

Synthetic, spectroscopic and thermal studies of some complexes of unsymmetrical Schiff base ligand

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Abstract New unsymmetrical Schiff base ligand (H₂L) is prepared via condensation of 2-hydroxy-5-methyl acetophenone, 2-hydroxy-5-chloro-3-nitro acetophenone and carbohydrazide in 1:1:1 ratio. Metal complexes of VO(IV), Cr(III), Mn(III), Fe(III), Zr(IV), MoO₂(VI), WO₂(VI) and UO₂(VI) have been prepared. These complexes were characterized by elemental analysis, UV–Vis and IR spectroscopy and magnetic moment and thermogravimetric analysis. The purity of the ligand and the metal complexes is confirmed by microanalyses, while unsymmetrical nature of ligand was further corroborated by ¹H NMR. All the complexes are air stable and insoluble in water and common organic solvents but fairly soluble in DMSO. The elemental analysis shows 1:1 metal to ligand stoichiometry for all the complexes. Thermal behaviour of the complexes was studied, the complexes were found to be quite stable and their thermal decomposition was generally via partially loss of the organic moiety and ended with respective metal oxide as a final product. Comparison of the IR spectrum of ligand and its metal complexes confirm that Schiff base behave as a dibasic tetradentate ligand towards the central metal ion with an ONNO donor sequence. The dc electrical conductivity is studied and data obtained obeyed the relation $\sigma = \sigma_0 \exp(-E_a/kT)$ over the temperature range 40–130 °C. X-ray diffraction study of VO(IV) complex shows its crystalline nature with triclinic crystal system.

Keywords Unsymmetrical Schiff base · Metal complexes · Thermal analysis · dc Conductivity

Introduction

Schiff base complexes of transition metals are of particular interest to inorganic chemists because of their structural, spectral and chemical properties are often strongly dependant on the nature of the ligand structure. Coordination complexes with substituted ketones have shown diverse structural and properties generating a variety of stereochemistry and a wide range of bonding interactions. The interest in the construction of unsymmetrical coordination complexes by reacting transition metal ions with tetradentate has been constantly growing over the past years [1–4]. Within this understanding lies an increased knowledge of molecular self-assembly [5, 6] metal–ligand complexation [7, 8] and disposition of metal binding sites [9]. By mastering these areas, new improved systems related to the fields of catalysis [10] supramolecular chemistry [11, 12] and bioengineering [7] can be achieved and due to this application of coordination complexes. The synthesis and characterization of symmetrical tetradentate Schiff base complexes have been thoroughly studied but comparatively less studies seem to have been done on complexes of unsymmetrical Schiff base derived from acetophenone. A search of the literature revealed that no work has been done on transition metal complexes of the unsymmetrical Schiff base derived from acetophenones and carbohydrazide. The synthesis of unsymmetrical tetradentate Schiff base formed by the condensation of 2-hydroxy-5-methyl acetophenone, 2-hydroxy-5-chloro-3-nitro acetophenone and carbohydrazide (Fig. 1) is reported. The complexes of VO(IV), Cr(III), Mn(III), Fe(III), Zr(IV), MoO₂(VI), WO₂(VI) and

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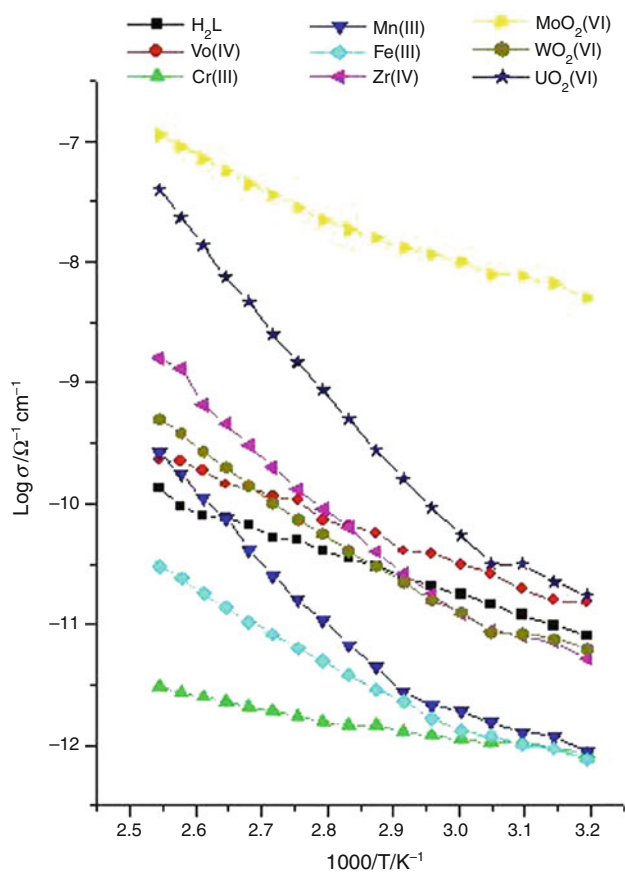
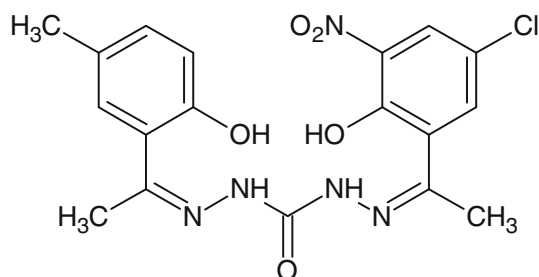


Fig. 1 Temperature dependence of $\log \sigma$



Scheme 1 Structure of the Schiff base (H_2L)

$UO_2(VI)$ with this ligand were also prepared in the solid state and characterized by different physicochemical methods (Scheme 1).

Experimental

All the chemicals and solvents were of analytical grade and used as received. Vanadyl sulphate pentahydrate, chromium chloride hexahydrate, anhydrous ferric chloride, dioxotungsten tetrathiocyanate, zirconium acetate, uranyl nitrate hexahydrate and carbohydrazide were of Rankem and SD fine chemicals and used as received. $Mn(OAc)_3 \cdot 2H_2O$ was

prepared by the oxidation of $Mn(OAc)_2 \cdot 4H_2O$ using Christensen's method [13] and bis(acetyl acetonato) dioxomolybdenum(VI) was synthesized according to literature method [14, 15].

Synthesis of N'' -[(1-(2-hydroxy-5-methylphenyl)ethylidene)- N''' -(1-(2-hydroxy-5-chloro-3-nitrophenyl)ethylidene)]carbonohydrazide (H_2L)

The unsymmetrical Schiff base ligand (H_2L) was prepared by modification of literature method [16, 17]. A mixture of 2-hydroxy-5-methyl acetophenone (2.4 g, 0.016 M), 2-hydroxy-5-chloro-3-nitro acetophenone (3.12 g, 0.016 M) and carbohydrazide (1.44 g, 0.016 M) in ethanol was refluxed for about 3 h. The reaction mixture was cooled to room temperature and solvent was then partially evaporated under air and faint brown yellow coloured solid compound formed was filtered and washed with ethanol, petroleum ether and then dried over anhydrous calcium chloride vacuo (Yield: 66%, m.p. 283 °C).

12.58 (S, 1H, OH, phenolic), 12.47 (S, 1H, OH, phenolic), 10.10 (S, 1H, imino, NH), 10.17 (S, 1H, imino, NH), 2.33 (S, 3H, Ar- CH_3), 2.81 (S, 3H, CH_3), 2.97 (S, 3H, CH_3), 6.84–8.07 (m, 5H, aryl-H).

Synthesis of $VO(IV)$, $Cr(III)$, $Mn(III)$, $Fe(III)$, $MoO_2(VI)$, $Zr(IV)$ and $UO_2(VI)$ complexes

To a hot DMF solution (25 mL) of the ligand (1.0 mmol), ethanolic solution (25 mL) of the desired metal salt (1.0 mmol) was added under continuous stirring. The resulting mixture was refluxed for 3–4 h. On cooling to room temperature the precipitated solid was filtered, washed with ethanol, DMF and petroleum ether and then dried over anhydrous calcium chloride vacuo, yields obtained ranged from 65 to 70%.

Synthesis of $WO_2(VI)$ complexes

Sodium tungstate dihydrate (1.2 g; 0.00363 M) and ammonium thiocyanate (2.9 g; 0.038 M) were dissolved in water (30 mL) at room temperature and 7.5 mL of 11 M HCl was added to it. The resulting yellow solution was cooled in an ice bath and DMF solution (10 mL) of ligand (0.00363 M) was added to it. The yellow precipitate was so obtained was filtered washed with water containing few drops of HCl and dried in vacuo. The yield was 67%.

Physical measurements

Elemental analyses carbon, hydrogen and nitrogen were obtained using Carlo Erba 1108 analyzer in micro

analytical laboratory, CDRI, Lucknow, India. The IR spectra of the complexes were recorded on a Perkin-Elmer 597 spectrophotometer using KBr pallets at SAIF Punjab University, Chandigarh, India. ^1H NMR spectrum of ligand was obtained using a Bruker Aavance-II 400 NMR spectrophotometer in DMSO solvent at SAIF Punjab University, Chandigarh while solid reflectance spectra were recorded on a Varian SE UV-NIR spectrophotometer. Magnetic susceptibilities were measured at room temperature by Gouy's method using $\text{Hg}[\text{CO}(\text{NCS})_4]$ as a calibrant and the diamagnetic corrections were made using Pascal's constant. The solid state dc electrical conductivity of compounds was measured by Zentech Electrometer in their compressed pellet form over 313–403 K temperature range. TG analysis of the complexes was carried out on Perkin Elmer TG-2 thermobalance in ambient air with a heating rate of 10 °C per minute. Metal contents of the complexes were analyzed gravimetrically after decomposing the complexes with a mixture of HClO_4 , H_2SO_4 and HNO_3 and then igniting to metal oxide. The XRD measurement of the complexes was recorded with a Bruker AXS, D8-ADVANCE (Gmbh, Karlsryhe, West Germany) equipped with θ/θ goniometer and a Lynv Eye detector.

Results and discussion

The physical characterization and microanalytical data of ligand and its coordination complexes are given in Table 1. ^1H NMR data of ligand revealed that the unsymmetrical Schiff base were isolated, while microanalysis confirms the purity of the ligand as formulated. The formulation of symmetrical and unsymmetrical analogue could be distinguished from the microanalytical data since they have different molecular masses. The complexes are stable in air, insoluble in water but slightly soluble in DMSO. The purity of the Schiff base and its complexes, as formulated, was established by microanalyses. Thus it can be concluded that the Schiff base behaves as tetradentate ligand coordinating via the azomethine N and the phenolic O.

Infrared spectra

For studying the bonding mode of unsymmetrical schiff base to the metal ion in the coordination complexes, IR spectra of the complexes were interpreted by comparing the spectrum with that of the free ligand as shown in Table 2. The comparison of the IR spectral bands of the free ligand and its metal complexes indicate that the band at 2971 cm^{-1} due to intramolecular hydrogen bonded $\nu(\text{OH})$ group in the free ligand spectrum disappeared in all complexes and the $\nu(\text{CO})$ (phenolic) band at 1232 cm^{-1} , shifted to a higher frequency, suggesting the coordination

Table 1 Analytical data of H_2L complexes

Sr. no.	Compound	Formula weight/g mol^{-1}	MP*/half decomp. temp./°C	Colour	Elemental analyses % found (calcd.)				Electrical conductivity $\sigma/\Omega^{-1}\text{ cm}^{-1}$ at 373 K	Activation energy/eV
					C	H	N	M		
1	H_2L	374.82	283	Avocado	57.32 (57.68)	5.02 (5.11)	14.12 (14.95)	—	6.67×10^{-11}	0.951
2	$[\text{VO L}] \text{H}_2\text{O}$	502.76	354	Green grey	9.37 (10.13)	42.28 (43.00)	2.81 (3.61)	13.09 (13.93)	1.35×10^{-10}	0.929
3	$[\text{Cr L} \cdot \text{H}_2\text{O} \cdot \text{Cl}] \cdot \text{H}_2\text{O}$	541.28	365	Umber	9.22 (9.61)	39.32 (39.94)	2.97 (3.72)	11.62 (12.94)	2.08×10^{-12}	1.063
4	$[\text{Mn L} \cdot \text{OAc}]$	531.78	332	Deep umber	9.37 (10.33)	44.25 (45.17)	3.09 (3.60)	12.84 (13.17)	1.07×10^{-12}	1.084
5	$[\text{Fe L} \cdot \text{H}_2\text{O} \cdot \text{Cl}] \cdot \text{H}_2\text{O}$	545.13	377	Black cherry	9.72 (10.24)	38.57 (39.66)	3.15 (3.70)	11.88 (12.85)	1.05×10^{-11}	1.011
6	$[\text{Zr L}(\text{OH})_2 \text{H}_2\text{O}] \text{H}_2\text{O}$	579.07	330	Avocado	14.51 (15.75)	36.49 (37.33)	2.71 (3.83)	11.75 (12.09)	3.01×10^{-10}	0.903
7	$[\text{MoO}_2 \text{ L}]$	545.74	388	Honey dew	16.46 (17.58)	38.66 (39.61)	2.24 (2.96)	11.97 (12.83)	4.47×10^{-08}	0.742
8	$[\text{WO}_2 \text{ L} \cdot \text{NCS}]$	691.72	344	Vanilla	25.47 (26.58)	32.18 (32.99)	1.89 (2.33)	11.63 (12.15)	1.41×10^{-10}	0.927
9	$[\text{UO}_2 \text{ L}]$	687.83	331	Khaki	33.91 (34.61)	30.47 (31.43)	1.79 (2.34)	9.67 (10.18)	4.68×10^{-09}	0.815

Table 2 Infrared spectral data (cm^{-1}) of H_2L and its complexes

Sr. no.	Ligand/complex	Phenolic O–H	N–H	C=N	C=O	C–O	N–N	M–O	M–N	H_2O
1	H_2L	2971	3297	1647	1729	1232	985	–	–	–
2	[VO L] H_2O	–	3286	1621	1702	1244	1025	528	485	3448, 1490
3	[Cr L- H_2O -Cl]- H_2O	–	3275	1614	1693	1256	1017	523	476	3433, 1528 878, 762
4	[Mn L-OAc]	–	3294	1635	1687	1238	998	507	487	–
5	[Fe L- H_2O -Cl]- H_2O	–	3290	1639	1695	1248	989	526	456	3450, 1534 857, 787
6	[Zr L(OH) $_2$ H_2O] H_2O	–	3277	1624	1712	1251	1013	536	472	3453, 1487 834, 741
7	[MoO $_2$ L]	–	3282	1642	1682	1235	1019	547	464	–
8	[WO $_2$ L-NCS]	–	3283	1634	1675	1266	995	528	458	–
9	[UO $_2$ L]	–	3302	1629	1697	1278	1004	554	461	–

of ligand through phenolic oxygen via deprotonation. Besides, the bands at 1647 cm^{-1} (azomethine C=N) shifted its position on complexation [18]. The $\nu(\text{N-H})$ and $\nu(\text{C=O})$ bands of the ligand at 3297 and 1729 cm^{-1} do not change their positions after complexation, indicating that ligand exists in keto form in free state as well as in all the complexes [19]. The coordination of water in VO(IV), Cr(III), Fe(III) and Zr(IV) complexes is indicated by the appearance of bands at $3453\text{--}3433$, $1534\text{--}1487$, $878\text{--}834$ and $787\text{--}741 \text{ cm}^{-1}$ assignable to $\gamma(\text{O-H})$, $\delta(\text{O-H})$, $\rho_r(\text{H}_2\text{O})$ and $\rho_w(\text{H}_2\text{O})$ mode, respectively [18, 20]. The coordination of the acetate group is confirmed due to the difference between the two bands ($\Delta\nu > 179 \text{ cm}^{-1}$) in Mn(III) complex, appeared at 1607 and 1428 cm^{-1} which are assignable to $\nu_{\text{asy}}(\text{OCO})$ and $\nu_{\text{sym}}(\text{OCO})$ modes. The spectra of VO(IV) and Zr(IV) complexes show new bands at around 973 and 1129 cm^{-1} , respectively, due to $\nu(\text{V=O})$ and $\nu(\text{ZrOH})$ vibrations. Also, the absence of a band at $850\text{--}950 \text{ cm}^{-1}$ in Zr(IV) complex due to $\nu(\text{Zr=O})$ stretch [21]. The MoO $_2$ (VI), UO $_2$ (VI), WO $_2$ (VI) complexes show new bands around 974 , 968 , 949 cm^{-1} due to $\nu_{\text{asym}}(\text{O=Mo=O})$, $\nu_{\text{asym}}(\text{O=U=O})$ and $\nu_{\text{asym}}(\text{O=W=O})$ vibrations [21–24]. The WO $_2$ (VI) complex shows bands around 2082 (CN), 795 (CS) and 470 cm^{-1} (NCS) suggesting that the thiocyanate group act as ligand in which bonding through nitrogen takes place [25]. In addition to the above bands all the complexes display the new bands in the far-infrared region $554\text{--}507$ and $487\text{--}456 \text{ cm}^{-1}$ were assigned to $\nu(\text{M-O})$ and $\nu(\text{M-N})$ vibrations, respectively [26].

Electronic spectra and magnetic properties

The information about geometry of the coordination complexes is obtained from their electronic spectral data and magnetic moments, which are given in Table 3. The electronic spectrum of VO(IV) complex shows absorption bands at 852 , 537 and 386 nm corresponding to square pyramidal geometry [27], these bands may be assigned to $d_{xy}(b_2) \rightarrow d_{xy}d_{yz}(e^*)$, $d_{xy}(b_2) \rightarrow d_{x^2-y^2}(b_1^*)$ and $d_{xy}(b_2) \rightarrow$

$d_{z^2}(a_1^*)$ transitions, respectively. The magnetic moment of the VO(IV) complexes 1.64 B.M. which is located in the region of square pyramidal geometry. The Cr(III) complex shows absorption band at 620 , 476 and 289 nm due to ${}^4A_{2g}(\text{F}) \rightarrow {}^4T_{2g}(\text{F})$, ${}^4A_{2g}(\text{F}) \rightarrow {}^4T_{1g}(\text{F})$ and ${}^4A_{2g}(\text{F}) \rightarrow {}^4T_{1g}(\text{P})$, transitions indicating an octahedral geometry around the Cr(III) ion [28]. The Cr(III) complexes show magnetic moment to be very close to the spin only value for three unpaired electron (3.87 B.M.). The crystal field parameters for Cr(III) complexes are found to be $Dq = 1612.9 \text{ cm}^{-1}$, $B = 481 \text{ cm}^{-1}$, $\beta = 0.523$ and % covalency = 47.7 . The reduction of the Racah parameter (B) and the nephelauxetic ratio (β) from the value of free ion suggested appreciable amount of covalent character in the metal ligand bonds. The Mn(III) complex shows absorption bands at 754 , 612 , 507 and 360 nm due to ${}^5B_1 \rightarrow {}^5B_2$, ${}^5B_1 \rightarrow {}^5A_1$ and ${}^5B_1 \rightarrow {}^5E$ and LMCT transitions, corresponding to square pyramidal geometry of complex [29]. The measured magnetic moment for Mn(III) complex was found to be 4.75 B.M. The Fe(III) complex shows absorption band at 754 , 641 and 448 nm due to ${}^6A_{1g} \rightarrow {}^4T_{1g}$, ${}^6A_{1g} \rightarrow {}^4T_{2g}$ and ${}^6A_{1g} \rightarrow {}^4E_g$ transitions, respectively, towards octahedral geometry for the complex [30, 31] and the magnetic moment value found to be 5.83 B.M. with d^2sp^3 hybridization.

Electrical conductivity measurements

The solid state dc electrical conductivity was measured in the form of compressed pellet from room temperature to 403 K . The solid state dc electrical conductivity increases with increases in the temperature [32]. The electrical conductivity (σ) varies according to the relation $\sigma = \sigma_0 \exp(-E_a/kT)$ where σ_0 is a constant, E_a is the activation energy of electrical conduction, T is the absolute temperature and k is the Boltzmann constant. The solid state conductivity measurements show that the plot of $\log \sigma$ versus $1/T$ (Fig. 1) are linear over studied temperature ranged which indicates their semiconducting nature [33]. The value of electrical conductivity lies in the range

Table 3 Electronic and magnetic data of H₂L and its complexes

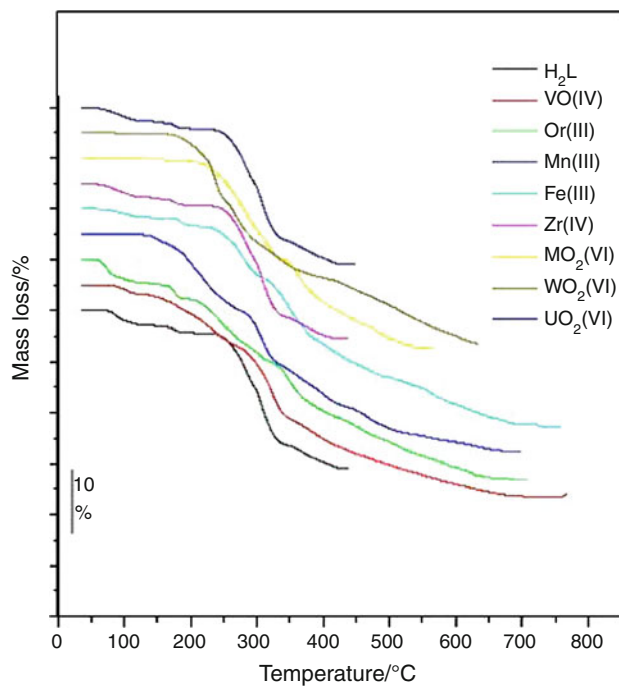
Sr. no.	Compound	μ_{eff} B.M.	Electronic spectra		
			Absorption band/nm	Absorption band/cm ⁻¹	Assignment
1	H ₂ L	–	–	–	–
2	[VO L] H ₂ O	1.64	852	11737	$d_{xy}(b_2) \rightarrow d_{xy} d_{yz}(e^*)$
			537	18622	$d_{xy}(b_2) \rightarrow d_{x^2-y^2}(b_1^*)$
			386	25907	$d_{xy}(b_2) \rightarrow d_{z^2}(a_1^*)$
3	[Cr L·H ₂ O·Cl]·H ₂ O	3.87	620	16129	${}^4A_{2g}(F) \rightarrow {}^4T_{2g}(F)$
			476	21008	${}^4A_{2g}(F) \rightarrow {}^4T_{1g}(F)$
			289	34602	${}^4A_{2g}(F) \rightarrow {}^4T_{1g}(P)$
			754	754	${}^5B_1 \rightarrow {}^5B_2$
4	[Mn L·OAc]	4.75	612	612	${}^5B_1 \rightarrow {}^5A_1$
			507	507	${}^5B_1 \rightarrow {}^5E$
			360	360	LMCT
			754	13263	${}^6A_{1g} \rightarrow {}^4T_{1g}$
5	[Fe L·H ₂ O·Cl]·H ₂ O	5.83	641	15601	${}^6A_{1g} \rightarrow {}^4T_{2g}$
			448	22321	${}^6A_{1g} \rightarrow {}^4E_g$
			–	–	–
6	[Zr L(OH) ₂ H ₂ O] H ₂ O	Diamagnetic	–	–	–
7	[MoO ₂ L]	Diamagnetic	–	–	–
8	[WO ₂ L·NCS]	Diamagnetic	–	–	–
9	[UO ₂ L]	Diamagnetic	–	–	–

1.07×10^{-12} to $4.47 \times 10^{-8} \Omega^{-1} \text{cm}^{-1}$ at 373 K. The conductivity of the free ligand (H₂L) is increased in complexing with metal ions.

Thermogravimetric analysis

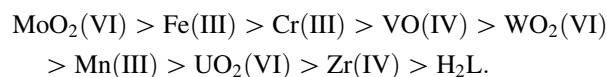
Thermogravimetric analyses for the complexes were performed from room temperature to 700 °C at a heating rate 10 °C min⁻¹ under a dynamic air atmosphere as shown in Fig. 2. In order to know the presence of water molecules and decomposition pattern of ligand, and its complexes TG analysis have been carried out.

The analysis of TG curves of H₂L and its metal complexes reveals that three stage decomposition pattern for Cr(III), Fe(III) and Zr(IV) complexes and two stage decomposition patterns for VO(IV), Mn(III), MoO₂(VI), WO₂(VI) and UO₂(VI) complexes. The TG curve of VO(IV), Cr(III), Fe(III) and Zr(IV) complexes show elimination of a water molecule takes place between 75 and 130 °C indicating the presence of lattice water molecule whereas Cr(III), Fe(III) and Zr(IV) complexes also eliminated in between 140 and 240 °C indicating the presence of these water as coordinated water molecule in the complexes [wt% loss, obs./calcd. VO(IV): 3.87/3.58; Cr(III): 3.59/3.32; Fe(III): 3.61/3.30 and Zr(IV): 3.45/3.10 for lattice water and Cr(III): 3.68/3.32; Fe(III): 3.72/3.30 and Zr(IV): 3.64/3.10 for coordinated water] [34]. The thermogram of Mn(III) complexes is almost stable up to

**Fig. 2** Thermograms of H₂L and its complexes

250 °C and then after shows gradual weight loss up to ~305 °C corresponding to loss of one acetate group [35]. MoO₂(VI) and UO₂(VI) complexes are almost stable up to 200 °C indicating that absence of any lattice or coordinated

water molecule [36]. The $\text{WO}_2(\text{VI})$ complex shows weight loss in the range 175–238 °C, which corresponds to loss of one thiocyanato group [37]. In complexes, a rapid weight loss has been observed between 280 and 410 °C due to quantitative elimination of ligand followed by a gradual weight loss up to 700 °C due to complete decomposition of coordinated ligand. Above 700 °C, nature of the curve is almost horizontal indicating the formation of corresponding metallic oxides. The thermal decomposition data of the compounds are given in Table 1. The half decomposition temperature of the compounds decreases in the order:



Powder XRD study

The X-ray diffractogram of $\text{VO}(\text{IV})$ complex exhibits sharp peaks indicating the crystalline nature of the complex. The peaks have been indexed using appropriate methodology and computer program (PowdMult, Version 2.3). The indexing is confirmed on the basis of correction obtained between observed and calculated values. The unit cell lattice parameters of $\text{VO}(\text{IV})$ complex are $a = 11.6164 \text{ \AA}$, $b = 12.7326 \text{ \AA}$, $c = 10.7906 \text{ \AA}$, $\alpha = 113.655^\circ$, $\beta = 105.0^\circ$, $\gamma = 101.950^\circ$, volume (V) = 1322.04 \AA^3 , therefore, system is triclinic.

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