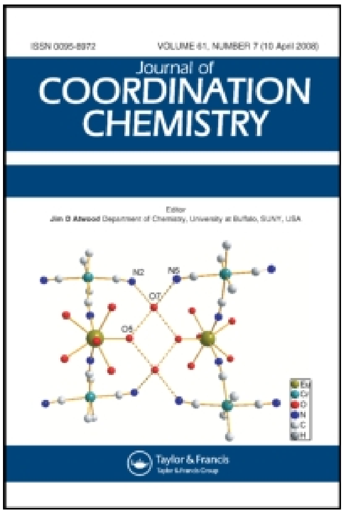

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Synthesis, spectral, and thermal studies of oxomolybdenum(V) Schiff-base complexes derived from heterocyclic β-diketone

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Synthesis, spectral, and thermal studies of oxomolybdenum(V) Schiff-base complexes derived from heterocyclic *β*-diketone

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Six mononuclear Mo(V) Schiff-base complexes were prepared by the reaction of $MoCl_5$ with Schiff bases, namely HL^1–HL^3 and HL^4–HL^6, such as 5-hydroxy-3-methyl-1(2-chloro)phenyl-1H-pyrazolone-4-carbaldehyde (I), 5-hydroxy-3-methyl-1(3-chloro)phenyl-1H-pyrazolone-4-carbaldehyde (II), and 5-hydroxy-3-methyl-1(3-sulfoamido)phenyl-1H-pyrazolone-4-carbaldehyde (III) with ethanolamine and propanolamine, respectively, in aqueous ethanolic medium. The resulting complexes have been characterized by elemental analyses, molar conductance, FT-IR, ^{1}H-NMR, electronic, electron spin resonance (ESR) spectra, magnetic susceptibility, and thermal study. The molar conductivity data show them to be non-electrolytes. IR and ^{1}H-NMR spectral data suggest that the ligand is a dibasic bidentate with ON donor toward metal ion. Electronic, magnetic, and ESR spectral data suggest that the oxomolybdenum(V) complexes have distorted octahedral geometry. One chloride coordinated to molybdenum is confirmed by thermal study.

Keywords: Schiff bases; Oxomolybdenum(V) complexes; FT-IR; ESR spectrometry; Thermal studies

1. Introduction

Schiff bases have been of great importance in macrocyclic coordination chemistry [1]. Transition metal complexes of Schiff bases have been among the most widely studied coordination compounds, important as biochemical, analytical, and antimicrobial reagents [2–4]. Schiff bases containing polyfunctional groups offer many practical advantages for complexation [5] and have produced stable metal complexes of transition, non-transition, inner-transition, and actinide metal ion which played a significant role in stereochemistry, structure, isomerism, magnetism, spectroscopy, kinetics and mechanism of reactions, reaction of coordinated ligands, model systems of biochemical interest, analytical chemistry, catalysis, stabilizers, polymers, pigments and dyes, photography, electro-optical display device, and agriculture [6], catalyze a large number of transformations of exoxides including hydrogenation, hydroformylation,

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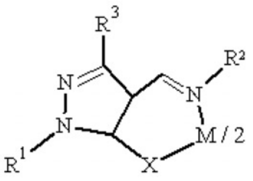
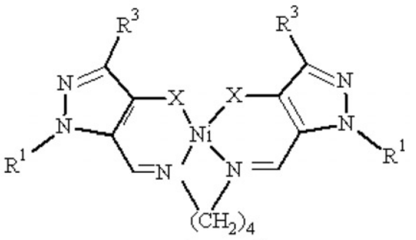
carbonylation, and deoxygenation [7], exhibit interesting fluorescence [8], and are applied in stereoselective organic transformations [9]. Polymetallic systems are of interest to biologists and bioinorganic chemists because their structure is similar to those found in polynuclear metal centers in proteins and to physicists and physical inorganic chemists who investigate new magnetic materials [10–14]. A review containing various types of mononuclear complexes of Schiff bases involving aldehyde and amine fragments (structure-1 and -2) were reported recently [15].



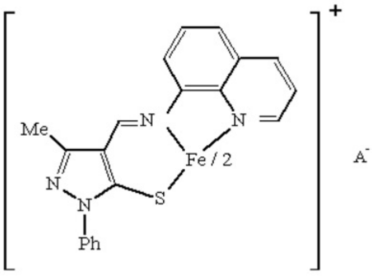
X = NR, O, S, Se

Structure-1



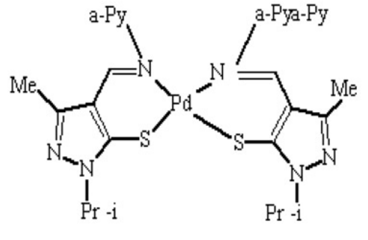
Structure-2

Most acyclic Schiff-base ligands containing transition metals with electropositive metals like Li, Al, Sn, Ga, and Sb have tetra, penta, and hexa coordination. A number of S- and Se-containing azomethine metal chelates are among the complexes of heterocyclic Schiff bases, including the unusual cationic complexes of iron (structure-3) [16], as well as *cis*-(structure-4) and *trans*-(structure-5) of palladium, obtained from imine derivative of 5-thiopyrazole with coordinative [17] and sterically hindered [18] substituents at nitrogen of the C=N bond and nickel complexes with 4-imino-5-aminopyrazolone [18, 19].

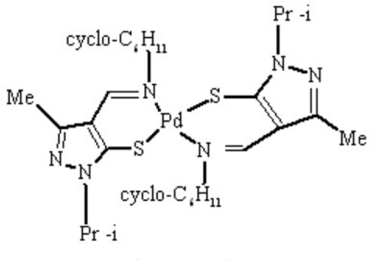


$A^- = FeCl_4, ClO_4$

Structure-3

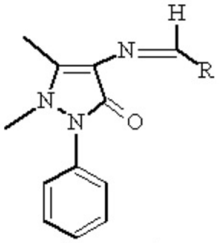


Structure-4



Structure – 5

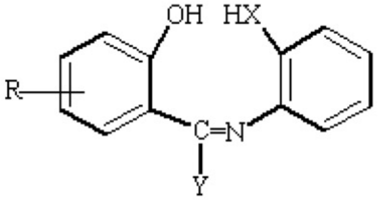
Another review [20] has recently appeared on the transition metal complexes of Schiff-base ligands involving 4-antipyrine-based derivatives only (structure-6).



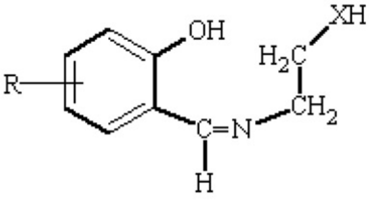
Structure – 6

Molybdenum is one of the most biologically active transition elements and is an essential micronutrient for microorganisms, plants, and animals. The propensity of oxomolybdenum species in higher oxidation states to form di-, tri-, and polynuclear complexes is well known [21]. Changes in the coordination number, observed particularly between Mo (IV), Mo (V), and Mo (VI) are important especially in industrial and biochemical catalysis [22]. Molybdenum is present in a number of redox enzymes [23], such as aldehyde oxidase, sulfite oxidase, xanthine oxidase, nitrate reductase, and nitrogenase, the last two are involved in the nitrogen cycle of plants [6]. Many molybdenum(IV) and (V) Schiff-base complexes have been found as simple models for redox [24] and in nitrogenase enzymes [25]. The oxygen transfer of oxomolybdenum plays a significant role in investigating the mechanism of molybdenum oxotransferase [26, 27].

Zelentsov *et al.* [28] reported the synthesis of dioxomolybdenum(IV) complexes of the ON donor Schiff base derived from salicylaldehyde and aniline. Extensive studies have been reported on the synthesis and characterization of dioxomolybdenum(VI) complexes with tridentate Schiff bases. Complexes MoO_2L_2 and MoO_2LA (where LH_2-tridentate Schiff base, A = monodentate ligand) have been prepared with (I) and (II) starting from MoO_2Cl_2, $MoO_2(acac)_2$, and $MoO_2(sal)_2$.

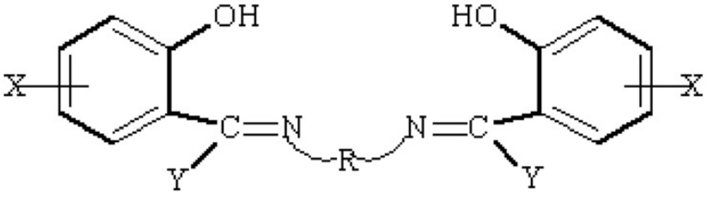


(I)



(II)

Oxomolybdenum(V) and dioxomolybdenum(VI) complexes of 1,2-dihydro-1,5-dimethyl-2-phenyl-4-(2,4-dihydroxy phenylazo)-3-H pyrazole-3-one and Schiff-base complexes of 1,2-dihydro-1,5-dimethyl-2-phenyl-4-amino-4-3H-pyrazol-3-one were synthesized by Nair and Prabhakaran [29]. Oxomolybdenum(V) complexes of Schiff bases have been reported in which Schiff-base ligand (III) is a neutral bidentate through azomethine nitrogen [6], although the Schiff bases are potential tetradentate ligands.



(III)

Pyrazolone and its derivatives have attracted much attention because of their high pesticide efficiency, low human toxicity, variety of structures, and application in diverse areas. They are used in laser materials as ^{1}H-NMR shift reagents, in chromatography, in petrochemical industry [30–34] and as dye intermediates. Pyrazolone derivatives (β-diketones) are useful reagents in the extraction and separation of metal ions [35–39].

Soni and Shah [40] reported the synthesis and characterization of Mn(II), Ni(II), Co(II), Cr(II), Cu(II), and Zn(II) complexes with 4-formyl-1,3-diphenyl-2-pyrazoline-5-one. Rana and Shah [41] reported complexes of 4-benzoyloxime-3-methyl-1-phenyl-2-pyrazoline-5-one with Cr(II), Ni(II), Co(II), Cu(II), UO_2(II), VO(II), and Zn(II). Shavaleev *et al.* [42] reported the synthesis, structure, and luminescence of new rare earth metal complexes with 1-phenyl-3-methyl-4-acylpyrazoline-5-one. Yasutaka *et al.* [43] reported 4,4-dichloro-1-(2,4-dichlorophenyl)-3-methyl-5-pyrazolone as a potent catalytic inhibitor of human telomerase [44–47]. Telomerase activity is controlled through the development and differentiation of cells or tissues, and the improper control of telomerase activity is associated with several diseases such as human immunodeficiency virus (HIV) and cancer [48–50].

Most pyrazolone derivatives have an aryl ring at position 1, which diminishes the solubility, but is known to display diverse pharmacological activities, such as antibacterial [51], antifungal [52], anti-inflammatory, analgesic, and antipyretic [53]. Researches have been done on pyrazole and heterocyclic β-diketones [54–56] due to their stability and easy synthesis. Pyrazolones exist in tautomeric forms, such as CH, OH, and NH [57–60].

2. Experimental

2.1. *Materials*

$MoCl_5$ (Aldrich, USA) was used as received. 1-Phenyl-3-methyl-5-pyrazolone and its chloro and sulfoamido derivatives (E-Merck), ethanolamine (BDH), and 3-amino 1-propanol (Alfa-Alser) were used.

2.2. *Instruments*

Elemental analyses (C, H, and N) were performed at RSIC, Lucknow. Molybdenum was estimated by decomposing the complexes with concentrated HNO_3, igniting at 650°C and then weighting as MoO_3 [61]. Conductance measurements of these complexes were carried out on the systronics direct reading conductivity meter type CM-82T. Infrared spectra were recorded with a Perkin Elmer IR spectrophotometer (4000–200 cm^{-1}) using KBr pellets. ^{1}H-NMR spectra of the compounds and their metal complexes were recorded with a Bruker Avance II 400 using $CDCl_3$ for ligands and DMSO-d_6 for metal complexes with tetramethylsilane (TMS) as an internal reference, at SAIF, Punjab University, Chandigarh. UV-Vis spectra from 200 to 800 nm were obtained in DMSO on a "SHIMADZU" UV 160A using a quartz cell of 1 cm^3 optical path. Magnetic measurements of metal complexes at room temperature (RT) were carried out on a Gouy balance as per the method suggested by Prasad *et al.* [62]. ESR spectra of all MoO(V) complexes were recorded by ESR Laboratory, SAIF, IIT, Mumbai, at RT and liquid nitrogen temperature (LNT) for polycrystalline and solution state. Thermogravimetric analysis (TGA)/differential thermal analysis (DTA) of the complexes were obtained by a model 5000/2960 SDT, TA Instruments, at a heating rate of 10°C min^{-1} at SP University, Vallabh Vidyanagar. The sample sizes ranged in mass from 4.5 to 10 mg. The differential scanning calorimetry (DSC) of the complexes were performed on a METTLER, at a heating rate of 10°C min^{-1} at Mantra, Surat.

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

The ligands (I), (II), and (III) were prepared by the 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), cooled to 0°C in an ice bath, and phosphoryl chloride (5.5 mL, 0.06 mol) was added dropwise at a rate to maintain the temperature between 10°C 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, and then poured into 1 L of ice water in a beaker. The resulting mixture was allowed to stand overnight, collected by filtration, washed with water, and dried. Crystallization was done with ethanol.

2.4. *Synthesis of Schiff-base ligands*

The Schiff bases HL^1–HL^3 and HL^4–HL^6 were synthesized by refluxing the methanolic solution of ligands I (2.33 g, 0.01 mol), II (2.33 g, 0.01 mol), and III (2.82 g, 0.01 mol) with ethanolamine (0.6 mL, 0.01 mol) and 3-amino-1-propanol (0.78 mL, 0.01 mol), respectively, in a water bath for 4 h. The dark liquid was allowed to cool overnight and the solid obtained was filtered and washed with ether. Crystallization was done with ethanol and the product was dried.

2.5. *Synthesis of Schiff-base complexes of oxomolybdenum(V)*

All the oxomolybdenum(V) Schiff-base complexes were prepared at 1 : 2 mole proportion of metal : ligand. A methanolic solution of $MoCl_5$ (2.73 g, 0.01 mol) was added with stirring to a hot solution of the Schiff-base ligands HL^1–HL^2 (5.28 g, 0.02 mol), HL^3 (6.16 g, 0.02 mol), HL^4–HL^5 (5.87 g, 0.02 mol), and HL^6 (6.12 g, 0.02 mol) dissolved in 80 mL of methanol. The pH of the reaction mixture was adjusted to 6 with NaOAc/HOAc buffer with stirring and the reaction mixture was refluxed for 4–4.5 h. During reflux, the color of the reaction mixture changed; the reaction mixture was concentrated to half of its volume, cooled, and kept overnight. The resulting precipitates were filtered, washed successively with water and ethanol, and dried.

3. Results and discussion

The elemental analyses, FT-IR, and ^{1}H-NMR spectral data are shown in Panel A of table 1 for I, II, and III and in Panel B for their Schiff bases HL^1–HL^6. The physical data of metal Schiff-base complexes of MoO(V) that are in agreement with the proposed stoichiometry are shown in table 2.

3.1. *Molar conductance*

The molar conductances of the oxomolybdenum(V) complexes in 10^{-3} mol L^{-1} in DMSO in the range of 6.4–16.2 $Ohm^{-1}\,cm^2\,mol^{-1}$ indicate that all complexes are non-electrolytes [63, 64].

3.2. *FT-IR spectra of Schiff-base ligands*

FT-IR spectra of HL^1–HL^6 exhibit a medium band due to υ(OH) at 3375–3312 cm^{-1} from ethanol or propanol amine. Phenyl substituted at position 4 by $-SO_2NH_2$ has a sharp but less intense band at 3274 cm^{-1} in III, HL^3, and HL^6 compounds which is unaffected by Schiff-base formation. ν(N–H) is expected at 3300–3200 cm^{-1} due to the tautomerism of ligand, but has not appeared [65, 66]. Band at ~2916–2860 cm^{-1} is due to ν(C–H) of $-CH_3$ or $-CH_2$. In Schiff-base ligands, a strong band at 1673–1656 cm^{-1} is due to ν(C=O) of pyrazoline, which remains unaffected on Schiff-base formation. The band in 4-carbaldehyde due to ν(H–C=O) at 1628–1627 cm^{-1} disappears and a new band at 1603–1601 cm^{-1} due to ν(C=N) at position 4 on Schiff-base formation appears. Single crystal study of this compound shows that the Schiff-base molecule in solid state is in keto-immine form [67].

3.3. *^{1}H-NMR spectra of Schiff bases*

^{1}H-NMR spectra of HL^1–HL^6 show high-intensity singlet at δ 2.14–2.21 ppm due to $-CH_3$ of pyrazoline. The free –OH proton of alkanolamine gives medium intense singlet at δ 5.34–5.44 ppm. The signals having different multiplicities observed from δ 7.0–8.1 ppm are due to phenyl substituted at position 1 of pyrazoline. The less

Table 1. Analytical, physical, and spectral data of complexes.

				Elemental analysis found (calculated) (%)			Functional group IR frequencies (cm^{-1})		Functional group and chemical shifts δ (ppm)		
Ligands	Color	Yield (%)	m.p. (°C)	C	H	N	ν(C=O) cyclic	ν(C=O) aldehydic	–CH$_3$ proton	Phenyl multiplets proton	Aldehyde proton
Panel A: Ligands											
I	Yellow	62.32	128	55.80(55.82)	3.70(3.83)	11.50(11.83)	1658	1628	2.20	7.26–7.42	9.75
II	Yellow	76.70	76	55.50(55.82)	3.70(3.83)	11.80(11.83)	1659	1627	2.13	7.25–7.40	9.74
III	Yellow	75.01	243	46.94(46.84)	3.90(3.94)	14.56(14.94)	1672	1628	2.14	7.43–7.63	9.45

				Elemental analysis found(calculated) (%)			Functional group IR frequencies (cm^{-1})			Functional group and chemical shifts δ (ppm)			
Schiff-base ligands	Color	Yield (%)	m.p. (°C)	C	H	N	ν(C=O) cyclic	ν(C=N) azomethine	–OH alkane	–CH$_3$ proton	–OH alkane	Phenyl multiplets proton	–CH=N proton
Panel B: Schiff-base ligands													
HL1	Orange	71.73	161	55.50(55.82)	5.06(5.04)	15.09(15.02)	1658	1603	3313	2.21	5.37	7.08–7.87	8.03
HL2	Light orange	75.74	115	55.50(55.82)	5.06(5.04)	15.09(15.02)	1659	1602	3361	2.17	5.40	7.07–7.86	8.02
HL3	Pink	71.98	98	48.18(48.13)	4.98(4.97)	17.04(17.02)	1672	1601	3375	2.15	5.44	7.43–8.13	8.63
HL4	Reddish brown	72.60	144	57.25(57.24)	5.53(5.49)	14.05(14.03)	1656	1603	3312	2.20	5.37	7.06–7.87	7.90
HL5	Orange brown	73.12	117	57.25(57.24)	5.53(5.49)	14.05(14.03)	1661	1602	3369	2.18	5.34	7.07–7.88	7.91
HL6	Reddish brown	75.17	200	49.70(49.69)	5.40(5.36)	16.60(16.55)	1673	1601	3372	2.14	5.44	7.44–8.15	8.64

Table 2. Elemental analysis and physical data of oxomolybdenum(V) complexes.

				Elemental analysis found (calculated) (%)					
Complexes	Color	Yield (%)	m.p. (°C)	C	H	N	M	Molar conductivity (Ohm^{-1} cm^2 mol^{-1})	μ_{eff} (B.M.)
[MoO(L^1)$_2$Cl]	Brown	60.95	>300	44.96(44.90)	4.02(3.96)	11.85(11.89)	13.60(13.57)	6.49	1.73
[MoO(L^2)$_2$Cl]	Brown	65.24	>300	44.96(44.90)	4.02(3.98)	11.85(11.89)	13.61(13.57)	6.47	1.74
[MoO(L^3)$_2$Cl]	Yellowish brown	65.99	>300	39.28(39.23)	4.07(4.02)	14.05(14.07)	11.98(12.05)	10.8	1.69
[MoO(L^4)$_2$Cl]	Brown	53.15	>300	45.69(45.77)	4.48(4.40)	11.41(11.43)	13.08(13.05)	11.9	1.73
[MoO(L^5)$_2$Cl]	Brown	56.55	>300	45.69(45.77)	4.48(4.40)	11.41(11.43)	13.08(13.05)	11.5	1.73
[MoO(L^6)$_2$Cl]	Yellowish brown	59.96	>300	43.06(43.04)	4.09(4.04)	14.02(14.00)	12.02(11.99)	16.2	1.68

Table 3. IR and ^{1}H-NMR spectral data of oxomolybdenum(V) complexes.

Functional group and IR frequencies (cm^{-1})					Functional group and chemical shifts (ppm)			
Complexes	ν(–OH) (broad band)	ν(C=N) coordination	ν(C–O) coordination	ν(M=O)	Methyl proton singlet	–CH$_2$O alkane and =N–CH$_2$	–OH alkane	Phenyl proton multiplets
[MoO(L^1)$_2$Cl]	3370	1586	1327	948	2.35	2.56–3.25	5.57	7.44–7.87
[MoO(L^2)$_2$Cl]	3375	1588	1325	972	2.30	2.57–3.27	5.58	7.48–7.90
[MoO(L^3)$_2$Cl]	3386	1590	1329	975	2.40	2.59–3.20	5.60	7.40–7.77
[MoO(L^4)$_2$Cl]	3377	1587	1325	949	2.35	2.56–3.25	5.57	7.44–7.87
[MoO(L^5)$_2$Cl]	3380	1589	1326	968	2.30	2.57–3.27	5.58	7.48–7.90
[MoO(L^6)$_2$Cl]	3389	1590	1327	970	2.40	2.58–3.20	5.60	7.33–7.75

intense signal near δ 7.90–8.64 ppm is due to aldehydic C–H. There is a quintet at δ 3.4–3.5 ppm due to the middle –CH$_2$- proton of propanol [$C{=}N{-}CH_2{-}\underline{CH_2}{-}CH_2{-}OH$] group in HL^4–HL^6. The keto-enol tautomerism is so fast in solution that 4-$\bar{C}$–H or 5-OH could not be detected in ^{1}H-NMR spectra.

3.4. *FT-IR spectra of Schiff-base complexes of oxomolybdenum(V)*

The coordination site of the ligand could be determined by employing FT-IR-LD method. Recently, such a method has been used to determine the coordination site of 4-amino-pyridine in Cu(II) complexes [68, 69].

IR spectra of the Schiff-base complexes of MoO(V) (table 3) exhibit broad bands at ~3370–3389 cm^{-1} due to ν(O–H) of alkanol amine, indicating that –OH is undissociated during complexation. Therefore, this –OH group of ethanolamine and propanolamine does not take part in the bond formation with metal. The Schiff bases exhibits a band at 1603–1601 cm^{-1} attributed to ν(C=N) of azomethine. On complex formation this band shifts to 1585–1590 cm^{-1}, indicating coordination through N of azomethine >C=N [70]. This lowering may be due to reduction in electron density in the azomethine as the nitrogen coordinates to the metal [61]. Appearance of a new sharp band at 1325–1329 cm^{-1} due to ν(C–O) indicates complex formation through oxygen (which is present at position 5 of pyrazolone ring after enolization) to molybdenum. The IR spectra of Schiff-base complexes of oxomolybdenum(V) are dominated by a strong band at 948–975 cm^{-1} due to terminal ν(Mo=O) [6].

3.5. *^{1}H-NMR spectra of Schiff-base complexes of oxomolybdenum(V)*

The ^{1}H-NMR spectra of six Schiff-base complexes (table 3) exhibit singlets at δ 2.30–2.40 ppm due to –CH$_3$ of pyrazoline. The presene of a less intense signal observed at δ 2.56–3.27 ppm may be attributed to the –CH$_2$O and =N–CH$_2$ of ethanolamine and propanolamine. The –OH singlet at δ 5.57–5.60 ppm indicates that the –OH is undissociated during complexation. The phenyl is observed at δ 7.33–7.90 ppm in all

Table 4. Electronic spectral data of oxomolybdenum(V) complexes.

	d–d transition (cm^{-1})					
			$B_2 \rightarrow {}^2A_1$			
Complexes	${}^2B_2 \rightarrow {}^2E$	${}^2B_2 \rightarrow {}^2B_1^2$	$O(\pi) \rightarrow d(Mo)$	Charge transfer band (cm^{-1})		
$[MoO(L^1)_2Cl]$	17,889	22,522	26,666	32,894	34,129	36,900
$[MoO(L^2)_2Cl]$	16,949	23,148	24,691	32,890	24,691	32,894
$[MoO(L^3)_2Cl]$	15,748	22,573	26,737	22,573	26,737	29,781
$[MoO(L^4)_2Cl]$	16,000	22,471	26,315	26,315	34,482	37,593
$[MoO(L^5)_2Cl]$	16,393	21,505	24,691	28,169	28,169	32,894
$[MoO(L^6)_2Cl]$	15,037	22,624	26,746	26,737	26,737	29,761

the complexes. The aldehydic proton is observed at δ 8.15–8.20 ppm. In solution, keto-enol tautomerism [71] is very fast and it is difficult to show the –O–H formation at position 5 of pyrazoline. Due to coordination, a few signals shifted to down field. $[MoO(L^3)_2Cl]$ and $[MoO(L^6)_2Cl]$ exhibit singlets at δ 9.25–9.30 ppm due to –N–H of $-SO_2NH_2$.

3.6. *Magnetic moment and electronic spectra*

All six Schiff-base complexes of MoO(V) are paramagnetic with effective magnetic moments in the range of 1.68–1.74 B.M. (table 2) with no significant magnetic interactions between the neighboring oxomolybdenum(V) ions [72]. Electronic spectra of six oxomolybdenum(V) (table 4, Supplementary material) complexes in $10^{-3}\,mol\,L^{-1}$ DMSO solutions have high-intensity peaks in UV region or near UV region, due to intra-ligand $n \rightarrow \pi^*/\pi \rightarrow \pi^*$ transitions (37,593, 36,900, 34,482, 34,129, 32,679, and 32,894 cm^{-1} due to $n \rightarrow \pi^*$ or $\pi \rightarrow \pi^*$ transitions). In the visible region, two bands of low intensity at 17,889–15,037 and 23,148–21,505 cm^{-1} are due to the d–d bands assigned to ${}^2B_2 \rightarrow {}^2E$ (ν_1) and ${}^2B_2 \rightarrow {}^2B_1$ (ν_2), respectively, from distorted octahedral environment [73–75]. The third band of high energy having slightly lower intensity compared to the interligand band observed at 26,746–24,691 cm^{-1} is attributed to $O(\pi) \rightarrow d(Mo)$ involving excitation of an electron from highest filled π bonding molecular orbital (associated mainly with oxygen) to the d-orbital of molybdenum.

3.7. *ESR spectra*

ESR spectral data of $[MoO(L^{4-6})_2Cl]$ complexes are presented in table 5 and ESR spectra shown in figure 1 are recorded as powders at RT and LNT. Seventy-five percent of molybdenum are isotopes ${}^{94}Mo$ and ${}^{96}Mo$ with the nuclear spin quantum number $I = 0$, and these isotopes give one ESR line. The natural abundance of ${}^{95}Mo$ and ${}^{97}Mo$ is 15.78% and 9.60%, respectively, both with a nuclear spin $I = 5/2$. Thus, each isotope should give six ESR lines. ${}^{95}Mo$ overlaps with the six lines arising from ${}^{97}Mo$, and only six broad lines are observed in addition to the single central line originating from ${}^{94}Mo$

Table 5. g and A of the powder ESR spectra of Mo(V) complexes at RT and LNT.

	RT			LNT					
Complexes	$g_{\parallel}$	$g_{\perp}$	$\lvert g \rvert$	$g_{\parallel}$	$g_{\perp}$	$\lvert g \rvert$	$A_{\parallel} \times 10^{-4}\,\mathrm{cm}^{-1}$	$A_{\perp} \times 10^{-4}\,\mathrm{cm}^{-1}$	$\lvert A \rvert \times 10^{-4}\,\mathrm{cm}^{-1}$
$[MoO(L^4)^2Cl]$	1.97	2.04	2.01	1.81	2.00	1.93	10.81	11.71	11.41
$[MoO(L^5)^2Cl]$	1.95	1.89	1.91	1.83	2.00	1.94	6.35	4.54	5.14
$[MoO(L^6)^2Cl]$	2.02	1.98	1.99	1.94	2.00	1.98	8.34	6.48	7.10

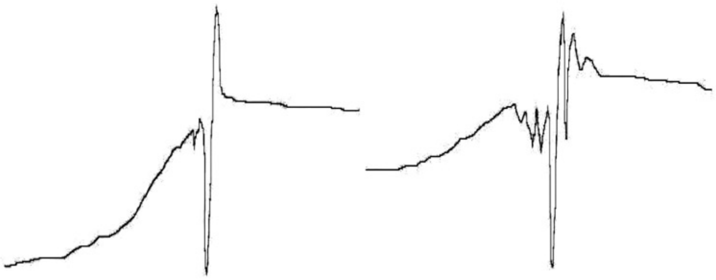


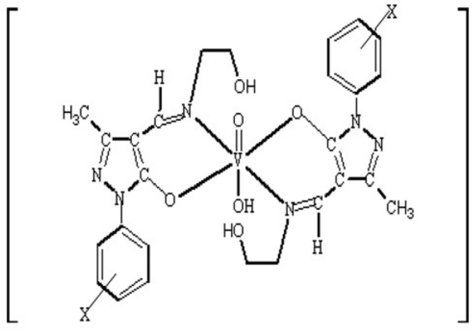
Figure 1. ESR spectra of $[MoO(L^4)_2Cl]$ complex at RT and LNT.

and ^{96}Mo [72]. ESR spectra of Schiff-base complexes exhibit a single line at RT, but six weak and broad ESR lines at LNT. Because of the poor solubility in DMF + pyridine (70 : 30), we could not find the ESR spectrum of these complexes in the solution.

The $g_{\parallel}$ and $g_{\perp}$ values were computed from the spectra using DPPH free radicals as g marker. The ESR parameters were $g_{\parallel} = 1.95$–2.02, $g_{\perp} = 1.89$–2.04, and $|g|$ or $g_{av} = 1.91$–2.01. $g_{\parallel} > g_{\perp}$ in most MoO(V) Schiff-base complexes [76]. Ligand spin–orbit interaction is evident in molybdenum complexes and therefore $g_{\parallel} > g_{\perp}$. The $|g|$ value indicates that the pentavalent Mo in the complexes is monomeric [77]. The $g_{\parallel}$, $g_{\perp}$, and $|g|$ values are in accordance with the unpaired electron localized in the d_{xy} orbital [76, 77] of a molecule which exists in distorted octahedral geometry. For molybdenum, the hyperfine contents $A_{\parallel}$ and $A_{\perp}$ were taken to be positive since ^{95}Mo and ^{97}Mo have negative nuclear moment. The $A_{\parallel}$ and $A_{\perp}$ are assigned a positive sign because the $^1B_2$ ground state places the unpaired electron in the d_{xy} (b_2) molecular orbital describing the in-plane π bonding [78]. The $A_{\parallel}$ and $A_{\perp}$ values are 6.35×10^{-4}–$10.81 \times 10^{-4}\,\mathrm{cm}^{-1}$ and 4.54×10^{-4}–$11.71 \times 10^{-4}\,\mathrm{cm}^{-1}$, respectively; these parameters have low values because of fact that the dipolar interactions of the unpaired electron in the ^3p_z chlorine orbital should be close to zero [78].

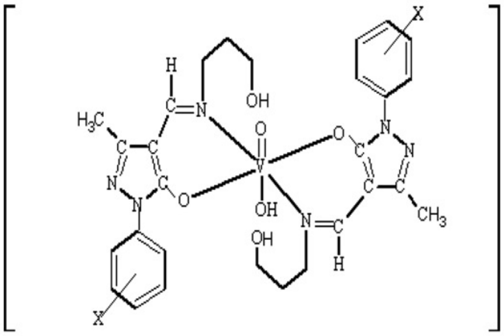
3.8. *Thermal study*

Very few references are available on thermal properties of Schiff-base metal complexes of MoO(V). From TGA/DTA curves (Supplementary material), there are two steps in the decomposition of Mo(V) complexes. The curves show no loss up to 40°C and then very small moisture removal completed at 80°C [79]. The first step starts at 185–208°C, due to the removal of chloride, found percentage is 5.25% (Calcd 5.01–4.45). The DTA



X = 6-Cl, 5-Cl or 5- SO_2NH_2

Figure 2. General structures of Schiff-base complexes of $[MoO(L^{1-3})_2Cl]$.



X = 6-Cl, 5-Cl or 5- SO_2NH_2

Figure 3. General structures of Schiff-base complexes of $[MoO(L^{4-6})_2Cl]$.

curve also shows endothermic peak at 185–210°C. Decomposition of organic ligand begins after 250°C and continues upto 450°C followed by exothermic process with the mass loss 80.5–83%, due to the pyrolysis of organic molecule. The stable MoO_3 forms at 700°C. The plot of $\ln(\ln(1/Y)) \rightarrow 1/T$ results in a straight line. From this plot, we calculated the activation energy ΔE^* by Broido's graphical method [80] and Broido's plots (Supplmentary material).

4. Conclusion

Mononuclear mono-oxo and dioxo Schiff-base complexes of Mo(IV) and Mo(VI) with NO donors are widely studied. However, mononuclear oxomolybdenum(V) complexes of ON chelator Schiff bases based on pyrazolone are less studied. This study provides a general way of synthesizing and characterizing mononuclear oxomolybdenum(V) Schiff-base complexes. The IR and ^{1}H-NMR spectral data suggest that the Schiff base is a dibasic bidentate with ON donor sequence toward molybdenum. The molar conductivity data show them to be non-electrolytes. Thermal stability of structures 1–3 is in the order $[MoO(L^3)_2Cl] > [MoO(L^1)_2Cl] > [MoO(L^2)_2Cl]$. Electronic, magnetic, and ESR spectral data suggest that all the oxomolybdenum(V) Schiff-base complexes have distorted octahedral geometry (figures 2 and 3).

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