

**CHARACTERIZATION OF HETEROBIMETALLIC
AND MIXED-VALENCE COMPLEXES OF MOLYBDENUM(V)
DERIVED FROM BIS(2-HYDROXY-1-NAPHTHALDEHYDE)
MALONOYLDIHYDRAZONE**

© A. Kumar,¹ O. B. Chanu,² R. Borthakur,² and R. A. Lal²

UDC 543.422:541.65:541.49:546.77

Heterobimetallic complexes $[\text{UO}_2\text{Mo}^{\text{V}}(\text{CH}_2\text{L})(\text{hzd})(\text{H}_2\text{O})_2]_n$, $[\text{ZnMo}^{\text{V}}(\text{CH}_2\text{L})(\text{hzd})(\text{H}_2\text{O})_2]_n$ and mixed-valence complexes $[\text{Mo}^{\text{VI}}\text{O}_2\text{Mo}^{\text{V}}(\text{CH}_2\text{L})(\text{hzd})(\text{H}_2\text{O})_2]_n$ (where $\text{hzdH}_3 = \text{inhH}_3$, $n = 1$; slhH_3 , $n = 2$) are synthesized from bis(2-hydroxy-1-naphthaldehyde)malonoyldihydrazone (CH_2LH_4) and monometallic precursor complexes $[\text{Mo}(\text{CH}_2\text{LH}_2)(\text{hzd})] \cdot n\text{H}_2\text{O}$ ($n = 0, 1$) in ethanol. The composition of the complexes is established based on the data obtained from the elemental analysis. The structure of the complexes is discussed in the light of data obtained from molar conductance, magnetic moment, electronic, EPR, and IR spectroscopic studies. All complexes have μ_B values in the range 1.59-1.64 B.M., slightly lower than that required for one unpaired electron. The heterobimetallic complexes show two bands, while mixed-valence complexes show only one band in the visible region assigned to the $d-d$ transition. The g -values decrease in going from uranyl-to-molybdenyl-to-zinc complexes containing the isonicotinoyldiazenido (inh) group, however, no such regular trend is observed in the case of complexes containing the salicyloyldiazenido (slh) group in the coordination sphere. In all complexes, the principal dihydrazone ligand is present in the *enol* form as a bridging hexadentate ligand in the *anti-cis* configuration where hydrazide ligands are coordinated to the metal centre as a trinegative bidentate ligand in the diazenido form.

Keywords: synthesis, characterization, molybdenum(V), heterometal, hydrazone, spectroscopic studies.

INTRODUCTION

Molybdoenzymes are found in nearly almost all the organisms in the oxo-form and catalyze the redox-reactions involving three oxidation states of molybdenum (Mo(IV), Mo(V), and Mo(VI)) to complete two-electron reduction-oxidation processes [1]. In addition to the presence of molybdenum in oxidases, it also occurs in nitrogenase found in blue algae and free living bacteria. In this enzyme, it is present in the non-oxo form together with iron and participates in the conversion of atmospheric nitrogen into ammonia in the soil [2]. Thus, molybdenum is present either alone in enzymes in the mixed-valence state or in combination with another metal giving the heterobimetallic character to the enzyme. Further, the Schiff base heterobimetallic chemistry is an area of active research due to the importance of heterobimetallic complexes in catalysis [3], and materials synthesis [4]. In catalysis, a heterobimetallic complex containing an electron deficient metal atom and an electron rich metal atom presents the possibility of Lewis acid activation of a substrate molecule bound to the electron rich

¹Department of Chemistry, University of the West Indies, St. Augustine, Trinidad and Tobago, West Indies; Arvind.Kumar@sta.uwi.edu. ²Department of Chemistry, North Eastern Hill University, Shillong, Meghalaya, India; ralal@rediffmail.com. The text was submitted by the authors in English. *Zhurnal Strukturnoi Khimii*, Vol. 53, No. 5, pp. 887-895, September-October, 2012. Original article submitted November 5, 2011.

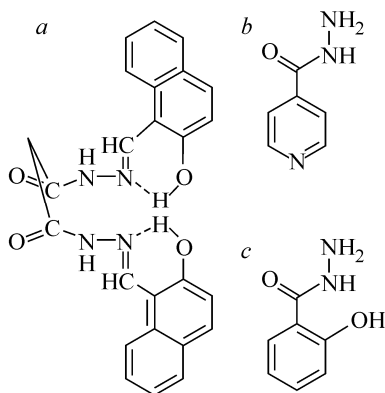


Fig. 1. Structure of the ligands: (a) bis(2-hydroxy-1-naphthaldehyde)malonoyldihydrazone (CH_2LH_4), (b) isonicotinoylhydrazine (inhH_3), and (c) salicyloylhydrazine (slhH_3).

metal centre [5, 6]. These complexes might be helpful in investigating the mutual influence of two metal centres on the electronic, magnetic, and redox properties of such systems [7, 8].

In view of the above importance of the heterobimetallic and mixed-valence complexes of molybdenum, the present paper describes the synthesis of some mixed-valence and heterobimetallic complexes of molybdenum in the +5 oxidation state, derived from polyfunctional CH_2LH_4 , inhH_3 , and slhH_3 ligands (Fig. 1), in which zinc, molybdenyl, and uranyl ions are the other metals. The complexes were mainly characterized based on the elemental analyses. The structure of the complexes has been discussed in the light of molar conductivity, magnetic moment, electronic, EPR, and IR spectral data.

EXPERIMENTAL

Ammonium molybdate $(\text{NH}_4)_6\text{Mo}_6\text{O}_{24} \cdot 4\text{H}_2\text{O}$, $\text{UO}_2(\text{OAc})_2 \cdot \text{H}_2\text{O}$, $\text{Zn}(\text{OAc})_2 \cdot \text{H}_2\text{O}$, diethylmalonate, hydrazine hydrate, 2-hydroxy-1-naphthaldehyde, acetylacetone, and isonicotinoyl hydrazine (inhH_3) were of Aldrich or equivalent grade. Salicyloylhydrazine (slhH_3) was prepared by reacting ethyl salicylate (1 mol) with hydrazine monohydrate (1 mol) and recrystallized from hot benzene [9]. Malonoyldihydrazone (MDH) was prepared by reacting a dilute solution of diethylmalonate in ethanol with hydrazine hydrate in the 1:2 molar ratio and recrystallized from hot water at $\sim 110^\circ\text{C}$. $\text{MoO}_2(\text{acac})_2$, $[\text{Mo}(\text{CH}_2\text{LH}_2)(\text{inh})] \cdot \text{H}_2\text{O}$, and $[\text{Mo}(\text{CH}_2\text{LH}_2)(\text{slh})]$ were prepared by literature methods [10, 11]. The determination of uranium, molybdenum, and zinc was performed following the standard literature procedures [12]. Magnetic susceptibility measurements were carried out on a Model 155 BAR vibrating sample magnetometer fitted with a Walker Scientific L75BAL magnet. The molar conductance of the complexes was measured on a Direct Reading Conductivity meter-303 with a dip type conductivity cell at room temperature in DMSO (10^{-3} M). Molecular weights were determined in the DMSO solution by the freezing point depression method. Infrared spectra were recorded on a paragon 500-model, Infrared spectrophotometer in the range $4000\text{--}350\text{ cm}^{-1}$ in KBr discs. The electronic spectra of the complexes were recorded on a Milton Roy Spectronic-21 spectrometer. The EPR spectra of the complexes in the powdered form at LNT were recorded at the X-band frequency on a Varian E-112 E-line century series ESR spectrometer using TCNE ($g = 2.00277$) as the internal field marker.

Preparation of bis(2-hydroxy-1-naphthaldehyde)malonoyldihydrazone (CH_2LH_4). The ligand bis(2-hydroxy-1-naphthaldehyde)malonoyldihydrazone (CH_2LH_4) was prepared by reacting a warm dilute solution of malonoyldihydrazide (1.32 g, 10.0 mmol) in ethanol (40 ml) with 2-hydroxy-1-naphthaldehyde (4.40 g, 25.0 mmol) also in ethanol (100 ml) at 70°C with gentle stirring for ca. 30-45 min. The yellow polycrystalline precipitate thus obtained was filtered and washed repeatedly with warm ethanol and dried under vacuum. The observed C, H, N analysis values (calcd. values are in

parentheses) for $C_{25}H_{20}N_4O_4$ (mol. wt., 440.45; m.p. 265°C) are C, 68.45 (68.17); H, 4.62 (4.58); N, 13.00 (12.72). Yield: 3.5 g (79.5%).

Preparation of $[M\text{Mo}^V(\text{CH}_2\text{L})(\text{inh})(\text{H}_2\text{O})_2]$ {where M = UO_2 (1), MoO_2 (3), and Zn (5)} and $[M\text{Mo}^V(\text{CH}_2\text{L})(\text{slh})(\text{H}_2\text{O})_2]$ {where M = UO_2 (2), MoO_2 (4), and Zn (6)}. All the complexes have been synthesised under the dinitrogen atmosphere.

In order to prepare complex $[\text{UO}_2\text{Mo}^V(\text{CH}_2\text{L})(\text{inh})(\text{H}_2\text{O})_2]$ (1), the complex $[\text{Mo}^V(\text{CH}_2\text{LH}_2)(\text{inh})]\cdot\text{H}_2\text{O}$ (0.684 g, 1.0 mmol) was taken in ethanol (50 ml) and stirred gently over a period of 10-15 min to make the suspension homogeneous. This was added to a solution of $\text{UO}_2(\text{OAc})_2\cdot 2\text{H}_2\text{O}$ (0.51 g, 1.20 mmol) in ethanol (50 ml) containing a trace of acetic acid, maintaining the molar ratio at 1:1.2. The reaction mixture was further stirred for about 30 min, and refluxed for 3 h, which produced a dark-red precipitate. The precipitate was filtered, washed with ethanol, ether and dried under vacuo over anhydrous CaCl_2 . Yield: 0.59 g (60%).

Complexes (3) and (5) were also prepared essentially by adopting the above procedure using $\text{MoO}_2(\text{acac})_2$ or $\text{Zn}(\text{OAc})_2\cdot 2\text{H}_2\text{O}$ instead of uranyl acetate. Yield 60-65%.

Similarly, complexes (2), (4), and (6) were also synthesised essentially by the above procedure using the precursor complex $[\text{Mo}^V(\text{CH}_2\text{LH}_2)(\text{slh})]$ instead of the complex $[\text{Mo}(\text{CH}_2\text{LH}_2)(\text{inh})]\cdot\text{H}_2\text{O}$. Yield: 60-65%.

RESULTS AND DISCUSSION

The heterobimetallic complexes of Mo(V) were synthesised by adopting the strategies developed by Lintvedt et al. [13] and Davies et al. [14]. The monometallic molybdenum (V) complex $[\text{Mo}^V(\text{CH}_2\text{LH}_2)(\text{inh})]\cdot\text{H}_2\text{O}$ or $[\text{Mo}^V(\text{CH}_2\text{LH}_2)(\text{slh})]$ was allowed to react with $\text{MoO}_2(\text{acac})_2$ or $\text{UO}_2(\text{OAc})_2\cdot 2\text{H}_2\text{O}$ or $\text{Zn}(\text{OAc})_2\cdot 2\text{H}_2\text{O}$ in the 1:1.2 molar ratio in absolute ethanol under the inert atmosphere. All the complexes with their color, analytical, magnetic moment, molar conductance and absorption data are given in Table 1. These complexes are air-stable and dark-red to orange in color and decompose or melt with decomposition in the temperature range 260-280°C. The complexes are insoluble in water and common organic solvents such as ethanol, methanol, ether, chloroform, dichloromethane, acetone, etc., but are soluble in CH_3CN , DMSO, and DMF. Many attempts to crystallize the complexes either from the saturated solution or by diffusing ether into the saturated solution in CH_3CN , DMSO, and DMF in a closed system resulted into amorphous solids. This prevented the X-ray analysis of these compounds. The molar conductance value of the complexes in the DMSO solution at 10^{-3} M concentration is in the range 2.5-7.0 $\text{Ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ suggesting that they are non-electrolytes in this solvent [15]. All complexes were heated at 110°C and 180°C and the weight loss was determined. None of the complexes showed weight loss at 110°C ruling out the possibility of the presence of water molecules in their lattice structure. On the other hand, the complexes showed weight loss corresponding to two water molecules at 180°C suggesting that they are coordinated to the metal centre. The vapours evolved at 180°C were passed through a trap containing anhydrous CuSO_4 that turned blue indicating that they originate from water molecules.

Molecular weight. The molecular weight data for the complexes (given in Table 1) have been determined in spectral grade DMSO by the freezing point depression method. The experimental values of molecular weights for complexes (1), (3), and (5) are very close to the values calculated based on their monomer formulas confirming their monomeric nature. On the other hand, the experimental values of the molecular weights for the remaining complexes agree with their dimeric character. However, the experimental values of the molecular weights are slightly higher than those calculated based on the suggested dimer compositions. Such higher values of the molecular weights strongly suggest that the structure of the complexes is altered in the strongly coordinating solvent as compared to that in the solid state. Most probably, the coordinated water molecules are substituted by DMSO molecules, which accounts for the higher molecular weights of the complexes.

Magnetic moment. The magnetic moment values for heterobimetallic molybdenum(V) complexes (1), (2), (5), and (6) and mixed-valence molybdenum(V)-molybdenum(VI) complexes (3) and (4) fall in the range 1.59-1.65 B.M. This value lies well within the range reported for Mo(V) complexes without any significant metal-metal interaction. Slightly lower

TABLE 1. Complex, Color, Analytical, Molar Conductance, Magnetic Moment and Electronic Spectral Data for Heterobimetallic and Mixed-Valence Molybdenum(V) Complexes

Sl. No.	Complex (Color)	Mol. Wt. (calc)	Elemental analyses: Found (calc), %					Molar cond. Λ_M , $\text{ohm}^{-1} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$	Magnetic moment μ_{eff} (BM)	Electronic spectral band λ_{max} , nm (ϵ_{max} , $\text{dm}^3 \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$)
			Mo	M	C	H	N			
	CH_2LH_4	—	—	—	68.45 (68.18)	4.62 (4.55)	13.00 (12.73)	—	—	320 (9500), 390 (15700)
1	$[\text{UO}_2\text{Mo}(\text{CH}_2\text{L})(\text{inh}) \times (\text{H}_2\text{O})_2]$ (dark-red)	1085±70 (972)	10.15 (9.88)	25.05 (24.49)	38.95 (38.27)	2.41 (2.47)	9.88 (10.08)	4.5	1.65	340 (11225); 390 (12750), 430 (10250), 500 (7560), 650 (290)
2	$[\text{UO}_2\text{Mo}(\text{CH}_2\text{L})(\text{slh}) \times (\text{H}_2\text{O})_2]$ (Dark-red)	2150±90 (1974)	10.20 (9.73)	23.82 (24.11)	39.25 (38.91)	2.45 (2.53)	8.95 (8.51)	6.0	1.63	350 (7980), 410 (10750), 500 (6720), 640 (310)
3	$[\text{MoO}_2\text{Mo}(\text{CH}_2\text{L})(\text{inh}) \times (\text{H}_2\text{O})_2]$ (red)	930±40 (830)	23.62 (23.13)	—	45.28 (44.82)	2.85 (2.89)	11.26 (11.81)	5.0	1.60	340 (8970), 420 (12750), 520 (5670), 630 (230)
4	$[\text{MoO}_2\text{Mo}(\text{CH}_2\text{L})(\text{slh}) \times (\text{H}_2\text{O})_2]$ (dark-red)	1880±40 (1690)	23.18 (22.72)	—	46.02 (45.44)	2.90 (2.96)	10.10 (9.94)	4.0	1.59	420 (10750), 510 (6780), 640 (250)
5	$[\text{ZnMo}(\text{CH}_2\text{L})(\text{inh}) \times (\text{H}_2\text{O})_2]$ (orange)	890±35 (797.38)	12.05 (12.51)	8.15 (8.36)	48.92 (48.48)	3.10 (3.13)	12.53 (12.77)	3.5	1.64	360 (9750), 430 (12480), 640 (48)
6	$[\text{ZnMo}(\text{CH}_2\text{L})(\text{slh}) \times (\text{H}_2\text{O})_2]$ (reddish-brown)	1750±70 (1564.76)	11.86 (12.27)	8.81 (8.36)	49.83 (49.08)	3.11 (3.20)	10.51 (10.74)	2.7	1.60	340 (8950), 420 (10570), 630 (58)

values than that required for one unpaired electron may be attributed to spin-orbit coupling.

Electronic spectra. The complexes have been characterized by electronic spectroscopy in DMSO solutions. The electronic spectral bands together with molar extinction coefficients for the complexes have been set out in Table 1. The free ligand CH_2LH_4 shows two bands at 320 nm (ϵ_{max} , 9500 $\text{dm}^3 \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$) and 390 nm (ϵ_{max} , 15700 $\text{dm}^3 \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$) in the region 300-400 nm. The band at 320 nm is assigned to the intraligand $\pi \rightarrow \pi^*$ transition, while the band at 390 nm is assigned to the $n \rightarrow \pi^*$ transition, a characteristic of the naphthalaldimine part of the ligand, as has been reported for several monoacylhydrazones [16, 17]. The electronic spectra for the complexes also show two bands in the region 300-450 nm. Both ligand bands at 320 nm and 390 nm showed a red shift on complexation to the metal. The absorption band appearing in the region 340-390 nm in the absorption spectra of the complexes is attributed to the $\pi \rightarrow \pi^*$ transition corresponding to the ligand band at 320 nm. On the other hand, the band appearing in the region 410-430 nm may be assigned to arise due to the ligand band at 390 nm and could be attributed to the $n \rightarrow \pi^*$ transition. The red shift of the ligand bands by 20-70 nm and 20-40 nm provides good evidence of the chelation of dihydrazone to the metal centre. The shift magnitude of the ligand bands on complexation indicates strong bonding between the ligand and the metal centre. All of the complexes show strong bands in the region 340-450 nm, which is indicative of their discrete molecularly [11, 18]. In addition to the ligand bands, complexes (1) to (4) show two new bands in the regions 650-630 nm and 520-500 nm respectively. The bands in this region have been

TABLE 2. EPR Spectral Data for Heterobimetallic and Mixed-Valence Molybdenum(V) Complexes at LNT in DMSO Solution

Sl. No.	Complex	Temp	g_{av}	g_1 or $g_{ }$	g_2	g_3 or $g_{\perp}$	A_{av}	A_1 or $A_{ }$ ($\times 10^{-4} \text{ cm}^{-1}$)	$A_2(g)$	A_3 or $A_{\perp}$
1	[Mo(CH ₂ LH ₂)(inh)]·H ₂ O	LNT (solid)	1.995	2.111	—	1.933	40	70	—	80
	[Mo(CH ₂ LH ₂)(slh)]	LNT (solid)	1.987	2.053	1.993	1.915	40	40	40	40
	[UO ₂ Mo(CH ₂ L)(inh)(H ₂ O) ₂] (dark-red)	LNT (solid)	2.096	2.171	—	1.968	35	65	—	20
	[UO ₂ Mo(CH ₂ L)(slh)(H ₂ O) ₂] ₂ (dark-red)	LNT (solid)	1.975	2.111	1.980	1.833	58	70	40	64
	[MoO ₂ Mo(CH ₂ L)(inh)(H ₂ O) ₂] (red)	LNT (solid)	2.027	2.149	—	1.967	48	40	—	52
	[MoO ₂ Mo(CH ₂ L)(slh)(H ₂ O) ₂] ₂ (dark-red)	LNT (solid)	2.008	2.106	1.980	1.938	—	47	15	—
5	[ZnMo(CH ₂ L)(inh)(H ₂ O) ₂] (orange)	LNT (solid)	1.995	2.005	—	1.965	42	46	—	40
6	[ZnMo(CH ₂ L)(slh)(H ₂ O) ₂] ₂ (reddish-brown)	LNT (solid)	2.030	2.125	2.031	1.933	41	50	20	53

reported to correspond to ligand field transitions ${}^2B_2 \rightarrow {}^2E_1$ and ${}^2B_2 \rightarrow {}^2B_1$ respectively in D_{4h} symmetry [19]. However, the molar absorptivity of the band in the region 520-500 nm lies in the range $7560\text{-}5670 \text{ dm}^3\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$. Such a high molar extinction coefficient for this band suggests that it mainly arises due to charge-transfer transitions masking weak ligand-field band occurring in this region. Further, the molar extinction coefficient for the band in the region 650-630 nm lies in the range $330\text{-}250 \text{ dm}^3\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$. The enhancement in the intensity of this band is probably due to the intensity borrowing from the adjacent charge transfer band. On the other hand, heterobimetallic Zn–Mo(V) complexes (5) and (6) show a single band at 630 nm, and the molar extinction coefficient of this band is $48 \text{ dm}^3\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ and $58 \text{ dm}^3\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ respectively. In these complexes, this band is ascribed mainly to the ligand field transition that is ${}^2B_2 \rightarrow {}^2E_1$ in character. The position of the ligand field bands remains almost the same as in the precursor monometallic complexes, indicating that the second metal centre present in the complexes does not affect the energy gap of the first electronic excitation transition.

Electron paramagnetic resonance (EPR). All complexes have been characterized by EPR spectroscopy at LNT in the solid state. Various EPR parameters for the complexes have been set out in Table 2. The EPR spectra for complexes (1), (4), (5), and (6) have been shown in Fig. 2.

The two types of heterobimetallic and mixed-valence molybdenum complexes (1) to (6) show anisotropic spectra, but still there are significant differences between the spectral features of these complexes which are dependent on the type of the secondary ligands, i.e. isonicotinoylhydrazine and salicyloylhydrazine coordinated to the metal centres. The EPR spectra of the complexes show the features similar to their corresponding precursor monometallic complexes [Mo(CH₂LH₂)(inh)]·H₂O and [Mo(CH₂LH₂)(slh)] [11]. This observation indicates that the essential features of the molybdenum(V) centre in these complexes remain the same as those in their precursor monometallic complexes. The spectra of heterobimetallic molybdenum(V) and mixed-valence Mo(V)–Mo(VI) complexes (1), (3), and (5), containing coordinated isonicotinoyldiazenido groups in the coordination sphere, possess axial symmetry [20]. The $g_{||}$ value for these complexes lies in the range 2.171-2.055, while the $g_{\perp}$ value lies in the range 1.968-1.965. On the other hand, heterobimetallic Mo(V) and mixed-valence Mo(V)–Mo(VI) complexes (2), (4), and (6), containing coordinated salicyloyldiazenido groups in the coordination sphere, show complete anisotropy in their spectral features, and the g -values are in the regions 2.106-2.125,

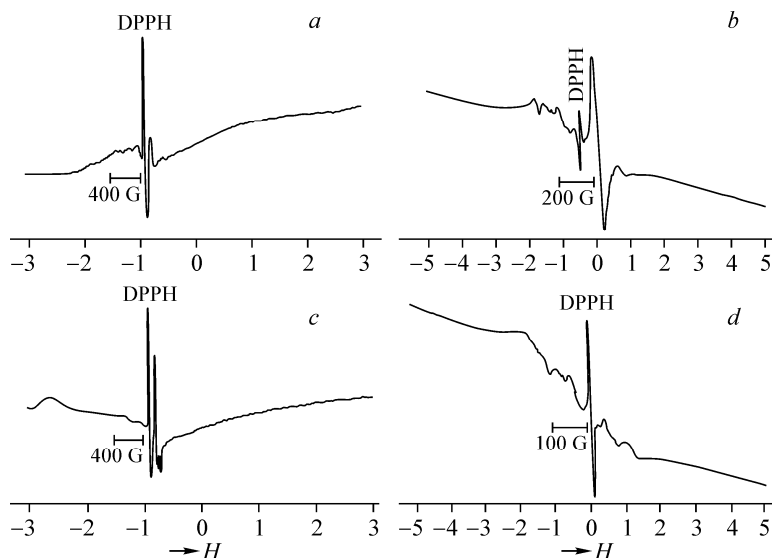


Fig. 2. EPR spectra of the complexes at 293 K in the solid state: (a) 1; (b) 4; (c) 5; and (d) 6.

1.980–2.031, and 1.838–1.938 respectively. This feature suggests that the x , y , and z coordinate axes are highly misaligned, which may be related to the coordination of the salicyloyl–OH group to the metal centre in complexes (2), (4), and (6). Further, the EPR spectral features for these complexes are consistent with the rhombic symmetry of the complexes [21]. However, the derived g and A tensor components are different from those of the precursor complexes, which is obviously due to the effect of another metal present in the same molecular unit of the complex. It is imperative to mention that the g_{av} and $g_{\parallel}$ values decrease in going from UO_2 –Mo(V) complex (1) to MoO_2 –Mo(V) complex (3), and to Zn–Mo(V) complex (5). Although, the $g_{\perp}$ value for the complexes also decreases in the same order, but it is not so pronounced. No such trend is observed in other complexes (2), (4), and (6) containing the coordinated salicyloyldiazenido group.

Infrared spectra. Structurally significant IR spectral bands for CH_2LH_4 , precursor monometallic complexes, and heterobimetallic and mixed-valence Mo(V) complexes have been set out in Table 3. A comparison of the IR spectra of the heterobimetallic complexes with those of the ligand and their precursor complexes suggests that dihydrazone is present in the *enol* form in both types of the complexes. The ligand shows strong broad bands centred at 3450 cm^{-1} , 3200 cm^{-1} , and 3047 cm^{-1} . These bands are assigned to arise from the stretching vibrations of naphtholic–OH and secondary –NH groups respectively [11, 22]. Complexes (2), (4), and (6) show a strong broad band in the 3550 – 3000 cm^{-1} region with peaks in the 3420 – 3400 cm^{-1} and 3220 – 3186 cm^{-1} regions respectively, and the remaining complexes show only a single strong broad band in the region 3550 – 3000 cm^{-1} with a broad peak in the 3420 – 3400 cm^{-1} region. The essential feature of the band in the region 3420 – 3400 cm^{-1} in all complexes is similar in its shape and position to those commonly observed for water or ethanol and accordingly, has been assigned to the $\nu(\text{OH})$ mode. However, from its position and intensity it is not possible to distinguish whether they are coordinated to the metal centre or present in the lattice. But the presence of a band in the region 670 – 644 cm^{-1} in the complexes assigned to the ρ_r mode of coordinated water suggests that these are water molecules that are present in the first coordination sphere around the metal centre in the complexes rather than the ethanol molecules [23]. Moreover, all complexes show weight loss at 180°C corresponding to two water molecules lending credence to the suggested number of coordinated water molecules. The fact that the weight loss occurs due to the water molecules was confirmed by passing the ensuing vapors through a trap containing anhydrous copper sulphate that turned blue. This further ruled out the possibility of the presence of ethanol molecules in the complexes and withal unambiguously establishes the water molecules coordinated to the metal centre. On the other hand, complexes (2), (4) and (6) show a new band in the region 3220 – 3212 cm^{-1} , which is not observed in complexes (1), (3), and (5). This band is relatively broader than the common νNH band, which rules

TABLE 3. Infrared Spectral Data for Heterobimetallic and Mixed-Valence Molybdenum(V) Complexes

Sl. No.	Ligand/complex	$\nu(\text{OH})+\nu(\text{NH})$	Amide I $\nu(\text{C=O})$	$\nu(>\text{C}=\text{N}-\text{N}=\text{C}<)$	Amide II $\nu(\text{C-O})$ (phenolic)	$\nu(\text{NCO})$	$\nu(\text{N=N})$	$\beta(\text{C-O})$	$\nu(\text{N-N})$	$\nu(\text{MO}_2^{2+})$	$\nu(\text{M-O})$ (naphtholate)	$\nu(\text{M-O})$ (carbonyl)
1	CH_2LH_4	3450sbr 3200s 3047s	1699vs 1661vs	1617vs 1596vs	1532vs	—	—	1278s	1030w	—	—	—
	$[\text{Mo}(\text{CH}_2\text{LH}_2)(\text{inh})]\text{H}_2\text{O}$	3500- 3000sbr	1671 s	1618 s 1594 s	1534 s	—	1504 s	1272 s	1057 w	—	—	—
	$[\text{Mo}(\text{CH}_2\text{LH}_2)(\text{slh})]$	3395s 3212s	1669 m	—	1535 s	—	1481 s	—	1031 w	—	—	—
	$[\text{UO}_2\text{Mo}(\text{CH}_2\text{L})(\text{inh})(\text{H}_2\text{O})_2]$ (dark-red)	3550- 3000sbr	—	1661vs 1597vs	1540s	—	1508s	1272s	1060w	907vs	587m 529w	473m
	$[\text{UO}_2\text{Mo}(\text{CH}_2\text{L})(\text{slh})(\text{H}_2\text{O})_2]_2$ (dark-red)	3550- 3300sbr 3217s	—	1617s 1598s	1539vs	—	1486s	1292m	1033w	919m	591m 530m	459w 433w
	$[\text{MoO}_2\text{Mo}(\text{CH}_2\text{L})(\text{inh})(\text{H}_2\text{O})_2]$ (red)	3550- 3000sbr	—	1617vs 1600vs	1544vs	1517m	1486s	—	1039m	939vs 913vs	592w 513w	464w 434w
2	$[\text{MoO}_2\text{Mo}(\text{CH}_2\text{L})(\text{slh})(\text{H}_2\text{O})_2]_2$ (dark-red)	3400sbr 3213s 3133s	—	1616s 1597vs	1540s	1503m	1503w	1275m	1066w	947s 906vs	595s	437w
3	$[\text{ZnMo}(\text{CH}_2\text{L})(\text{inh})(\text{H}_2\text{O})_2]$ (orange)	3550- 3000sbr	—	1617vs 1600vs	1540vs	1504s	1504s	1272m	1036w	—	568w	442w
4	$[\text{ZnMo}(\text{CH}_2\text{L})(\text{slh})(\text{H}_2\text{O})_2]_2$ (reddish-brown)	3400sbr 3220s 3134s	—	1616vs 1599vs	1540s	1520s	1486m	1278m	1040w	—	595w	470w

out the possibility of its origin from secondary NH groups; instead it suggests that this band originates from the stretching vibration of the OH group. The shape and position of this band is similar to that observed for complexes containing salicyloyl-based hydrazides and hadrazones, where the salicyloyl–OH group has been reported to coordinate to the metal centre.

The $\nu(\text{C=O})$ band present at 1699 cm^{-1} and 1661 cm^{-1} in free dihydrazone is absent in both types of heterobimetallic and mixed-valence molybdenum complexes, indicating the collapse of the amide structure of dihydrazone as a result of enolization on introduction of the second metal centre as a consequence of the heterometallic complex formation. The $\nu(\text{C=N})$ band appears as a couple of bands in these complexes, similar to those observed in free dihydrazone. This feature of the C=N band observed in the complexes suggests that the two $>\text{C=N}$ groups are inequivalent in these complexes. Such an inequivalency in the $>\text{C=N}$ groups arises due to the coordination of dihydrazone to the metal centre in the *anti-cis* configuration, where the molecule is oriented in such a manner that half of hydrazine is out of the molecular plane and the other half remains in the molecular plane [22]. Another interesting observation is that the $\nu(\text{C=N})$ band shifts to a higher frequency by $1\text{--}3\text{ cm}^{-1}$ in all complexes. This shift of the $\nu(\text{C=N})$ band to higher frequencies indicates an increase in the $>\text{C=N}$ bond order. This increase in the bond order of the $>\text{C=N}$ group in the complexes manifests the flow of electron density from the naphthyl ring to the metal centre through the azomethine nitrogen atom. This process gives rise to a stronger azomethine nitrogen-to-metal bond, which may be related to the nature of the metal ion bonded to the azomethine nitrogen atom.

Complexes (3) to (6) show a band in the region $1520\text{--}1503\text{ cm}^{-1}$, which is characteristic of the newly created NCO^- group produced as a result of enolization of dihydrazone [23, 24]. A strong to very strong band in the $1544\text{--}1531\text{ cm}^{-1}$ region is observed for all the complexes, which is assigned to the $\nu(\text{C--O})$ (naphtholate) vibration. The position of this band is consistent with the bonding of the naphtholate oxygen atom to the metal centre. However, in complex (2), this band has a contribution due to the stretching vibration of the NCO^- group produced as result of enolization of dihydrazone. The $\beta(\text{C--O})$ band appears in the region $1292\text{--}1272\text{ cm}^{-1}$ in the complexes. The $\nu(\text{N--N})$ band appears in the region $1095\text{--}1030\text{ cm}^{-1}$, similar to that in the precursor monometallic complexes indicating the coordination of only one hydrazinic nitrogen atom to the metal centre [25].

All complexes do not show any band in the region $1630\text{--}1700\text{ cm}^{-1}$, which could be assigned either to $>\text{C=O}$ or δNH_2 vibrations of the hydrazide ligand. Further, complexes (5) and (6) do not show any strong band in the region $850\text{--}1000\text{ cm}^{-1}$ due to the $\nu\text{Mo=O}$ vibrations of the *cis*- MoO_2^{2+} group. The absence of any band characteristic of $>\text{C=O}$ and $-\text{NH}_2$ groups in the region $1630\text{--}1700\text{ cm}^{-1}$ along with the $\nu\text{Mo=O}_t$ vibration indicates the condensation of the $-\text{NH}_2$ group of hydrazides with the Mo=O group. This is further confirmed by that these complexes show a new band in the region $1486\text{--}1508\text{ cm}^{-1}$, which is a characteristic of the newly created (N=N) group [26, 27]. All these facts together account for the presence of pyridoyldiazenido and salicyloyldiazenido groups in the coordination sphere of the complexes. It is assumed that the parent metal ion, i.e., the Mo(V) ion retains the N_2O_2 coordination chamber. This assumption regarding the retention of the N_2O_2 coordination chamber by Mo^{V} is entirely on IR spectroscopic evidences and is merely tentative.

Mixed-valence $\text{MoO}_2(\text{VI})\text{--Mo(V)}$ complexes (3) and (4) show two new bands in the region $947\text{--}906\text{ cm}^{-1}$; on the other hand, heterobimetallic $\text{UO}_2(\text{VI})\text{--Mo(V)}$ complexes (1) and (2) show only one band at 907 cm^{-1} and 919 cm^{-1} respectively. The two bands observed in the region $947\text{--}907\text{ cm}^{-1}$ for complexes (3) and (4) are assigned to the symmetric and asymmetric vibrations of the *cis*- MoO_2^{2+} group, while only one band is observed in this region at 907 cm^{-1} and 919 cm^{-1} for complexes (1) and (2) is assigned to the $\nu_3(\text{UO}_2^{2+})$ vibration of the linear oxo-uranyl group respectively [28]. The absence of any band assignable to the oxo-molybdenum group for complexes (1), (2), (5), and (6) suggests that molybdenum is present in the non-oxo form, similar to that in the precursor complexes. The IR spectra of the complexes in the region below 600 cm^{-1} are very complicated and have several other weak bands in addition to the ligand bands. This is obviously due to the split of ligand vibrations as well as the presence of $\nu(\text{M--O})$ (naphtholic), $\nu(\text{M--O})$ (carbonyl), and $\nu(\text{M--O})$ (aquo) bands. On the careful analysis of the spectra of the ligand and metal complexes in this region, the bands appearing in the $595\text{--}525\text{ cm}^{-1}$ and $474\text{--}433\text{ cm}^{-1}$ regions are tentatively assigned to $\nu(\text{M--O})$ (naphtholic) [29] and $\nu(\text{M--O})$ (carbonyl) [30] respectively.

CONCLUSIONS

The heterobimetallic complexes of molybdenum(V) with dioxouranium(VI) and zinc(II) and mixed-valence dioxomolybdenum(VI)-molybdenum(V) complexes were synthesised from dihydrazone and proton donor ligands. Dihydrazone is coordinated to the metal centres in the *anti-cis*-configuration in all the complexes. In this form, the naphthalaldimine fraction of dihydrazone is bonded to one metal centre, while carbonyl oxygen atoms are bonded to the second metal centre. The isonicotinoylhydrazide co-ligand is bonded to the molybdenum(V) centre in the condensed form as a trinegative-bidentate ligand through the terminal azenido nitrogen atom and the carbonyl oxygen atom in the enol form, while the salicyloylhydrazide co-ligand is bonded to the metal centre as a trinegative-tridentate ligand through the terminal azenido nitrogen atom, enolic-carbonyl oxygen atom, and salicyloyl-OH group. The molybdenum(V) metal centre in the N_2O_2 coordination chamber retains its original six-coordinate stereochemistry in heterobimetallic complexes (1), (3), and (5), whereas it attains seven-coordinate pentagonal bipyramidal stereochemistry in complexes (2), (4), and (6).

The tentative structures of the complexes are shown in Fig. 3.

Arvind Kumar thanks to the Campus Research and Publication Fund, the University of West Indies, St. Augustine and Ram A. Lal thanks UGC, New Delhi, India for the grant of financial assistance through the major research project.

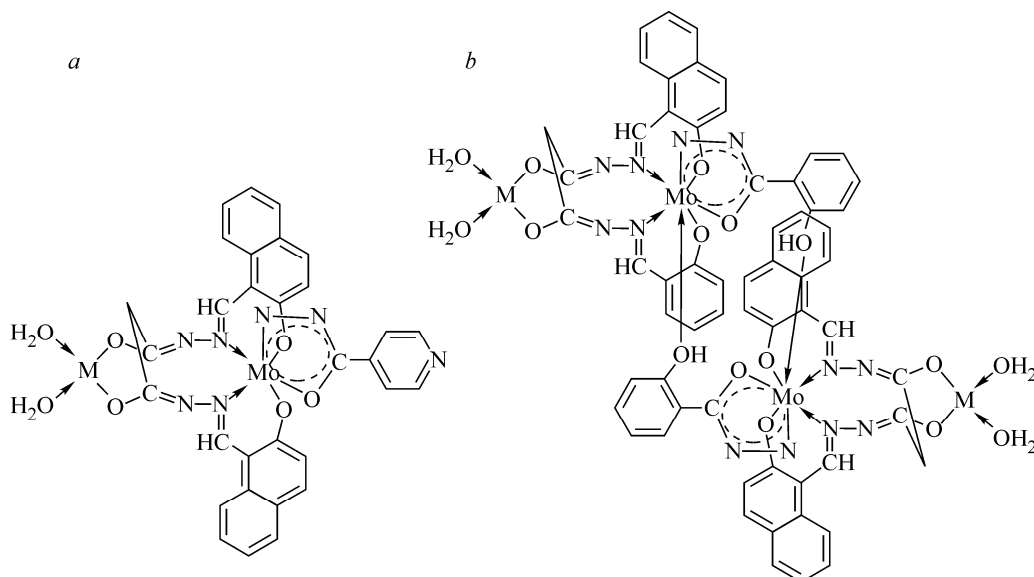


Fig. 3. Tentative structure of the complexes: (a) $[\text{MMo}(\text{CH}_2\text{L})(\text{inh})(\text{H}_2\text{O})_2]$ ($\text{M} = [\text{O}=\text{U}=\text{O}]^{2+}$ (1), MoO_2^{2+} (3), Zn (5)) and (b) $[\{\text{MMo}(\text{CH}_2\text{L})(\text{slh})(\text{H}_2\text{O})_2\}_2]$ ($\text{M} = [\text{O}=\text{U}=\text{O}]^{2+}$ (2), MoO_2^{2+} (4), Zn (6)).

REFERENCES

1. G. Schwarz, R. R. Mendel, and M. W. Ribbe, *Nature*, **460**, 839-847 (2009).
2. B. K. Burgess and D. J. Lowe, *Chem. Rev.*, **96**, No. 7, 2983-3011 (1996).
3. C. Liu, H. Zhang, W. Shi, and A. Lei, *Chem. Rev.*, **111**, No. 3, 1780-1824 (2011).
4. J. H. Therston, A. Kumar, C. Hofmann, and K. H. Whitmire, *Inorg. Chem.*, **43**, No. 26, 8427-8436 (2004).
5. G. M. Sammis, H. Danjo, and E. N. Jacobsen, *J. Am. Chem. Soc.*, **126**, No. 32, 9928/9929 (2004).
6. S. Leelasubcharoen, P. A. Zhizhko, L. S. Kuzmina, A. V. Churakov, J. A. K. Howard, and G. I. Nikonov, *Organometallics*, **28**, No. 15, 4500-4506 (2009).
7. B. P. Greenwood, S. I. Forman, G. T. Rowe, C. H. Chen, B. M. Foxman, and C. M. Thomas, *Inorg. Chem.*, **48**, No. 13, 6251-4560 (2009).
8. M. Andruh, *Chem. Commun.*, **47**, No. 11, 3025-3042 (2011).
9. H. Galoms, C. Cave, M. Miocque, P. Rinijard, G. Tran, and P. Binet, *Eur. J. Med. Chem.*, **25**, No. 9, 785-788 (1990).
10. O. A. Rajan and A. Chakravorty, *Inorg. Chem.*, **20**, No. 3, 660-664 (1981).
11. R. A. Lal, O. B. Chanu, R. Borthakur, M. Asthana, A. Kumar, and A. K. De, *J. Coord. Chem.*, **64**, No. 8, 1393-1410 (2011).
12. A. I. Vogel, *A Text Book of Quantitative Inorganic Analysis*, Longman, London (1973).
13. R. L. Lintvedt, W. E. Lynch, and J. K. Zehetmair, *Inorg. Chem.*, **29**, No. 16, 3009-3013 (1990).
14. J. B. Carlson, G. Davies, and P. Vouros, *Inorg. Chem.*, **33**, No. 11, 2334-2340 (1994).
15. W. J. Geary, *Coord. Chem. Rev.*, **7**, No. 1, 81-122 (1971).
16. A. A. R. Despaigne, J. G. da Silva, A. C. M. do Carmo, F. Sives, O. E. Piro, E. E. Castellano, and H. Beraldo, *Polyhedron*, **28**, No. 17, 3797-3803 (2009).
17. S. C. Chan, L. L. Koh, P. H. Leung, J. D. Ranford, and K. Y. Sim, *Inorg. Chim. Acta*, **236**, Nos. 1/2, 101-108 (1995).
18. S. A. Patil and V. H. Kulkarni, *Inorg. Chim. Acta*, **95**, No. 4, 195-199 (1984).
19. C. S. J. Chang, D. Callison, F. E. Mabbs, and J. H. Enemark, *Inorg. Chem.*, **29**, No. 12, 2261-2267 (1990).
20. S. B. Kumar and M. Chaudhury, *Dalton Trans.*, No. 8, 2169-2174 (1991).

21. I. K. Dhawan and J. H. Enemark, *Inorg. Chem.*, **35**, No. 12, 4873-4882 (1996).
22. R. A. Lal, S. Choudhury, A. Ahmed, R. Borthakur, M. Asthana, and A. Kumar, *Spectrochim. Acta*, **75**, No. 1, 212-224 (2010).
23. M. P. Degaonkar, V. G. Puranik, S. S. Tavale, S. Gopinathan, and C. Gopinathan, *Bull. Chem. Soc. Jpn.*, **67**, No. 7, 1797-1801 (1994).
24. R. A. Lal, M. Chakrabarty, S. Choudhury, A. Ahmed, R. Borthakur, and A. Kumar, *J. Coord. Chem.*, **63**, No. 1, 163-175 (2010).
25. A. Braibanti, F. Dallavalle, M. A. Pellinghelli, and E. Leporati, *Inorg. Chem.*, **7**, No. 7, 1430-1433 (1968).
26. H. Kang, S. Liu, S. N. Saikh, T. Nicholson, and J. Zubietta, *Inorg. Chem.*, **28**, No. 5, 920-933 (1989).
27. M. D. Fitzroy, J. M. Frederiksen, K. S. Murray, and M. R. Snow, *Inorg. Chem.*, **24**, No. 20, 3265-3270 (1985).
28. J. Topich and J. O. Bachert III, *Inorg. Chem.*, **31**, No. 3, 511-515 (1992).
29. G. C. Percy, *J. Inorg. Nucl. Chem.*, **37**, No. 10, 2071-2073 (1975).
30. L. Sacconi, A. Sabatini, and P. Gans, *Inorg. Chem.*, **3**, No. 12, 1772-1774 (1964).