal decomposition data.

Keywords: Hydrazone, metal complexes, spectral study, thermal analysis

Introduction

In the development of coordination chemistry Schiff base hydrazones play an important role as they easily form stable complexes with most of the transition metal ions in different oxidation state to adopt octahedral and tetrahedral geometries. The coordination compounds derived from aryl hydrazones have been reported to act as enzyme inhibitors and are useful due to their wide range of applications in organic synthesis, analytical chemistry and medicine [1-3]. The chemistry of Schiff base hydrazones and their complexes gained much attention due to potentially useful biological properties such as antifungal, antibacterial, anticonvulsant, and analgesic, anti-inflammatory, antimalarial, antimicrobial, antituberculosis, anticancer, and antiviral activities, antinociceptive and anti-inflammatory activity [4-6]. The bases derived from salicylaldehydes are well known as polydentate ligands and possess a broad level of antibacterial and antifungal activity. Hydrazones containing an azomethine have demonstrated significant role in the field of medicinal chemistry for the iron chelators in vivo as well as in vitro for the treatment of iron overload [7-8]. The interest in the study of hydrazone compounds has recently been grown up due to their good donating property through the enolate/amide oxygen (nucleophile), azomethine nitrogen (nucleophile) and phenolate oxygen. Additionally, piperidone based carbohydrazone are known to have strong coordinating properties and complexing ability towards metal ions adopting several geometries e.g. bidentate, tridentate or polydentate mode of linkages via NO, ONO, N₂O₄ [9-11]. Recently we described the biologically active hydrazone Schiff base metal complexes. Their interesting biological and structural properties encouraged us to extend our study to metal complexes of 1-(2, 5-dihydroxyphenyl) propylidene) pyrazine-2-carbohydrazideligand to see its effect on such properties compared to (H₂L, Scheme 1) analog. Moreover, the literature survey revealed that no metal complexes have been reported so far on the hydrazone obtained from 2-5-dihydroxy propiophenone with pyrazine-2-carbohydrazide.

In this paper, we report the synthesis of, spectral characterization and thermal analysis of Fe (III), Cr (III), Ti (III), VO (IV), Th (IV), MoO₂ (VI) and WO₂ (VI) complexes with 1-(2,5-dihydroxyphenyl) propylidene) pyrazine-2-carbohydrazide (H₂L) (Scheme 1).

Experimental**Materials and Methods**

All the chemicals and solvents used were of Analytical Grade (AR) and purchased commercially. All the solvents were purified by standard method and used [12]. 2-hydroxypropiophenone (Aldrich Chemical Company, USA), anhydrous titanium chloride, chromium chloride hexahydrate, anhydrous ferric chloride, Vanadyl sulphate pentahydrate and thorium nitrate hexahydrate were of analytical reagent grade and obtained from SD's fine chemicals, Mumbai, India were used as supplied.

Precursor molecule Pyrazine-2-carbohydrazide was prepared by reacting methyl-2-pyrazine carboxylate with hydrazine hydrate in ethanol using usual standard method. $\text{MoO}_2(\text{acac})_2$ and $\text{WO}_2(\text{acac})_2$ were prepared according to literature methods^[13-14].

The carbon, hydrogen and nitrogen analysis were performed on a 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 $400\text{--}4000\text{cm}^{-1}$. Magnetic measurements were carried out by the Sherwood magnetic susceptibility balance MK1 at room temperature. ^1H and ^{13}C NMR spectra were recorded on Bruker Advance II, 400 MHz, NMR spectrophotometer in d_6 -DMSO with TMS as an internal standard at SAIF, Punjab University, Chandigarh, India. 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. Thermogravimetric analysis were performed on a Perkin Elmer, Diamond TG thermal analyzer in the temperature range $40\text{--}750\text{ }^\circ\text{C}$ with a heating rate of $10\text{ }^\circ\text{C min}^{-1}$. The metal contents of the complexes were analyzed gravimetrically by decomposing the complexes with a mixture of HClO_4 , H_2SO_4 and HNO_3 and then igniting to metal oxide. The molar conductance values were recorded using 10mg per mole solution in DMSO with an Elico conductivity bridge and dip type cell calibrated with KCl solution.

Synthesis of Ligand (H_2L) 1-(2, 5-dihydroxyphenyl) propylidene pyrazine-2 carbohydrazide

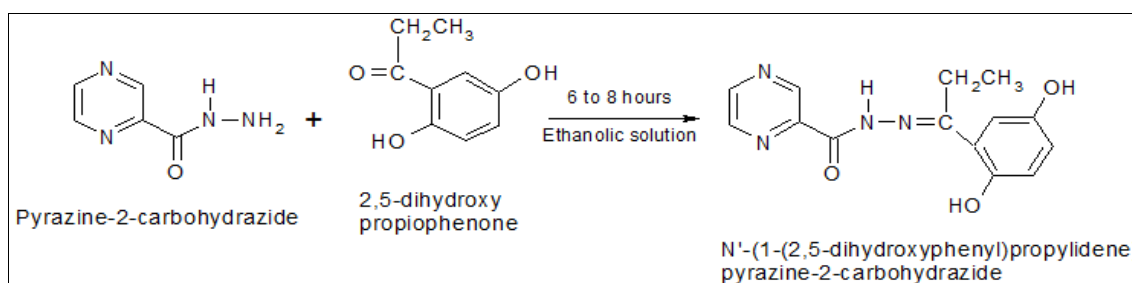
An ethanolic solution of 2-5-dihydroxy propiophenone (12g, 0.07239 moles) was added to a hot ethanolic solution of pyrazine-2-carbohydrazide (10g, 0.07239 moles) in equimolar ratio with 2-3 drops of conc. H_2SO_4 as catalyst with constant stirring on a magnetic stirrer. The resulting mixture was refluxed for 6 to 8 h. After completion of reaction time, the reaction mixture was cooled at room temperature and kept in refrigerator for overnight. A pale yellow coloured product was precipitate out which was filtered off, washed with distilled water, cold ethanol and lastly dried in desiccator using silica gel as moisture absorbent. Yield: 73% M. P.: $253\text{ }^\circ\text{C}$.

^1H -NMR (DMSO- d_6 , 400MHz): δ 12.25 (d, 1H, O-H), 11.33 (d, 1H, N-H), 9.28(s, 1H, O-H), 9.28(d, 1H, C2-H), 9.28 (d, 1H, C2-H), 8.94 (d, 1H, C5), 8.89 (d, 1H, C6-H), 7.01 (d, 1H, C9-H), 6.78 (s, 1H, C12-H), 6.75 (s, 1H, C10-H), 2.92 (s, 2H, CH_2) 1.19 (s, 3H, CH_3) fig. 1

^{13}C -NMR (DMSO- d_6 , 400MHz): δ 162.83 (C=N), 159.51 (C=O), 151.87 (C12), 149.30 (C6), 147.95 (C2), 144.03 (C3), 143.37 (C5), 119.17 (C8), 117.97(C7), 113.51 (C9), 19.37 (CH_2), 10.78 (CH_3) fig. 2

IR (KBr disc cm^{-1}): 3328 (OH), 3025 (NH), 1685 (C=O), 1572m (C=N), 1319 (C-O), 1057 (N-N)

The general scheme for the synthesis of ligand H_2L is shown below. The analytical data and physical properties are provided in table 1.



Synthesis of Ligand H_2L

Synthesis of $\text{VO}(\text{IV})$, $\text{Cr}(\text{III})$, $\text{Fe}(\text{III})$, and $\text{UO}_2(\text{VI})$ complex

Metal complexes of $\text{VO}(\text{IV})$, $\text{Cr}(\text{III})$, $\text{Fe}(\text{III})$, and $\text{UO}_2(\text{VI})$ were prepared by following general method. An equimolar amount of ligand (H_2L) (2.91 g, 0.01 mol) and respective metal salt (0.01 mol) were dissolved separately in DCM+ MeOH (50:50, v/v) (25 mL). Both the solutions were filtered and mixed in warm conditions with continuous stirring. The reaction mixture was further refluxed for ca. 5 h on an oil bath. The pH of the reaction mixture was adjusted ca. 7.0 by adding methanolic solution of sodium acetate (0.5 g) and refluxing further continued for another 1 h. The reaction mixture was cooled to room temperature, the precipitate separated out was filtered, washed with cold DCM, methanol and petroleum ether and finally dried under vacuum over CaCl_2 Yield: 55-68%.

Synthesis of $\text{MoO}_2(\text{L})\text{H}_2\text{O}$ and $\text{WO}_2(\text{L})\text{H}_2\text{O}$ complex

A hot methanolic solution (25mL) of $[\text{MoO}_2(\text{acac})_2]$ (0.44 g, 1 mmol) was mixed in drop wise 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 volume of the solution to 10 mL and cooling at $10\text{ }^\circ\text{C}$ overnight, the separated coloured product obtained was

filtered, washed with ethanol followed by petroleum ether and finally dried in desiccator over anhydrous CaCl_2 . Yield: 65%. The $[\text{WO}_2(\text{L})(\text{H}_2\text{O})]$ complex was prepared under similar condition as above using $[\text{WO}_2(\text{acac})_2]$ 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 DMF and DMSO. The proposed compositions, formula weights and elemental analysis of the complexes are included in Table 1.

Results and Discussion

The reaction between 2-5-dihydroxy propiophenone with pyrazine-2-carbohydrazide in ethanol produced a new hydrazone ligand (H_2L). Physico-chemical studies confirmed its structure. Reaction of this ligand with metal salts resulted in the formation of complexes in good yield. 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 of these complexes suggest 1:1 metal: ligand stoichiometry for all the complexes and it is in good agreement with the proposed structures and geometry of complexes. Most of the

complexes are decomposed at higher temperature without melting. The observed low value of conductivity in DMSO reveals their non-electrolytic nature [15-16].

Elemental analysis and solution conductivity

All the complexes synthesized from H₂L ligand are coloured solids, air stable and non-hygroscopic in nature. These complexes are insoluble in water and most of the organic solvents but found to be sparingly soluble in DMF and DMSO. At high temperature without melting most of the complexes gets decomposed. The solution conductivities of complexes (10⁻³M) are presented in Table 1. The low conductivity values in DMSO revealed their non-electrolytic nature. The elemental analysis (Table 1) suggest 1:1 metal to ligand stoichiometry for all complexes.

Magnetic susceptibility and reflectance spectral studies of metal complexes of 2, 4-dihydroxy benzophenone pyrazine-2-carbohydrazone [H₂L]

The solid reflectance bands and magnetic moment values provides information about the geometry of the compounds. Fe(III) complex, shows three weak bands at 13721, 18415 and 24320 cm⁻¹ due to ⁶A_{1g}→⁴T_{1g}(G), ⁶A_{1g}→⁴T_{2g}(G) and ⁶A_{1g}→⁴E_g(G), transitions, respectively of a typical octahedral structure. The room temperature value of magnetic moment is 5.97 B.M. corresponds to the presence of five unpaired electrons, indicating octahedral geometry of complex [17-18]. The reflectance spectrum of Cr(III) complex shows bands at 17405, 27519 and 34216 cm⁻¹ corresponding to the transitions ⁴A_{2g}→⁴T_{2g}(F), ⁴A_{2g}→⁴T_{1g}(F) and ⁴A_{2g}→⁴T_{1g}(P), respectively, suggesting an octahedral geometry for Cr(III) complex [19]. For Cr (III) octahedral system the ligand field parameters are found to be Dq=1740 cm⁻¹, B=635 cm⁻¹, v₂/v₁ = 1.49, β=0.69 and β₀=31 respectively. The B value for the complex is lower than free ion value which is indicative of orbital overlap and delocalization of d-orbitals. The observed magnetic moment 4.31 B.M. is also supports towards octahedral geometry for Cr (III) complex. The Ti (III) complex shows a broad band at 17892 cm⁻¹ due to ²T_{2g}→²E_g transition in an distorted octahedral geometry. The observed magnetic moment of 1.78 B.M., which is in good agreement with octahedral geometry for Ti (III) complex. The existence of three bands at 13892, 17541 and 24261 cm⁻¹ in the reflectance spectrum of VO(IV) complex observed as a consequence of ²B₂→²E₀, ²B₂→²B₁ and ²B₂→²A₁, transitions, respectively, suggesting square pyramidal geometry around VO(IV) ion. The observed magnetic moment at room temperature is 1.67 B.M. which also suggests square pyramidal geometry for VO (IV) complex [20-21]. MoO₂ (VI) and WO₂ (VI) complexes are found to be diamagnetic and do not show any d-d transitions in their reflectance spectra and may have octahedral geometry for both complexes [22]. Th (IV) complex exhibits a broad band at 19784 cm⁻¹ due to the ligand to metal charge transfer transition and complex is found to be diamagnetic for majority of Th (IV) octahedral complexes [23].

Infrared spectral studies of metal complexes of 2-5-

dihydroxy propiophenonepyrazine-2-carbohydrazone [H₂L]

The IR spectra of the metal complexes are compared with those of the free ligand in order to determine the coordination sites that may be involved in chelation. The position and or the intensities of these peaks are expected to be changed upon complexation.

The ligand exhibits a medium intensity band at 3328 cm⁻¹ which is attributed to intramolecular hydrogen bonded hydroxyl group (O-H-N). This band was found to be absent in the spectra of the metal complexes indicating deprotonation of the OH group upon bonding with metal ions. This is further supporting by shifting of the ν(C-O) phenolic band at 1319 cm⁻¹ to a higher frequency by 44-12 cm⁻¹ in complexes, suggesting the coordination of ligand through phenolic oxygen via deprotonation. The ligand spectrum exhibits a strong band at 1572 cm⁻¹ (azomethine C=N), which shifted to lower frequency (63-25 cm⁻¹) indicating the participation of azomethine nitrogen in coordination. The ligand spectrum shows a band at 1057 cm⁻¹ due to the ν(N-N) stretch. In the spectra of the complexes this band shifted to higher frequency by 14-33 cm⁻¹ also suggests coordination through azomethine nitrogen atom. The high frequency shift of the ν(N-N) band is expected because of diminished repulsion between the lone pairs of adjacent nitrogen atoms. The ligand spectrum showed bands ν(N-H) and ν(C=O) at 3006 and 1685 cm⁻¹ respectively. However, these bands are not found in all the complex suggests coordination arises through enolic oxygen. During this process the dissociation of proton occurs which destructs the carbonyl moiety and forms azomethine (>C=N-N=C<) group. In VO (IV) complex, strong band observed at 875 cm⁻¹ is assigned to ν(V=O) modes. The MoO₂ complex shows new bands at 948 and at 950 cm⁻¹ due to symmetric and asymmetric stretching frequency of *cis*-MoO₂. The WO₂ (VI) complex shows band at 844-895 cm⁻¹ due to (O=W=O) stretch. Besides this, complexes also show bands in the range 3377-3424, 1568-1592, and 847-884 cm⁻¹ due to ν (OH), δγ(H₂O) and δw (H₂O) vibrations for the coordinated water molecules. The IR spectra of complexes show new bands in the region 506-576 and 402-478 cm⁻¹ due to ν(M-O) and ν(M-N) vibrations respectively indicating the coordination of ligand through the phenolic oxygen and azomethine nitrogen atoms. From the IR spectral data, the tridentate nature of ligand was found and coordination arises through the phenolic oxygen, enolic oxygen and azomethine nitrogen [24].

Thermogravimetric analysis of ligand (H₂L) and its complexes

Thermal analysis is performed to determine the thermal stability of complexes and its degradation pattern in which the change in the weight of the substance is recorded as function of temperature or time. Thermogravimetric analysis (TGA) was performed in nitrogen atmosphere with heating rate 10°C min⁻¹ and thermograms are recorded in temperature range 40-800 °C. Using this technique several kinetic parameters such as activation energy (E_a), order of

reaction (n), entropy change (S) and frequency factor (Z) were calculated. The thermal data have been analyzed using Freeman-Carroll [25] and Sharp-Wentworth methods [26].

The TGA curves for ligand H_2L and its complexes were obtained by TG analysis in the temperature range 40-750 °C in air atmosphere with heating rate of 100 °C min^{-1} . The thermal decomposition curves are shown in Fig. 3. And fragments losses are given in Table 2. The pattern of decomposition shown by complexes was found to be similar reflecting their isostructural characteristics. The thermograms of the complexes suggests that they are thermally stable at different temperature ranges. A regular weight loss found in the complexes indicating decomposition by fragmentation decomposition taking place as we increase the temperature. The thermograms obtained from TGA analysis showed one-step decomposition for ligand and two and three steps decomposition for the metal complexes. The first step decomposition in complexes was due to the loss of coordinated water molecule/s in the temperature range 115-195 °C. Thus TG curve of Ti (III), Cr (III) and Fe (III) complexes exhibits elimination of two coordinated water molecules and VO (IV), MoO_2 (VI), WO_2 (VI) and Th (VI) complexes exhibit elimination of one coordinated water molecule in this temperature range

The second step decomposition in complexes corresponds to the loss of coordinated chloride ion and nitrate ion in the temperature range 195-300 °C. Thus TG curve of Ti (III), Cr (III) and Fe (III) complexes exhibits the elimination of one coordinated chloride ion and Th (VI) complex exhibits elimination of two nitrate ions [% wt. loss obs./calcd.: Ti(III): 8.56/8.80; Cr(III):8.17/8.71; Fe(III): 8.88/8.62; Th(IV): 19.78/19.24]. At the end of thermal analysis, all the

complexes arrays constant and fast weight loss above 343 °C, indicates the decomposition of the free parts of the coordinated ligand. Beyond 649 °C, the horizontal level formed suggesting the formation of final decomposition products corresponding to respective oxides.

Freeman and Carroll plots of $[\Delta \log(dw/dt)]/\Delta \log W_r V_s \Delta(1/T)/\Delta \log W_r$ should give on Y-axis ($x = 0$) an intercept for the value of n , the order of reaction and the slope $m = -E/2.303R$ were drawn. The activation energy (E_a) obtained for the decomposition process of complexes was calculated by both the methods FC and SW and the acquired values are comparable. These values of activation energy, decomposition temperature, other parameters like the Entropy change (ΔS), the free energy change (ΔF), frequency factor (z) and apparent entropy of activation (ΔS^*) were calculated and the computed data presented in Table 3. During decomposition process, it was found that activation energy (E_a) values increases from 13.28 to 34.56 and entropy change values decreases from -102.57 to -82.10 which indicates the more ordered nature of complexes than their ligands. Lower value of frequency factor (z) and higher activation energy (E_a) values favour the reaction to proceed more slowly than the normal. It was also found that the values of activation energy are less than free energy changes (ΔG) because decomposition reaction is non-spontaneous in all steps. The positive magnitude of (ΔG) confirmed that complex compound shows more thermal stability, endothermicity, and the non-spontaneous degradation reaction at higher temperature. Thus TGA analysis provides further support towards the elucidation of proposed structures and composition of synthesized metal complexes.

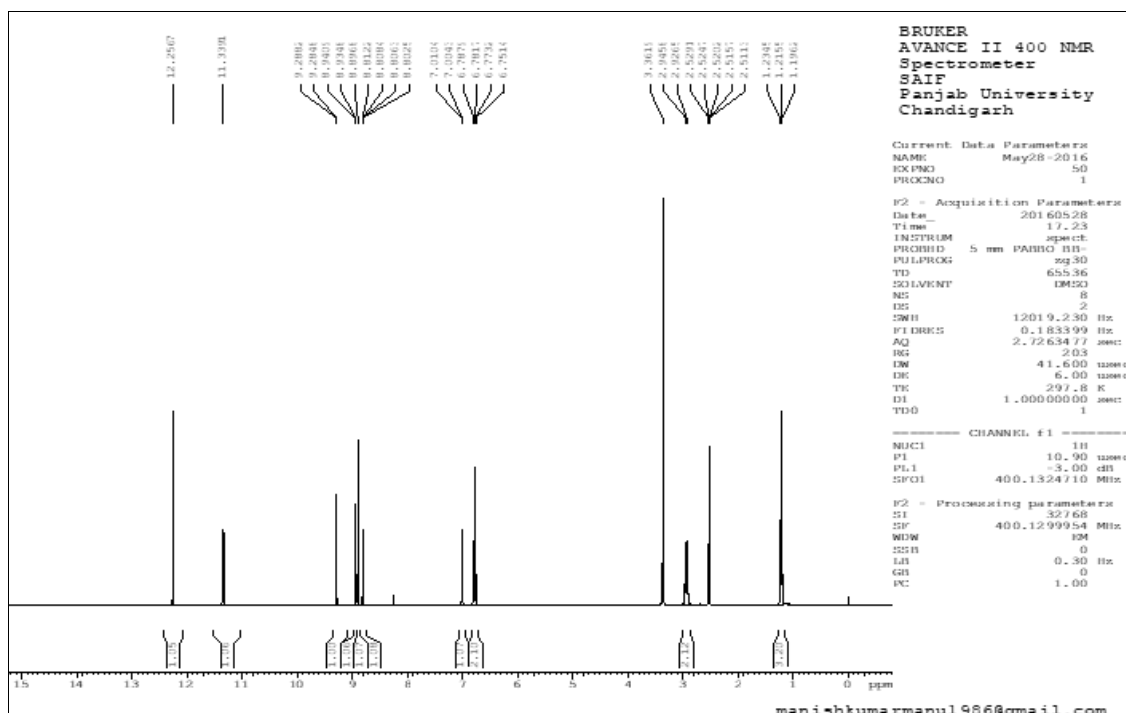
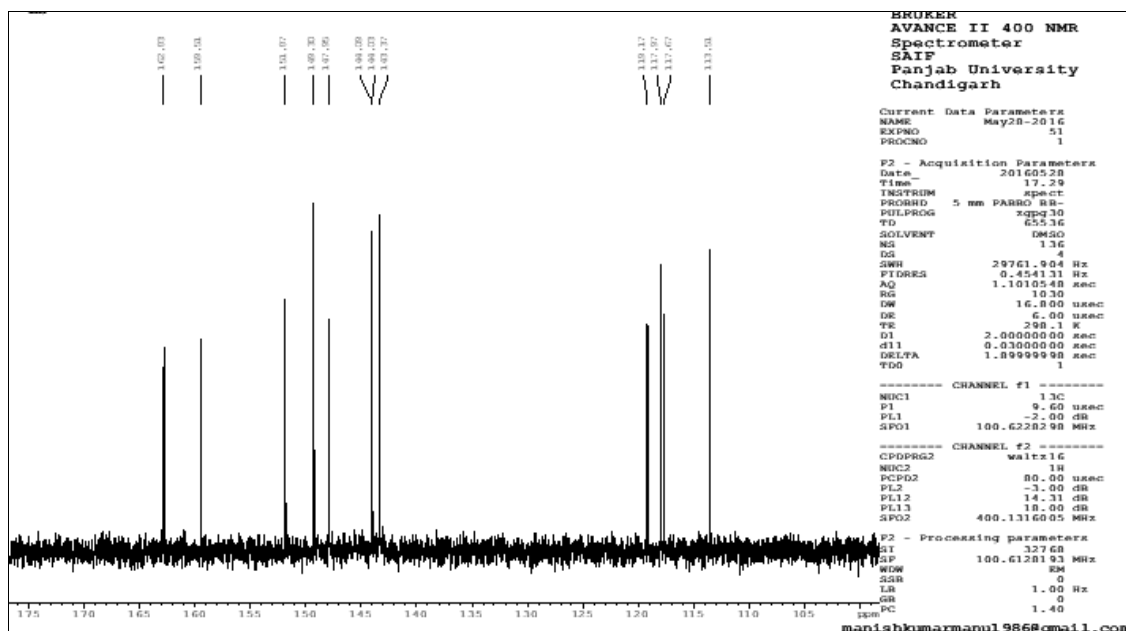
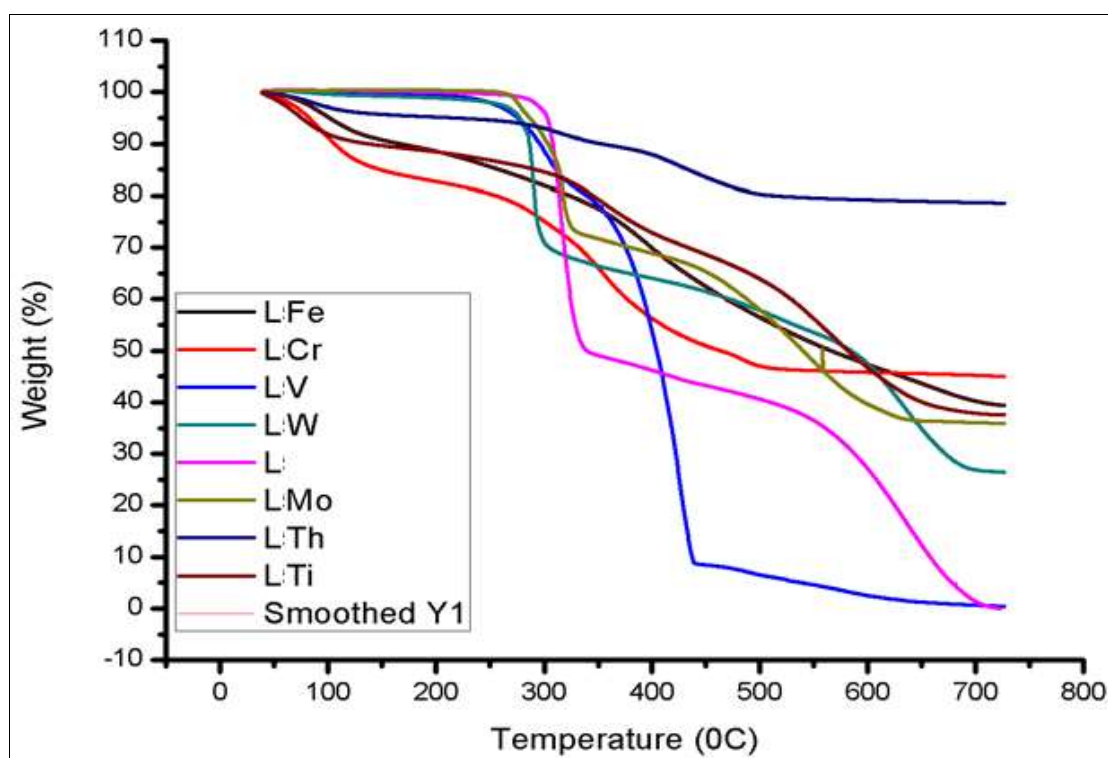


Fig 1: 1H NMR Spectrum of ligand H_2L

Fig 2: ^{13}C NMR Spectrum of Ligand H_2L Fig 3: Thermograms of Ligand H_2L and its complexesTable 1: Element analysis of the ligand H_2L and its metal complexes

Ligand and its complexes	Colour	Molecular formula	Formula Weight	Elemental analysis % found (calculated)						Molar conductance ($\Omega^{-1}\text{cm}^2\text{mol}^{-1}$)
				C	H	N	O	M	Cl	
H_2L	Yellow	$\text{C}_{14}\text{H}_{14}\text{N}_4\text{O}_3$	286.11	57.89 (58.74)	5.02 (4.98)	20.12 (19.57)	15.88 (16.77)			-
$[\text{Ti}(\text{L})(\text{Cl})(\text{H}_2\text{O})_2]$	Reddish brown	$\text{C}_{14}\text{H}_{16}\text{ClN}_4\text{O}_5\text{Ti}$	403.03	42.02 (41.66)	3.92 (4.00)	13.65 (13.88)	20.12 (19.82)	12.02 (11.86)	8.02 (8.78)	4.3
$[\text{Vo}(\text{L})(\text{H}_2\text{O})]$	Slate white	$\text{C}_{14}\text{H}_{14}\text{N}_4\text{O}_5\text{V}$	369.04	46.02 (45.54)	3.02 (3.82)	16.22 (15.17)	21.02 (21.67)	14.02 (13.80)		6.8
$[\text{Cr}(\text{L})(\text{Cl})(\text{H}_2\text{O})_2]$	Brown	$\text{C}_{14}\text{H}_{16}\text{ClN}_4\text{O}_5\text{Cr}$	407.02	42.02 (41.24)	4.02 (3.96)	14.68 (13.74)	19.98 (19.62)	13.02 (12.75)	8.88 (8.69)	7.6
$[\text{Fe}(\text{L})(\text{Cl})(\text{H}_2\text{O})_2]$	Blackish red	$\text{C}_{14}\text{H}_{16}\text{ClN}_4\text{O}_5\text{Fe}$	411.02	41.12 (40.85)	4.24 (3.92)	13.67 (13.61)	20.22 (19.44)	13.88 (13.57)	8.88 (8.61)	6.5
$[\text{MoO}_2(\text{L})(\text{H}_2\text{O})]$	Crèmy white	$\text{C}_{14}\text{H}_{14}\text{N}_4\text{O}_6\text{Mo}$	432	40.88 (39.08)	3.23 (3.28)	12.98 (13.02)	22.86 (22.31)	22.08 (22.30)		9.3

[WO ₂ (L)(H ₂ O)]	Greenish white	C ₁₄ H ₁₄ N ₄ O ₆ W	518.04	33.04 (32.45)	3.02 (2.72)	11.04 (10.81)	17.98 (18.53)	35.88 (35.48)		8.9
[Th(L)(NO ₃) ₂ (H ₂ O)]	Brown	C ₁₄ H ₁₄ N ₆ O ₉ Th	642.12	26.85 (26.18)	2.25 (2.20)	13.42 (13.08)	20.43 (22.42)	37.05 (36.12)		11.6

Table 2: Stepwise thermal degradation data for H₂L metal complexes

Compound	Temp. range (°C)	% mass loss		Assignments/Observation
		Found	Calcd.	
[Ti(L)(Cl)(H ₂ O) ₂]	120-230	8.88	8.93	Loss of 2 mol of coordinated water molecules
	230-250	8.56	8.80	Loss of 1 coordinated chloride ion.
	250-750	--	--	Deligation
[VO(L)(H ₂ O)]	130-290	4.73	4.88	Loss of 1 mol of coordinated water molecule.
	290-750	--	--	Deligation
[Cr(L)(Cl)(H ₂ O) ₂]	110-150	8.12	8.84	Loss of 2 moles of coordinated water molecules
	150-275	8.17	8.71	Loss of 1 coordinated chloride ion.
	275-750	--	--	Deligation
[Fe(L)(Cl)(H ₂ O) ₂]	120-225	8.16	8.76	Loss of 2 moles of coordinated water molecules
	225-295	8.88	8.62	Loss of 1 coordinated chloride ion.
	295-750	--	--	Deligation
[MoO ₂ (L)(H ₂ O)]	125-250	4.92	4.19	Loss of 1 mol of coordinated water molecule.
	250-750	--	--	Deligation
[WO ₂ (L)(H ₂ O)]	110-240	3.94	3.48	Loss of 1 mol of coordinated water molecule.
	240-750	--	--	Deligation
[Th(L)(H ₂ O)(NO ₃) ₂]	115-150	2.25	2.80	Loss of 1 moles of coordinated water molecule.
	150-313	19.78	19.24	Loss of 2 moles of Nitrate,
	313-750	--	--	Deligation

Table 3: Activation Energy, decomposition temperature and kinetic parameters of Ligand H₂L and its complexes

Sr. No.	Ligand and metal complexes	Decomposition temp. (°C)	Activation energy Ea (KJ mol ⁻¹)		Entropy change ΔS (Jmol ⁻¹ K ⁻¹)	Free energy change ΔG (KJ)	Frequency factor Z (s ⁻¹)	Apparent entropy change S*(KJ)	Order of reaction (n)
			FC	SW					
1	H ₂ L	300	27.80	26.92	-102.57	91.70	6.74x10 ⁻⁴	-37.50	0.84
2	[Ti(L)(Cl)(H ₂ O) ₂]	305	13.28	14.09	-92.54	82.04	5.156x10 ⁻⁴	-37.94	1.08
3	[VO(L)(H ₂ O)]	280	20.73	14.09	-84.18	91.21	5.101x10 ⁻⁴	-37.94	0.56
4	[Cr(L)(Cl)(H ₂ O) ₂]	385	21.23	19.89	-89.14	87.21	5.25x10 ⁻⁴	-33.25	0.90
5	[Fe(L)(Cl)(H ₂ O) ₂]	330	18.78	18.82	-86.68	77.98	1.49x10 ⁻³	-36.79	0.93
6	[MoO ₂ (L)(H ₂ O)]	375	20.33	19.55	-85.12	85.24	5.41x10 ⁻⁴	-36.88	0.96
7	[WO ₂ (L)(H ₂ O)]	295	34.56	30.96	-82.40	78.66	1.87x10 ⁻³	-36.60	0.79
8	[Th(L)(H ₂ O)(NO ₃) ₂]	310	27.80	25.90	-87.41	89.25	7.149x10 ⁻⁴	-37.56	0.84

Conclusion

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.

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