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Microwave assisted synthesis and characterization of unsymmetrical tetradentate Schiff base complexes of VO(IV) and MoO(V)

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Microwave synthesis, is green chemical method, simple, sensitive, reducing solvent amount and reaction time. The attempt was made to synthesize the unsymmetrical tetradentate N_2O_2 ligands and their VO(IV) and MoO(V) unsymmetrical tetradentate Schiff base complexes by classical and microwave techniques using domestic microwave oven. The resulting unsymmetrical Schiff base ligands L^1–L^3 characterized by different spectral methods. Their complexes with oxocations of VO(IV) and MoO(V) have been synthesized and characterized by elemental analyses, conductometric measurements, infrared and electronic absorption, ^1H NMR spectra, mass spectrometry, ESR spectra, magnetic susceptibility measurement and thermal study. The study suggests that the oxo metal ion is bonded to the ligand through the oxygen and imino nitrogen and the geometry around metal ion is distorted octahedral.

1. Introduction

Unsymmetrical Schiff base complexes have been applied as redox catalyst in some organic reactions [1], their use as ligands in metal complexation [2–5]. These metalloenzymes facilitate a variety of reactions, including redox reaction (carried out by oxidases and oxygenases), acid-catalyzed hydrolysis (hydrolases), and rearrangement of carbon–carbon bonds (synthases and isomerases) [6,7]. Schiff-base complexes of transition metal ions display biological activities such as treatment of cancer, fungicides, viracides, bactericides, and function as catalysts in industrial processes [8–12].

The coordination chemistry and reactivity of vanadium have continued to play a significant role not only because of the physiological relevance of the metal but also for its activity in various industrial processes. Most oxo-vanadium(IV) complexes with a tetradentate Schiff-base ligand like salen have green monomeric structures with square-pyramidal coordination geometry. However, orange polynuclear linear chain structures have been observed for the six-member N–N chelating ring for vanadyl Schiff-base complexes [13,14], especially for Schiff-base ligands with electron-withdrawing substituents [15]. Interest in the chemistry of metallacyclic oxomolybdenum(V) and (VI) complexes grows continuously, particularly due to their potential relevance as model systems for molybdenum enzymes [16]. In a number of enzymatic systems, molybdenum is believed to be associated with flavins and amino acid residues [17]. Microwave assisted reactions in solvent or solvent-free conditions have gained popularity because of rapid reaction rate, cleaner reactions, easy of manipulation, higher yields, often improved selectivity with respect to conventional reaction conditions [18]. Microwave assisted reactions used the formation of trinuclear cluster $[Ni_3(mimp)_5(CH_3CN)]ClO_4$, Co(II) cluster, $[M_7(OH)_6(mimmp)_6]X_2$ ($M = Zn$, $X = NO_3^-$; $M = Mn$, $X = ClO_4^-$), $[Ni(immp)_2]\cdot(H_2O)_2]$ (mimmp = anion of 2-methoxy-6-methyliminomethyl-phenolic; imp = anion of 2-iminomethyl-6-methoxyphenolic) [18]. The microwave heating is a new and extremely attractive method for synthesizing polymetallic clusters of paramagnetic transition metal ions [18].

Induced organic reaction enhancement (MORE) chemistry techniques are lowered energy consumption compared to conventional reactions performed under reflux, which also require the latent heat of vaporization. A major advantage is given by the usual reaction time which is a few minutes even on a few hundred grams scale. The reduction of solvents and formation of lowered amounts of by-products decrease pollution at the source and ensure high levels of "atomic economy". The present study investigates reaction of unsymmetrical tetradentate Schiff base and their metal complexes synthesized by classical and microwave technology. In our continuation of the work on pyrazolones ligands [19], an attempt has been made to synthesize, characterize and find their thermal behavior of novel unsymmetrical Schiff base complexes of oxocations such as VO(IV) and Mo(V) by both methods and to indicate in which by microwave process the yield is better.

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2. Experimental

2.1. Materials

For the synthesis of unsymmetrical tetradentate Schiff base ligands and their metal complexes, solvents like methanol, petroleum ether, N,N-dimethyl formamide (AR grade) were used. Dehydroacetic acid (DHA) (Merk), primary aromatic diamines viz: o-phenylene diamines (Atul Ltd.), 1-phenyl-3-methyl-5-pyrazolone, 1(2-chloro)-1-phenyl-3-methyl-5-pyrazolone and 1(3-sulfoamido)-1-phenyl-3-methyl-5- pyrazolone (Nutan Dye Chem., G.I.D.C., Sachin) were used. The metal salt like $VOSO_4 \cdot 5H_2O$ (National chemicals) and $MoCl_5$ (Aldrich, U.S.A.) were used as received.

2.2. Instruments

Microwave assisted condensation of Schiff base and their complexes were carried out in a domestic oven, 2450 MHz frequency, 800 W. The elemental analyses (C,H,N) were performed at RSIC, Lucknow. The vanadium metal was estimated by gravimetrically as V_2O_5. A 100 mg sample of VO(IV) complexes were placed in a silica crucible, decomposed by gentle heating and then treated with 2–3 ml of nitric acid, 2–3 times and igniting at 600 °C. Orange colored residues of V_2O_5 were obtained after decomposition and complete drying and weighing [20]. Similarly, molybdenum was also estimated by gravimetrically as MoO_3, yellowish white colored residues of MoO_3 were obtained after decomposition and complete drying and weighing [21]. The conductance of oxo cations complexes were carried out on the Equip-Tronics conductivity meter, model No. EQ-664 with range 20 $\mu\Omega$ to 20 mΩ at 306 K temperature. The IR spectra of the unsymmetrical Schiff base ligands and their complexes were recorded at Centre of Excellence, Quality Testing Facility & R&D Centre, GIDC, Vapi with a Perkin Elmer Spectrum-BX, IR spectrophotometer (4000–450 cm^{-1}) using KBr discs. The electronic spectra of complexes in the 200–800 nm were obtained in DMSO as a solvent on a SHIMADZU UV 160 A using quartz cell of 1 cm optical path. The magnetic measurement of metal complexes at room temperature was carried out on Gouy balance as per the method suggested by Prasad and coworkers [22] at M.S. University of Baroda, Vadodara. The mass spectra of VO(IV) and MoO(V) complexes were recorded by Electro impact mass spectrometer (GC–MS). The mass spectra were recorded at SAIF, Punjab University, Chandigarh. The ESR spectra of all VO(IV) and MoO(V) complexes were recorded by SAIF, IIT, Mumbai, at RT and LNT for polycrystalline state. TGA and DTG were performed on an Al_2O_3 crucible and samples under investigation decomposed in the N_2 atmosphere at a heating rate 10 °C/min at SAIF, Indian Institute of Technology, Madras, Chennai.

2.3. Synthesis of ligands: (I), (II) and (III)

The ligands (I), (II) and (III) were prepared by condensation of 1-(2-chloro)-phenyl-3-methyl-5-pyrazolone (10.4 g, 0.05 mol), 1-(3-chloro)-phenyl-3-methyl-5-pyrazolone (10.4 g, 0.05 mol) and 1-(3-sulfoamido)-1 phenyl-3-methyl-5- pyrazolone (12.6 g, 0.05 mol) dissolved in DMF (10 ml, 0.05 mol), then cooled to 0 °C in an ice bath. The phosphoryl chloride (5.5 ml, 0.06 mol) was added drop wise at a rate to maintain the temperature between 10 and 20 °C. After the addition was completed, the reaction mixture was heated for 2.5 h for (I) ligand and 3.5–4 h for (II) and (III) ligands, then poured into 1 l ice water in beaker. The resulting mixture was allowed to stand overnight; it was collected by filtration, washed with water, and dried. Recrystallization was done from ethanol.

2.4. Synthesis of unsymmetrical tetradentate Schiff base ligand L^1 to L^3

2.4.1. Classical method

2-Aminomono Schiff base ligand (3-[(1-E)-N-(2-aminophenyl) ethanimidoyl]-4-hydroxy-6-methyl-2H-pyran-2-one) is synthesized by refluxing of an equimolar mixture of dehydroacetic acid (DHA) and aromatic diamines in dry ethanol. The dehydroacetic acid (0.1 mol, 16.8 g) and o-phenylene diamine (10.8 g) dissolved in (100 ml) dry methanol in a round bottom flask and add to it one to two drops of concentrated sulphuric acid. The contents of the flask were refluxed for about 2 h. Then it was cooled, up to room temperature. On cooling, the solid Schiff base that separated out was filtered and washed with methanol. The Schiff base was further purified by recrystallization from dry methanol and dried.

0.01 mol of 2-amino mono Schiff base ligand dissolved in N,N-dimethyl formamide in round bottom flask. 0.01 mol of each ligands (I), (II) and (III) also dissolved in N,N-dimethyl formamide, and then added gradually into the round bottom flask in which previously containing the mono Schiff base. After the addition of ligands (I), (II) and (III), respectively, was completed, the reaction mixture was refluxed on water bath for 3–4 h, and then poured into 1 l ice water in beaker. Brown colored precipitate of unsymmetrical tetradentate Schiff base ligands obtained. The resulting mixture was allowed to stand overnight. It was collected by filtration, washed with distilled water and petroleum ether, and dried.

2.4.2. Microwave method

2-Amino mono Schiff base ligand was synthesized by ethanolic mixture of DHA (0.1 mol) and aromatic diamines (0.1 mol) were placed in a flask and irradiated in a microwave oven for 30 s at 800 W. Completion of the reaction was monitored by TLC. The reaction mixture was allowed to attain RT. The solid mass obtained and recrystallized from methanol.

0.01 mol of 2-amiono mono Schiff base ligand and each pyrazolone ligands (I), (II) and (III) dissolved in DMF in a flask. The resulting mixture was irradiated in a microwave oven for 1 min at 800 W. The solid mass separated was poured into 1 l ice water in beaker. Brown colored precipitate of unsymmetrical tetradentate Schiff base ligands obtained. The resulting mixture was allowed to stand overnight. It was collected by filtration, washed with distilled water and petroleum ether, and dried.

2.5. Synthesis of unsymmetrical tetradentate Schiff base metal complexes of VO(IV) and Mo(V)

2.5.1. Classical method

(A) *VO(IV) complexes*: 0.01 mol of each ligand in slight excess was taken in round bottom flask containing 30 ml of dimethyl formamide and dissolved completely. A solution of 0.01 mol of $VOSO_4 \cdot 5H_2O$ in 20 ml of DMF was then added drop wise to the solution of the ligand. The contents were refluxed for 2–3 h. Then the resulting solution was poured on ice cold distilled water. The precipitates were digested for 1 h. The solid metal complex separated out and filtered in hot condition. The complexes washed with petroleum ether and dried.

(B) *MoO(V) complexes*: In a flat bottom flask 0.01 mol of each ligand in slight excess was dissolved in a mixed solvents of chloroform (15 ml) + methanol (15 ml). The solution was stirred on magnetic stirrer for few minutes for dissolution of ligand. A solution of 0.01 mol $MoCl_5$ in 20 ml of methanol was added drop wise to the solution of ligand. The pH of resulting mixture was adjusted to 6 with NaOAc buffer and stirred for 8–10 h and checked the pH of the solution. The solid mass was separated. The precipitate was filtered, washed with methanol and petroleum ether

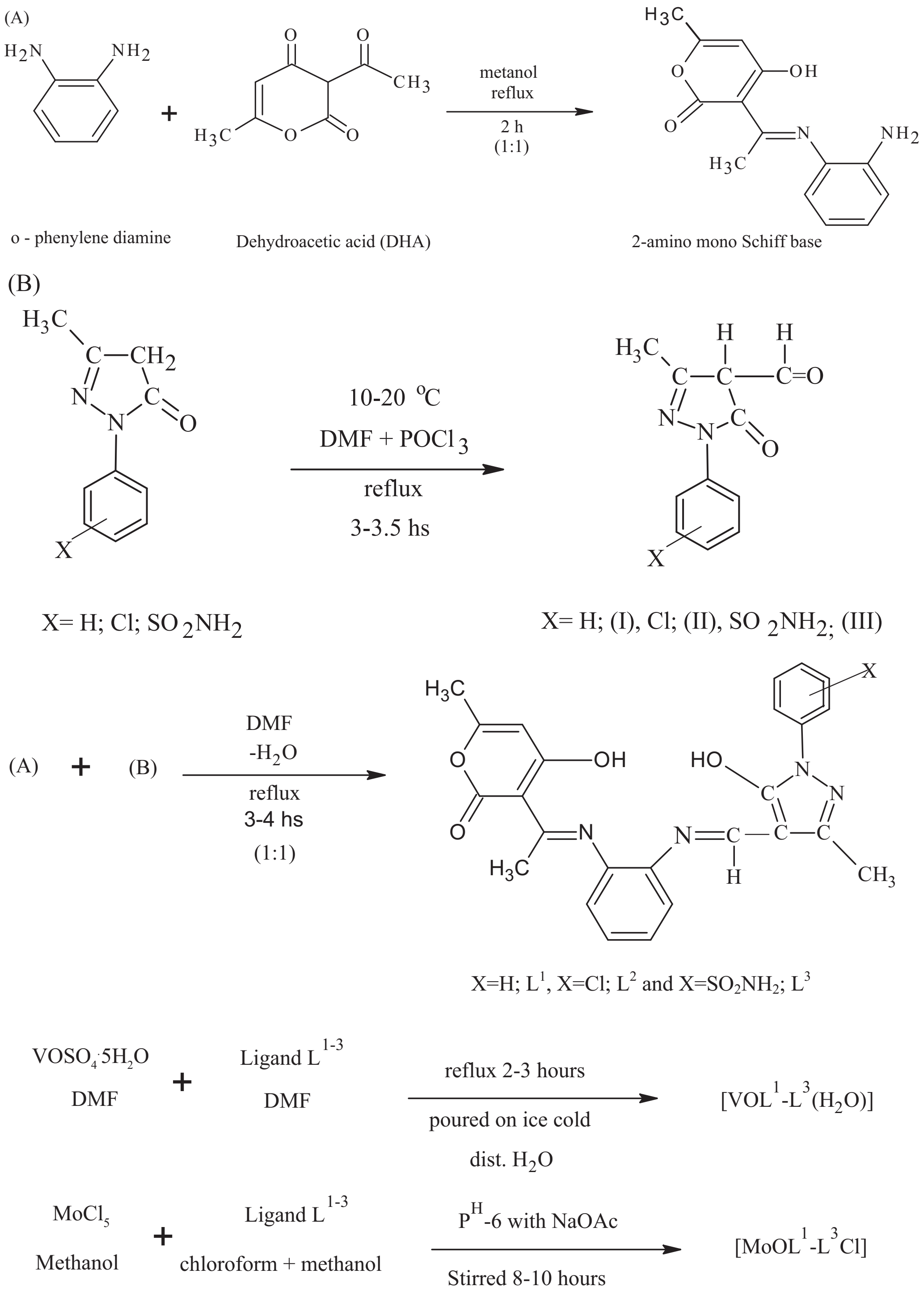


Fig. 1. Synthetic pathway of unsymmetrical tetradentate Schiff base complexes of VO(IV) and MoO (V).

successively and dried. Synthetic rout to unsymmetrical TSB complexes of VO(IV) and MoO(V) is shown in Fig. 1.

2.5.2. Microwave method

An equi molar solution of unsymmetrical tetradentate Schiff base ligands L^1–L^3 in DMF were added to a DMF solution of $VOSO_4{\cdot}5H_2O$ or methanolic solution of $MoCl_5$ in a flask. The resulting mixture was irradiated in microwave oven for 1 min at 800 W in both cases. The reaction mixture was kept at room temperature for few minutes. Thus, solid colored compound obtained, was filtered, washed thoroughly with methanol and petroleum ether and dried.

3. Result and discussion

Physical data and elemental analysis of unsymmetrical tetradentate ligands L^1–L^3 and their metal complexes are shown in Table 1. The elemental analyses are also in good agreement with expected stoichiometry of complexes which indicate that the metal to ligand ratio in all VO(IV) and Mo(V) complexes is 1:1. It is clear from the yield comparison plot shown in Fig. 2 of classical and microwave assisted (MWI) synthesis of the unsymmetrical tetradentate Schiff base and their metal complexes that MWI is easier, convenient

Table 1
Elemental analysis, molar conductivity and μ_{eff} physical data of unsymmetrical tetradentate Schiff base ligand and their metal complexes.

Compounds	Elemental analysis found % (calculated %)				Molar conductivity (ohm^{-1} cm^2 mol^{-1})	μ_{eff} (B.M.)
	C	H	N	M		
L^1	68.01(67.71)	5.20(5.01)	12.75(12.66)	–	–	–
L^2	63.16(62.96)	4.25(4.43)	11.86(11.74)	–	–	–
L^3	57.85(57.57)	4.60(4.44)	13.67(13.42)	–	–	–
$[VOL^1(H_2O)]$	57.26(57.15)	4.44(4.22)	10.89(10.66)	9.89(9.69)	0.24	1.76
$[VOL^2(H_2O)]$	53.78(53.53)	3.88(3.78)	17.21(17.14)	9.21(9.09)	0.96	1.76
$[VOL^3(H_2O)]$	49.91(49.67)	4.10(3.83)	11.68(11.58)	8.69(8.42)	1.16	1.77
$[MoOL^1Cl]$	45.15(45.02)	3.38(3.17)	10.62(10.50)	14.45(14.38)	0.85	1.71
$[MoOL^2Cl]$	48.46(48.25)	3.28(3.07)	9.14(9.00)	15.49(15.41)	1.16	1.71
$[MoOL^3Cl]$	51.32(51.10)	3.63(3.42)	9.64(9.53)	16.45(16.32)	1.47	1.69

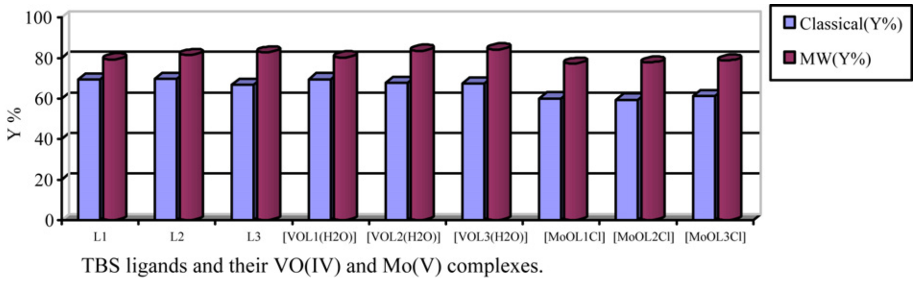


Fig. 2. Graphical representation of yield comparison between classical and microwave irradiations.

and yields of all products are better than classical method (Table 2).

3.1. Molar conductance

The molar conductance of the VO(IV) and Mo(V) complexes (Table 1) in 10^{-3} M in DMSO as solvent observed in the range 1.47–0.24 and 1.47–0.85 ohm^{-1} cm^2 mol^{-1}, respectively. The low conductivity values in DMSO reveal that all complexes are non-electrolytic in nature and there is no counter ion present outside the coordination sphere of oxocations complexes [23].

3.2. FT-IR spectra of unsymmetrical tetradentate Schiff base ligands

The broad band appeared at 3464–3220 cm^{-1} due to the intra molecular hydrogen bonding (O–H···N) present in TSB ligand L^1 to L^3 [24,25]. But in the IR spectra of L^3 ligand we observed new bands at 3356 cm^{-1} (N–H asymm.) and 3220 cm^{-1} (N–H symm.) of $-SO_2NH_2$ group of pyrazolone [26]. The lactone C═O band observed at 1710–1697 cm^{-1} [25]. The medium strong intensity band observed at 1632–1660 cm^{-1} in IR of ligands are assigned to azomethine C═N stretching vibrations [27–29]. The strong medium intensity bands appeared at 1569–1571 cm^{-1}, due to C═C aromatic ring stretching vibrations. The IR spectral band due to enolic C–O stretching vibrational mode is expected to appear around 1200 cm^{-1} [30]. A weak to strong intensity bands observed at 1250–1206 cm^{-1} is assigned to enolic C–O stretching vibrational mode (Table 3).

3.3. ^{1}H NMR spectra of unsymmetrical tetradentate Schiff base ligands

The chemical shift observed at δ 2.16–2.17 and δ 2.28–2.40 for the $-CH_3$ proton of three position of pyrazolone ring and DHA moiety, respectively. The base value for chemical shift of $-CH_3$ protons of azomethine carbon is δ 2. But the aromatic ring is bonded to nitrogen and π electron cloud of aromatic ring may dishield the methyl proton and thus δ value is shifted towards downfield to 2.63–2.66 [26]. Quartets signals are observed at δ 5.22–5.25 (ligands-$L^1$and L^2) and δ 6.72–6.76 (ligand-L^3) due to the coupling of C_5 proton of DHA with C_6 methyl protons of DHA moiety. A signal observed at δ 5.62–5.75 is due to –OH proton of pyrazolone ring. The H of C_3 of DHA is expected to resonate at δ 2.1 [20,21]. However, dehydroacetic acid exists in solution as a completely enolized species as the acidic hydrogen at C_3 being alpha to carbonyl groups and resonate at δ 15.35–15.65, which is the chemical shift of enolic –OH involved in hydrogen bonding with azomethine group. This enolic hydrogen undergoes tautomerism to form –NH shown in Fig. 3 and the signals are shifted at δ 7.98 and 8.50 [22] (Table 4).

Table 2
Physical properties of unsymmetrical tetradentate Schiff base ligand and their metal complexes.

Compounds	Color	Melting point (°C)	Microwave method		Classical method	
			Reaction time (s)	Yield (%)	Reaction time (h)	Yield (%)
L^1	Dark brown	69	60	79.35	3	69.30
L^2	Dark brown	65	60	81.47	3	69.74
L^3	Brown	130	60	82.79	4	66.79
$[VOL^1(H_2O)]$	Greenish brown	>250	60	80.32	2	69.52
$[VOL^2(H_2O)]$	Greenish brown	>250	60	83.63	2	67.79
$[VOL^3(H_2O)]$	Greenish brown	>250	60	84.21	3	67.50
$[MoOL^1Cl]$	Brown	>250	60	77.29	8	60.07
$[MoOL^2Cl]$	Brown	>250	60	77.80	9	59.42
$[MoOL^3Cl]$	Brown	>250	60	78.79	10	61.18

Table 3
FT-IR spectral data of unsymmetrical tetradentate Schiff base ligand and their metal complexes.

Functional group and IR frequencies (cm^{-1})									
Compounds	v(OH) of (H_2O) coord.	v(O–H–N)	v(C=O) lactone	v(C=N) free azomethine	v(C=N) after coord.	v(C–O) coord.	v(M=O)	v(M–O) str.	v(M–N) str.
L^1		3220	1700	1654					
L^2	–	3225	1710	1660	–	–	–	–	–
L^3	–	3464	1697	1632	–	–	–	–	–
$[VOL^1(H_2O)]$	3418	–	1715	–	1621	1290	969	502	478
$[VOL^2(H_2O)]$	3429	–	1716	–	1629	1267	972	512	482
$[VOL^3(H_2O)]$	3422	–	1726	–	1612	1236	975	514	485
$[MoOL^1Cl]$	–	–	1705	–	1630	1248	916	504	476
$[MoOL^2Cl]$	–	–	1704	–	1629	1246	918	501	472
$[MoOL^3Cl]$	–	–	1700	–	1611	1243	919	502	474

Table 4
^1H NMR spectral data of unsymmetrical tetradentate Schiff base ligand and their metal complexes.

Functional group and chemical shifts δ in ppm									
Compounds	$-CH_3$ pyrazolone	C_6-CH_3 DHA	$-CH_3$ bonded to C=N	C_5-DHA	–OH pyrazolone	Phenyl proton pyrazolone	Phenyl proton o-phenylene diamine	–CHO	–OH DHA (hump)
L^1	2.16	2.28–2.39	2.53–2.63	5.22–5.25	5.26	6.70–7.16	7.29–7.54	7.89	15.65
L^2	2.16	2.29–2.40	2.55–2.65	5.22–5.25	5.29	6.71–7.19	7.30–7.58	7.91	15.70
L^3	2.17	2.29–2.40	2.53–2.66	6.72–6.76	5.75	6.72–6.76	7.33–8.18	8.47	15.35
$[VOL^1(H_2O)]$	2.14	2.29–2.45	2.52–2.96	5.22	–	6.60–7.20	7.31–7.89	7.97	–
$[VOL^3(H_2O)]$	2.15	2.31–2.47	2.55–2.86	5.19	–	6.68–7.22	7.35–7.92	8.01	–
$[MoOL^1Cl]$	2.10	2.39–2.40	2.48–2.57	5.75	–	6.67–7.60	7.70–8.19	7.98	–
$[MoOL^3Cl]$	2.16	2.40–2.41	2.51–2.59	5.70	–	6.68–7.61	7.73–8.20	8.46	–

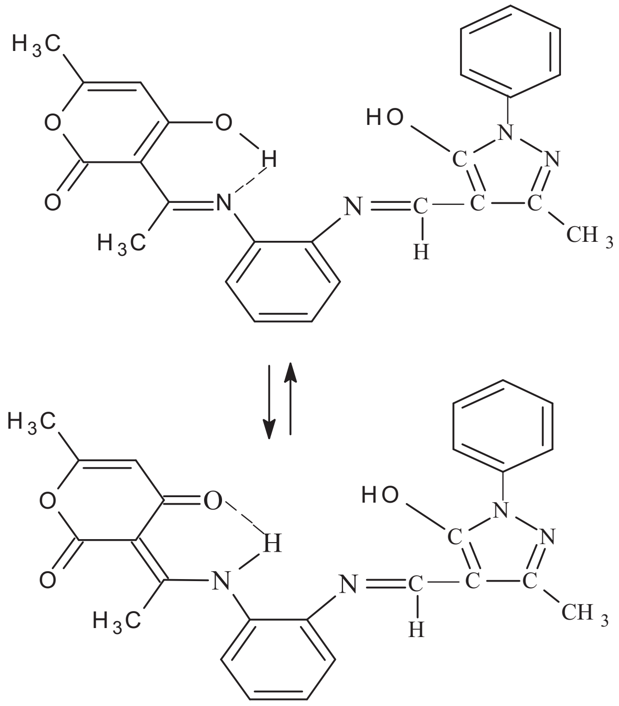


Fig. 3. Tautomerism form in unsymmetrical tetradentate ligands.

3.4. *Mass spectra of unsymmetrical tetradentate L[1]*

The molecular mass spectra of ligand L^1 is depicted in Fig. 4, which shows molecular ion peak at $m/z = 443.6$ $(M+1)^+$ which is also in agreement with molecular mass of the ligand L^1 ($C_{25}H_{22}O_4N_4 = 442.45$).

3.5. *FT-IR spectra of unsymmetrical tetradentate Schiff base complexes*

Some of the important applications of IR spectroscopy are the identification of major types of bonds, various functional groups and hydrogen bonding in metal complexes. One of the best features of IR spectroscopy in qualitative analysis is that, the absorption or lack of absorption in the specific frequency region can be corrected with specific stretching and bending modes and in some cases, with the relationship of these groups to rest of the molecule.

The broad band centred at ~3400 cm^{-1} due to v(O–H) of coordinated water molecule present in vanadium complexes. The sharp bands observed in the region 1612–1630 cm^{-1} were assigned to

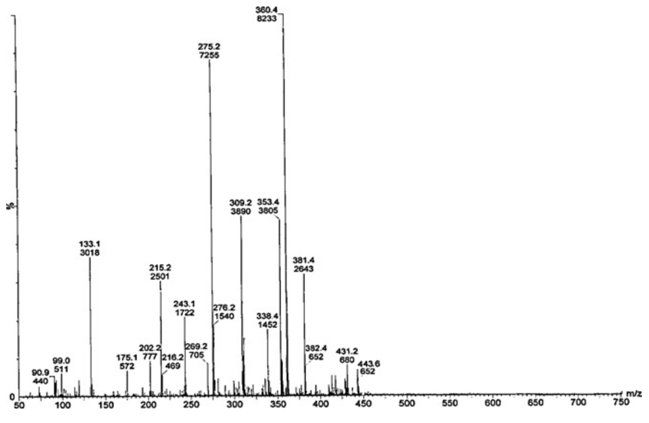


Fig. 4. Mass spectra of ligand L^1.

Table 5
Electronic spectral data of unsymmetrical tetradentate Schiff base ligand and their metal complexes.

Complexes	d–d transition (cm^{-1})			Charge transfer band (cm^{-1})			d–d transition (cm^{-1})		
	$d_{xy} \rightarrow d_{xy},d_{yz}$ (υ_1)	$d_{xy} \rightarrow d_{x^2-y^2}$ (υ_2)	$d_{xy} \rightarrow d_{z^2}$ (υ_3)				$^2B_2 \rightarrow {}^2E$	$^2B_2 \rightarrow {}^2B_1$	$^2B_2 \rightarrow {}^2A_1$ O(π) → d(Mo)
[$VOL^1(H_2O)$]	12,903	14,326	23,529	26,455	28,985	33,783			
[$VOL^2(H_2O)$]	13,037	14,492	17,853	26,315	28,901	35,971	–	–	–
[$VOL^3(H_2O)$]	13,020	14,556	17,953	23,923	28,409	35,460	–	–	–
[$MoOL^1Cl$]	–	–	–	29,069	31,446	33,444	14,388	17,513	26,737
[$MoOL^2Cl$]	–	–	–	28,901	30,769	32,467	14,064	18,315	27,173
[$MoOL^3Cl$]			–	28,725	30,303	32,051	13,888	16,750	26,525

C=N stretching vibrational mode. In the corresponding free TSB ligands the frequencies for C=N group are observed between 1632 and 1660 cm^{-1}. A downward shift of the band by 20–33 cm^{-1} in complexes indicate that the C=N group of the ligands is coordinated to the metal ion via its azomethine nitrogen [31,32]. This lowering may be due to reduction in electron density in the azomethine link as the nitrogen coordinates to the metal ion. The medium to strong bands observed at 1236–1290 cm^{-1} appeared in the spectra of complexes were assigned to enolic C–O stretching vibrations. The observed higher C–O frequency in metal complexes may be ascribed to delocalization σ-electron density from the oxygen to metal ion, resulting in an increase in electro negativity of oxygen atom. This will lead to greater ionic character of bond and consequently increase in C–O vibration frequency on metal complexation [32].

3.6. ^{1}H NMR spectra of unsymmetrical tetradentate Schiff base complexes

The very low intense singlet observed at δ 5.19–5.22 and 5.70–5.75 due to the C$_5$ -proton of DHA moiety. The disappearance of peaks –OH (hump) in the spectra of the complexes, which indicates that coordination occur through the ketonic oxygen atom of the –OH group (after enolization). One more signal observed near downfield region at δ 5.57 and δ 5.90 due to water molecule proton, indicating the presence of H_2O molecule in VO(IV) complexes. The multiplet signals observed at δ 6.60–7.61 and at δ 7.31–8.20 due to the aromatic protons of phenyl ring of pyrazolone moiety and o-phenylene diamines, respectively. In the spectra of the [VOL^3 H_2O] and [MOL^{3}Cl] complexes we observed a signal at δ 8.47 and δ 8.55 due to the proton of –SO_2NH_2 group substituted of phenyl pyrazolone.

3.7. UV/visible spectra of unsymmetrical tetradentate Schiff base complexes

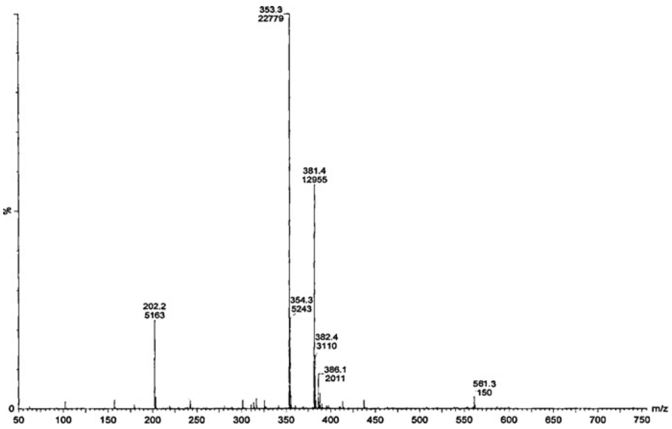
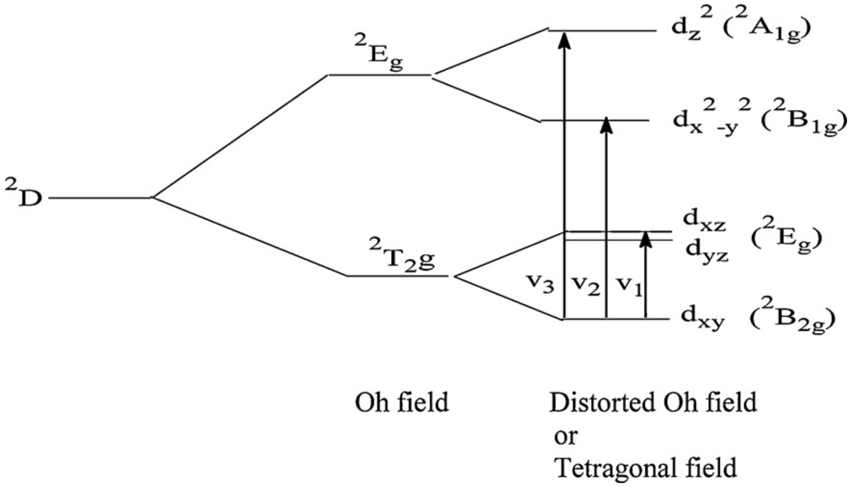


Fig. 5. The mass spectra of [VOL^2(H_2O)] complex.

The electronic spectra of oxovanadium (IV) complexes show intense band at 26,455–23,923 cm^{-1}, 28,945–28,409 cm^{-1} and 33,783–35,971 cm^{-1}, respectively, assigned to either a metal–ligand charge transfer band or to an electronic transition within the ligand [33,34]. In the visible region, the solution electronic spectra of VO(IV) Schiff base compounds exhibit three d–d bands in the region 23,529–12,903 cm^{-1}. These bands may be assigned to the following transitions. The electronic data of oxo complexes presented in Table 5.

$$v_1 \rightarrow {}^2B_{2g} \rightarrow {}^2E_g$$
$$v_2 \rightarrow {}^2B_{2g} \rightarrow {}^2B_{1g}$$
$$v_3 \rightarrow {}^2B_{2g} \rightarrow {}^1A_{1g}$$



Above transition have major contribution for distorted O$_h$ geometry of oxovanadium(IV) complexes, which is supported by the reported literature [35]. In addition, it also shows a high energy band above 30,000 cm^{-1}, which may be due to the first spin forbidden charge transfer transition [36]. The electronic absorption spectra of [MoOL^{1}Cl]–[MoOL^{3}Cl] complexes, we observed the high energy bands (in UV region or near UV region) observed at 33,444 cm^{-1}, 32,467 cm^{-1} and 32,501 cm^{-1} due to $n \rightarrow \pi^*$ or $\pi \rightarrow \pi^*$ transitions. In the visible region two bands observed with low intensity in the range 14,388–13,888 cm^{-1} and 18,315–16,750 cm^{-1} due to d–d band and this may be assigned to $^2B_{2g} \rightarrow {}^2E_g$ (υ_1) and $^2B_{2g} \rightarrow {}^2B_{1g}$ (υ_2), respectively. Thus, electronic spectra of these compounds indicate octahedral environment for all the complexes and are in conformity with an distorted octahedral geometry [37].

3.8. Mass spectra of unsymmetrical tetradentate Schiff base complexes

The mass spectrum of [VOL^2 (H_2O)] complex is shown in Fig. 5, which also gives molecular ion peak at m/z = 561.3 (M+2)$^+$, which are in agreement with molecular mass of the [VOL^2(H$_2$O)] (VC$_{25}$H$_{21}$O$_6$N$_4$Cl = 559.82) complex. The mass spectrum of [MoOL^{3}Cl] complex is shown in Fig. 6, which also gives molecular ion peak at m/z = 667.1 (M+1)$^+$, which is also in agreement with molecular mass of the [MoOL^{3}Cl] (MoC$_{25}$H$_{21}$O$_7$N$_5$Cl$_2$S = 666.87) complex.

3.9. Magnetic susceptibility

The magnetic susceptibility measurement of unsymmetrical tetradentate complexes of VO(IV) and MoO(V) complexes were carried out by Gouy method at room temperature. The observed magnetic moment (μ_{eff}) values is in the range 1.77–1.76 B.M., indicating the VO(IV) compounds are normal paramagnetic having one unpaired electron s = 1/2. There is no reduced magnetic moment, ruling out any anti ferromagnetic interaction present in the molecules [35]. Therefore, VO(IV) complexes are mono nuclear. MoO(V) are paramagnetic with effective magnetic moments in the range 1.69–1.71 B.M., with no significant magnetic interactions between the neighboring oxomolybdenum(V) ions, indicating mononuclear nature of unsymmetrical tetra dentate Schiff base

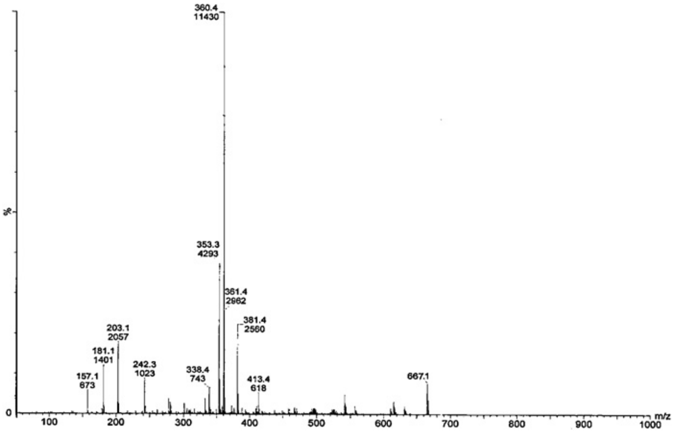


Fig. 6. The mass spectra of [MoOL^{3}Cl] complex.

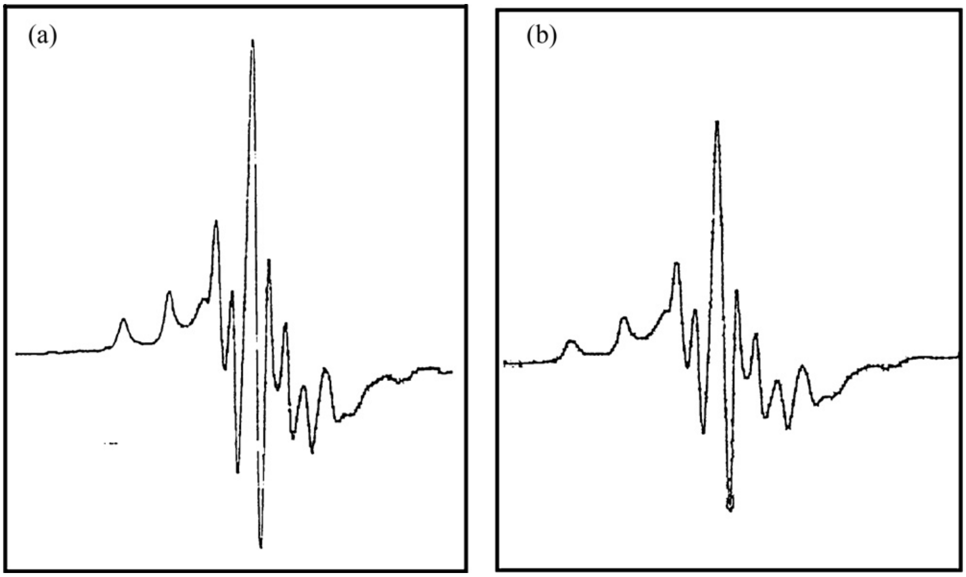


Fig. 7. The power ESR spectra of [VOL^1(H$_2$O)] complex at (a) RT and (b) LNT.

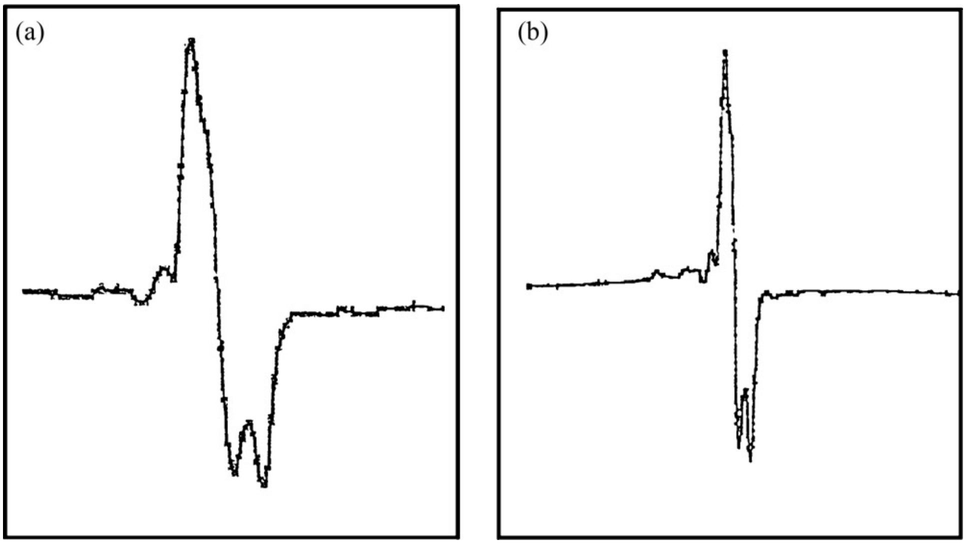


Fig. 8. The power ESR spectra of [MoOL^{3}Cl] complex at (a) RT and (b) LNT.

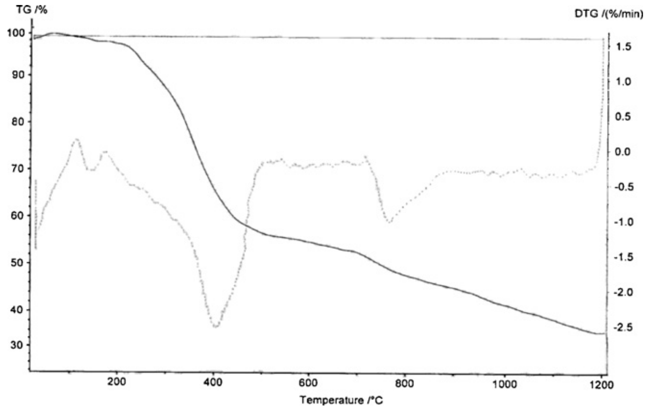


Fig. 9. TGA/DTG curve of [$VOL^1(H_2O)$] complex.

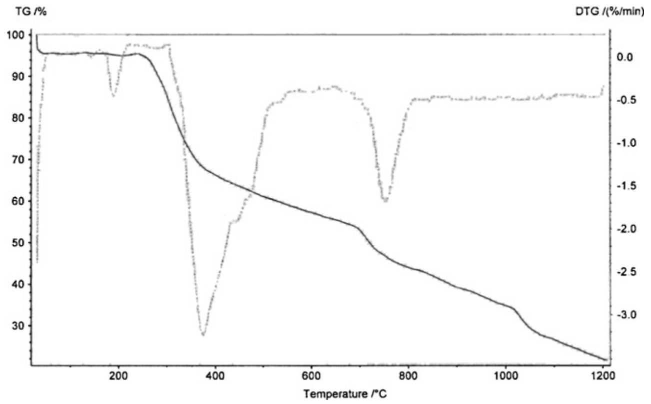


Fig. 11. TGA/DTG curve of [$MoOL^3Cl$] complex.

complexes [35]. The ESR spectral studies indicate that the all complexes are magnetically dilute in nature. The relevant data of magnetic moments are reported in Table 1.

3.10. *ESR spectra*

The RT and LNT ESR spectrum of [$VOL^1(H_2O)$] complex shows the typical eight line pattern indicating single vanadium is present in the molecules, i.e., it is a mononuclear. The $g_{||}$ and $g_{\perp}$ value were computed from the spectra using DPPH free radical as g marker. The observed $g_{||}, g_{\perp}, |g|$ $A_{||}, A_{\perp}$, and $|A|$ values are well in accordance with the complexes indicate that the unpaired electron localized in d_{xy} orbital [34–36] of a molecule which exists in distorted octahedral geometry [37–40]. The $g_{||} < g_{\perp}$ and $A_{||} > A_{\perp}$ relations are consistent with octahedral geometry in complexes with C_{4v} symmetry. The principal component of the g and A tensor were calculated from the observed spectra. $A_{||}$ $A_{\perp}$ and $|A|$ are the hyperfine coupling constants. The $g_{||}, g_{\perp}, A_{||}$ and $A_{\perp}$ were evaluated by using the expressions given in literature [41].

Table 6
g and A value of the powder ESR spectra [$VOL^1(H_2O)$] and [$MoOL^3Cl$] complexes at RT and LNT.

Complex	$g_{\|\|}$	$g_{\perp}$	$\|g\|$	Hyperfine contents × 10^{-4} cm^{-1}		
				$A_{\|\|}$	$A_{\perp}$	$\|A\|$
[$VOL^1(H_2O)$]						
RT	1.93	1.97	1.94	153.75	66.60	95.65
LNT	1.92	1.96	1.95	155.15	63.65	94.15
[$MoOL^3Cl$]						
RT	1.92	1.96	1.95	6.35	5.54	5.14
LNT	1.94	2.0	1.98	10.81	11.71	11.41

$|g| = 1/3(g_{||} + 2g_{\perp})$, $|A| = 1/3(A_{||} + 2A_{\perp})$.

The ESR spectra of [$MoOL^3Cl$] complex which was recorded in powder form at RT and LNT. The ESR spectra of [$MoOL^3Cl$] complex exhibited a six weak line in the powder form at room temperature. But [$MoOL^3Cl$] complex gave six intense and broad ESR lines at LNT, the intensity of these lines are very high. A typical six line pattern which shows that single molybdenum is present in the molecules, i.e., it is a mononuclear. The ESR parameters were found to be $g_{||} = 1.92–1.94$, $g_{\perp} = 1.96–2.0$ and $|g|$ or $g_{av} = 1.95–1.98$. An intensity point is that $g_{\perp} > g_{||}$ in most of MoO(V) unsymmetrical tetradentate Schiff base complexes [41]. The $A_{||}$ and $A_{\perp}$ value are 6.35×10^{-4} cm^{-1}–10.81×10^{-4} cm^{-1} and 5.54×10^{-4} cm^{-1}–11.71×10^{-4} cm^{-1}, respectively; these parameters are low because of the dipolar interactions of the unpaired electron in the $3p_z$ chlorine orbital should be near to zero [42]. The $g_{||}, g_{\perp}$ and $|g|$ value are well in accordance with the complexes indicates that the unpaired electron localized in the d_{xy} orbital [43,44] of a molecule which exists in distorted octahedral geometry. The ESR spectral data of [$VOL^1(H_2O)$] and [$MoOL^3Cl$] complexes are presented in Table 6 and their ESR spectra are given in Figs. 7 and 8, respectively.

3.11. *Thermal study*

From the TGA and DTG curves, it has been observed that there are main three steps in the decomposition of [$VOL^1(H_2O)$] complex. In complex, decomposition starts from 130 to 180 °C. The first mass loss 3.50% (3.42% cala.) up to 180 °C is in good agreement with loss of one coordinated water molecule. The second and third steps start from 340 to 480 °C and 720 to 900 °C, respectively, which is due to the pyrolysis of organic molecule into two steps. After 900 °C,

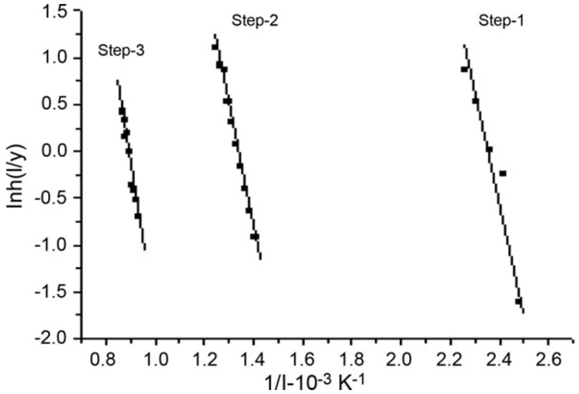


Fig. 10. Broido plots of [$VOL^1(H_2O)$] complex.

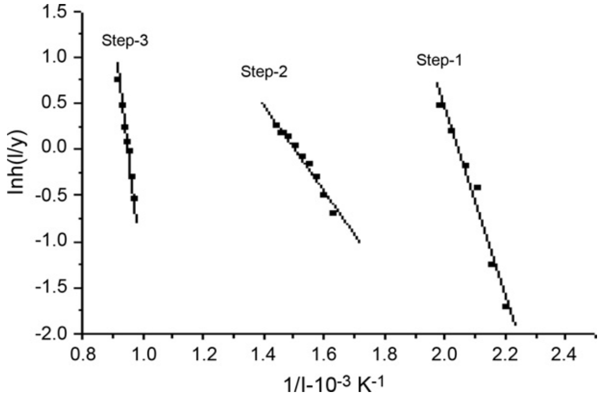
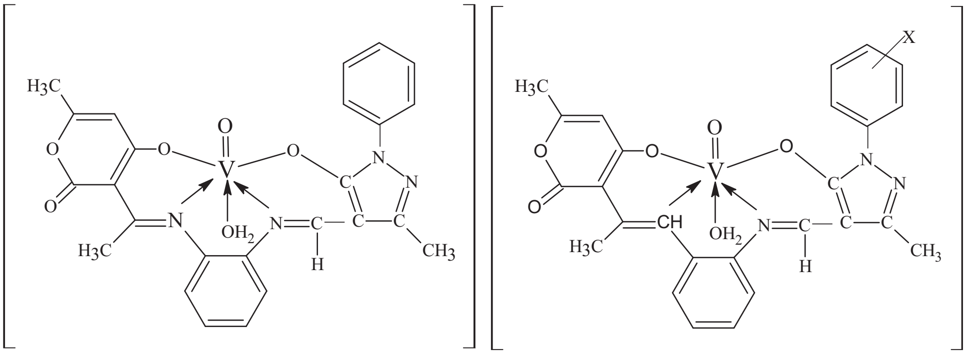


Fig. 12. Broido plots of [$MoOL^3Cl$] complex.

Table 7
Thermal behavior and thermodynamic parameters of [VOL^1(H$_2$O)] and [MoOL^{3}Cl] complexes.

Complexes	Step	Step analysis Temperature °C			ΔE^* kcal/mol	$C_s = W_s - W_f/W_0 - W_f$	Order of reaction
		T_i	T_{max}	T_f			
[VOL^1(H$_2$O)]	I	130	140	180	7.64	0.321	1
	II	340	405	480	5.60	0.430	3/2
	III	720	760	900	3.16	0.534	2
[MoOL^{3}Cl]	I	175	185	230	7.51	0.337	1
	II	305	375	520	7.08	0.398	1
	III	710	755	815	3.94	0.389	1

T_i, initial decomposition temperature.
T_{max}, temperature for maximum rate of decompositions.
T_f, final decomposition temperature.



Complex; [VOL^1(H$_2$O)]

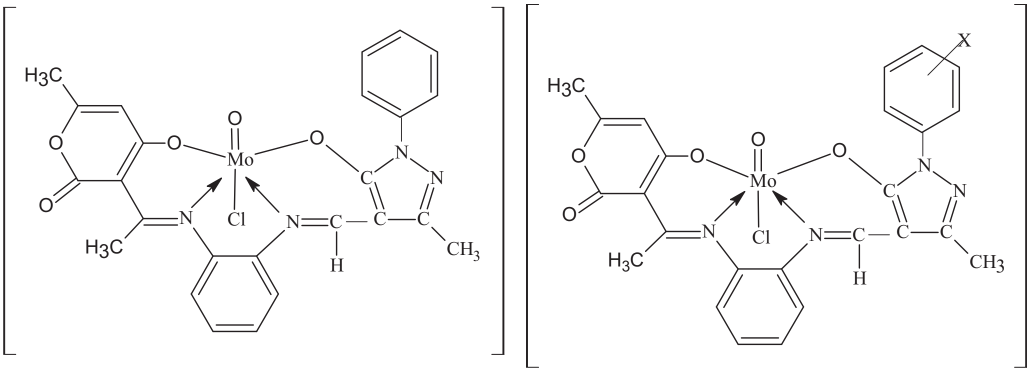
X=Cl; Complex; [VOL^2(H$_2$O)] and
X =SO$_2$NH$_2$; Complex; [VOL^3(H$_2$O)]

Fig. 13. Probable structures of unsymmetrical tetradentate Schiff base complexes of oxovanadium.

the stable metal oxide V_2O_5 was formed. The energy of activation E_a of thermal degradation of [VOL^1(H$_2$O)] is 7.64 kcal/mol in the N_2 for the first step and the corresponding values for the second and third steps are 5.60 and 3.16 kcal/mol, respectively. The thermal behavior and thermodynamic parameters presented in Table 7. The TGA/DTG curves of [VOL^1(H$_2$O)] complex of unsymmetrical tetradentate also shown in Fig. 9. The plot of lnln $(1/Y)$ vs $1/T$, results in straight line are shown in Fig. 10. From these plots we calculated the activation energy $\Delta E^*$and also calculated order of reaction.

From the TGA and DTG curves, it has been observed that there are also main three steps in the decomposition of [MoOL^{3}Cl] complex. In complex, decomposition starts from 175 to 230 °C. The first mass loss 5.40% (5.31% cala.) is due to the loss of one coordinated chlorine molecule, i.e., one chlorine atom coordinated with Mo(V) atom. The second step and third step start from 305 to 520 °C and 710 to 815 °C, respectively, which is due to the pyrolysis of organic molecule into two steps. After 850 °C, the stable metal oxide MoO_3 was formed. The thermal behavior and thermodynamic parameters presented in Table 7. The TGA/DTG curves of [MoOL^{3}Cl] complex of unsymmetrical tetradentate also shown in Fig. 11. The plot of lnln $(1/Y)$ vs $1/T$, results in straight line are shown in Fig. 12. From these plots we calculated the activation energy $\Delta E^*$and also calculated order of reaction.

Application of Broido's [45] method used to determine the kinetic parameter for complexes.



Complex; [MoOL^{1}Cl]

X=Cl; Complex; [MoOL^{2}Cl] and
X =SO$_2$NH$_2$; Complex; [MoOL^{3}Cl]

Fig. 14. Probable structures of unsymmetrical tetradentate Schiff base complexes of oxomolybdenum.

The Horowitz–Metzger equation [46,47]

$$C_s = n^{1/(1-n)},$$

$$C_s = \frac{W_s - W_f}{W_0 - W_f},$$

The above equation is used for the determination of the reaction order, where C_s is the mass fraction of the substance, W_s stands for the mass remaining at a given temperature, W_0 and W_f are the initial and final masses of the substance, respectively.

4. Conclusion

Microwave irradiation is becoming an increasingly popular method of heating, which replaces classical heating because it proves to be a clean and convenient method. It affords higher yields and results in shorter reaction times. In microwave synthesis the yield of all products are more than 75%. The reaction time is drastically reduced to 1 min instead of 2–10 h in the classical method. The IR and ^{1}H NMR spectral data suggest that the unsymmetrical tetradentate Schiff base ligands behave as O_2:N_2 donor sequence towards oxocations. The molar conductivity data show them to be non-electrolytes. From the magnetic measurement, electronic and ESR spectral data suggest that all the oxovanadium(IV) and oxomolybdenum(V) complexes have distorted octahedral geometry, shown in Figs. 13 and 14, respectively. The presence of one coordinated water molecule in the oxovanadium(IV) complexes is confirmed by thermal study such as TGA and DTG. Similarly, the presence of one coordinated chlorine atom in the unsymmetrical tetradentate Schiff base Mo(V)complexes is also confirmed by thermal study TGA and DTG.

References

[1] D.M. Boghaei, S.J.S. Sabouncheib, S. Rayatib, Synth. React. Inorg. Met. Org. Chem. 30 (8) (2000) 1535–1545.
[2] A.A. Osowole, G.A. Kolawole, O.E. Fagade, Synth. React. Inorg. Met. Org. Chem. 35 (2005) 829–836.
[3] D.M. Boghaei, S. Mohebi, J. Chem. Res. 2001 (2001) 224–226.
[4] M. Lashanizadegan, D.M. Boghaei, Synth. React. Inorg. Met. Org. Chem. 31 (2001) 1519–1529.
[5] R. Atkins, G.A. Brewer, E. Kokot, G.M. Mockler, E. Sinn, Inorg. Chem. 24 (1985) 127–134.
[6] I. Rousso, N. Friedman, M. Sheves, M. Ottolenghi, Biochemistry 34 (1995) 12035–12059.
[7] J.P. Costes, M.I. Fernandes-Garcia, Inorg. Chim. Acta 237 (1995) 57–63.
[8] P.E. Aranha, M.P. Do Santo, S. Romera, E.R. Dockal, Polyhedron 26 (2007) 1373–1382.
[9] Z. Afrasiabi, E. Sinn, J. Chen, Y. Ma, A.L. Rheingold, L.N. Zakharov, N. Rath, S. Padhye, Inorg. Chim. Acta 357 (2004) 271–278.
[10] D.C. Quenelle, K.A. Keith, E.R. Kern, Antiviral Res. 71 (2006) 24–30.
[11] H.A. Tang, L.F. Wang, R.D. Yang, Transit. Met. Chem. 28 (2003) 395–398.
[12] D.M. Boghaei, S. Mohebi, Tetrahedron 58 (2002) 5357–5366.
[13] A. Serrete, P.J. Carrol, T.M. Swager, J. Am. Chem. Soc. 114 (1992) 1887–1889.
[14] K. Nakajima, M. Kojima, S. Azuma, R. Kasahara, M. Tsuchimoto, Y. Kubozono, Y. Maeda, H. Kashino, S. Ohba, Y. Yoshikawa, J. Fojita, J. Bull. Chem. Soc. Jpn. 69 (1996) 3207–3216.
[15] M. Kojima, H. Taguchi, M. Tsuchimoto, K. Nakajima, Coord. Chem. Rev. 237 (2003) 183–196.
[16] P. Nag, R. Bohra, R.C. Mehrotra, R. Ratnani, Transit. Met. Chem. 27 (2002) 321–325.
[17] R.J. Butcher, B.R. Penfold, E. Sinn, J. Chem. Soc. Dalton Trans. (1979) 668–675.
[18] (a) S. Deshayes, M. Liagre, A. Loupy, J. Luche, A. Petit, Tetrahedron 55 (1999) 10851–10870;
(b) R.S. Varma, Pure Appl. Chem. 73 (2001) 193–198;
(c) P. Lidstrom, J. Tierney, B. Wathey, J. Westman, Tetrahedron 57 (2001) 9225–9583;
(d) S.H. Zhang, M.F. Tang, C.M. Ge, Z. Anorg. Allg. Chem. 635 (2009) 1442–1446;
(e) S.H. Zhang, Y. Song, H. Liang, M.H. Zeng, Cryst. Eng. Commun. 11 (2009) 865–872;
(f) S.H. Zhang, C. Feng, J. Mol. Struct. 977 (2010) 62–66;
(g) C.J. Millos, A.G. Whittaker, E.K. Brechin, Polyhedron 26 (2007) 1927–1933.
[19] B.T. Thaker, R.S. Barvalia, Spectrochim. Acta Part A 74 (2009) 1016–1024.
[20] B.S. Furniss, A.S. hannaford, V. Rogers, P.W.G. Smith, A.R. Tatchell (Eds.), Vogel's Text Book of Practical Organic Chemistry, fourth ed., ELBS Logman Group Ltd., London, 1978.
[21] B.T. Thaker, R.S. Barvalia, J. Coord. Chem. 63 (2010) 1597–1610.
[22] (a) M. Prasad, S.S. Dharmati, S.V. Gokhale, Proc. Ind. Acad. Sci. 20 A (1944) 224;
(b) C.N.R. Rao, University General Chemistry – An Introduction to Chemical Science, first ed., Macmillan, India, 1973.
[23] W.J. Geary, Coord. Chem. Rev. 7 (1971) 81–122.
[24] P.G. moe, R.B. Bhalvankar, J. Indian Chem. Soc. 81 (1) (2004) 13–17.
[25] P.J. bahad, N.S. bhave, S. Aswar, J. Indian Chem. Soc. 77 (8) (2000) 363–366.
[26] R.M. Silverstein, F.X. Webster, Spectrometric Identification of Organic Compounds, sixth ed., John Wiley & Sons, Inc., New York, 2002.
[27] D.L. Pavia, G.M. Lampman, G.S. Kriz, Introduction to Spectroscopy, third ed., Thomson, Harcourt College Publishers, Orlando, FL, 2001.
[28] A.K. Abdulla, K.Z. Ismail, Can. J. Chem. 72 (1994) 1785–1788.
[29] P.S. Mane, S.G. Shirodakar, B.R. Arbad, T.K. Chondhekar, Indian J. Chem. 40A (6) (2001) 648–651.
[30] W. Kemp, Organic Spectroscopy, second ed., Macmillan, London, 1991.
[31] K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, third ed., John Wiley & Sons, New York, 1978.
[32] K.R. Surti, B.T. Thaker, J. Coord. Chem. 59 (11) (2006) 1191–1202.
[33] T. Ghoshh, C. Bandyopadhyay, Trans. Met. Chem. 30 (2005) 404–410.
[34] I. Sakryan, N. Gunduz, T. Gunduz, Synth. React. Ingo. Met. Org. Chem. 31 (2001) 1175–1187.
[35] R.L. Datta, A. Syamal, Element of Magnetochemistry, second ed., 1993, East–West, New Delhi.
[36] J. Selbin, G. Mans, D.L. Johnson, J. Inorg. Nucl. Chem. 29 (1967) 1735–1744.
[37] A. Syamal, M.R. Maurya, Coord. Chem. Rev. 95 (1989) 183–238.
[38] C.R. Cornman, J. Kamp, M.S. Lah, V.L. Pecorato, Inorg. Chem. 31 (1992) 2035–2043.
[39] P. Basu, S. Pal, A. Chakravarty, J. Chem. Soc. Dalton Trans. (1991) 3217–3221.
[40] G.R. Hausan, T.A. Kabanos, A.D. Keramidas, D. MEntzatos, A. Terzis, Inorg. Chem. 31 (1992) 2587–2594.
[41] H.A. Kuska, M.T. Rogers, Electron Spin Resonance of Transition Metal Complexes Ions in Coordination Chemistry, Van-Nostrand Reinhdd Co., New York, 1971.
[42] A.E. Martell, Coordination Chemistry, VanNostrand Reinhold Co., New York, 1971.
[43] S.K. Gupta, D. Raina, Trans. Met. Chem. 22 (1997) 372–374.
[44] S.S. Dodwad, R.S. Dhamnaskar, P.S. Prabhu, Polyhedron 8 (1989) 1748–1750.
[45] A. Broido, J. Polym. Sci. 7A (1969) 1761–1773.
[46] M. Sekerci, F. Yakuphanoglu, J. Therm. Anal. Calorim. 75 (2004) 189–195.
[47] H.H. Horowitz, G. Metzger, Anal. Chem. 35 (1963) 1464–1468.