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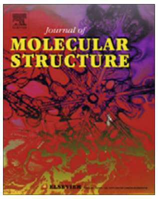

Synthesis, spectroscopic and electrochemical characterisation of binuclear dioxomolybdenum complexes derived from disalicylaldehyde succinoyldihydrazone

Aziz Ahmed [a,*], Oinam B. Chanu [b], Angira Koch [b], R.A. Lal [b]

[a] *Department of Chemistry, Indian Institute of Technology, Patna-13, Bihar, India*
[b] *Department of Chemistry, North Eastern Hill University, Shillong 793 022, Meghalaya, India*

HIGHLIGHTS

- ▶ Homobimetallic Complexes have been synthesized and characterised.
- ▶ The ligand present in enol form in the complexes.
- ▶ Bimetallic monomeric complexes.
- ▶ The dihydrazone coordinates to Mo(VI) centre as tetrabasic hexadentate tridentate ligand.

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ABSTRACT

The diamagnetic dioxomolybdenum (VI) complexes **$[(MoO_2)_2(L).(H_2O)_2]$** where $H_4L = H_4$slsh have been isolated in solid state from the reaction of $MoO_2(acac)_2$ and disalicylaldehyde succinoyldihydrazone (H_4L) in 3:1 molar ratio in ethanol at higher temperature. The reaction of the complex with electron donor bases gives diamagnetic molybdenum(VI) complexes having composition **$[(MoO_2)_2(L)(A)_2]\cdot H_2O$** (where A = pyridine (py, 2), 2-picoline (2-pic, 3), 3-picoline (3-pic, 4), 4-picoline (4-pic, 5). The composition of the complexes have been established by analytical, thermo-analytical data. The structure of the molybdenum (VI) complexes has been established by mass, electronic, IR, ^{1}H NMR and CV spectral studies. The dihydrazone is coordinated to the metal centres in *staggered* configuration in all the complexes. The electronic spectra of the complexes are dominated by strong charge transfer bands. All of the complexes involve six coordinated molybdenum centre with octahedral arrangement of donor atoms.

1. Introduction

Molybdenum is a versatile transition element possessing a large number of stable and accessible oxidation states. It is the only element from second transition series which occurs in the biological system [1]. In combination with oxo and imido ligands, molybdenum plays a very important role in its catalytic chemistry [2] and biochemistry [3]. Molybdenum complexes with highly reactive oxo ligands capable of participating in several reaction with saturated/unsaturated organic molecules constitute an active area of research for defining unprecedented bond constructions and functional group transformation. The oxo ligands have the potential to be a six-electron donors through a σ and two degenerate $p\pi$–$d\pi$ bonds to the metal. In certain configuration of the complexes containing multiply bonded ligands, for example, if mutually *cis*, the ligands compete for three molybdenum π-orbitals originating from the metal dxy, dyz and dxz orbitals [4]. Thus one of the multiply bonded ligands can form a triple bond to the metal as a six electron donor ($1\sigma + 2$pi) while the other can only form a metal–ligand double bond with four electron donor ($1\sigma + 1$pi) reflecting that the multiple bonding is brought about through p-pi/d-pi interactions. Metal–ligand bonding in such complexes involves σ-/π-electrons of *o*-hydroxy aromatic aldehydes and ketones. There have been numerous reports of transition metal complexes containing polyfunctional ligands derived from aromatic aldehydes and ketones [5] with two nitrogen and two oxygen donor atoms as well as other similar ligands [6] in which one or both aryl rings are electron-withdrawing. Dihydrazones derived from condensation of acyl-, aroyl-, pyridoyl-dihydrazines with *o*-hydroxy aromatic aldehydes and ketones are related ligands possessing four oxygen and four nitrogen donor atoms [7]. As the growth of interest in the use of polyfunctional ligands containing electron-withdrawing bulky fragments in their molecular skeleton becomes more

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[*] Corresponding author.
E-mail address: azizahmed@iitp.ac.in (A. Ahmed).

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significant [5,8], we are interested in the synthesis and characterisation of the metal complexes derived from polyfunctional ligand containing electron-withdrawing bulky phenyl fragments in its molecular skeleton and to see as if it could readily be prepared and how the chemical reactivity of these complexes varies relative to their corresponding complexes derived from dihydrazone obtained from condensation of acyl-, aroyl- and pyridoyl-dihydrazines with simple aldehydes and ketones. The ligand disalicylaldehyde succinoyldihydrazone, example of polyfunctional dihydrazone, has been selected in the present study. This ligand has been derived from condensation of salicylaldehyde with succinoyldihydrazine and possesses as many as eight oxygen and nitrogen donor atoms.

The dihydrazone is capable of giving rise to monometallic [9], homobimetallic [7] and heterobimetallic [9,10] complexes. Although, the ligand is a potential polyfunctional ligand, even then only meager amount of work has been done on its Zn^{II}, Cu^{II}, Ni^{II} and Mn^{II} complexes only [11]. It seems that no complexes of the ligand with oxo metal ions are yet known. In continuance of our interest in the chemistry of oxometal cations ligated to nitrogen and oxygen donors with NO_2 and N_2O_4 chromophores [12] the present work aims to pursue the synthesis and characterisation of some binuclear monomeric Mo(VI) complexes, derived from the title ligand disalicylaldehyde succinoyldihydrazone (Fig. 1) and its reactivity study with proton and electron donor reagents and the characterisation of the resulting compounds.

2. Experimental

Ammonium molybdate $(NH_4)_6Mo_6O_{24}\cdot4H_2O$, hydrazine hydrate $(N_2H_4\cdot H_2O)$, salicylaldehyde $(C_6H_4(OH)CHO)$, diethylsuccinate $(CH_2)_2(COOEt)_2$ were E-Merck or equivalent grade reagents. The ligand disalicylaldehyde succinoyldihydrazone was prepared in two steps. In the Ist step, succinoyl-(H_6sh) was prepared by reacting diethylsuccinate with hydrazine hydrate in 1:2 molar ratio. In the second step, succinoyldihydrazine thus obtained were allowed to react with salicylaldehyde in 1:2.2 molar ratio in ethanol which yielded the ligand H_4slsh(L). $MoO_2(acac)_2$ was prepared by a reported method [13].

The reactions were carried out in open air. The ethanol used as solvent is 95%. The estimation of molybdenum was done by following the standard literature procedure [14]. Room temperature magnetic susceptibility measurements were carried out on Sherwood Scientific Magnetic susceptibility Balance MBS-Auto. The molar conductance of the complexes at 10^{-3} M dilution in DMSO solution were measured on Wayne Kerr Precision Component Analyser 6440B with a dip-type conductivity cell at room temperature. Infrared spectra were recorded on Bomen (1) A-8FT-IR Spectrophotometer in the range 4000–450 cm^{-1} and (2) Spectrum-BX Perkin Elmer in KBr discs. Low frequency infrared spectra were recorded in the range 600–30 cm^{-1} on Perkin Elmer Spectrum 400 in CsI discs. The electronic spectra were recorded on a Perkin Elmer Lamda 25 UV/Vis spectrophotometer using DMSO solution. The mass spectra of the complexes were recorded on Liquid Chromatoghaphy–Mass Spectrometer Model: Waters ZQ-4000. The ^1H NMR spectra were recorded on AMX-400 MHz and Varian 400 MHz in DMSO-d_6 using TMS as internal standard. The Cyclic Voltammetric measurement of the complexes in DMSO (10^{-3} M) was done using CH Instruments Electrochemical Analyser under nitrogen atmosphere. The electrolytic cell comprises of 3-electrodes. The working electrode was a glassy carbon disc from BAS and the reference electrode was a aqueous SCE or Ag/AgCl separated from the sample solution by a salt bridge, 0.1 M TBAP was used as the supporting electrolyte.

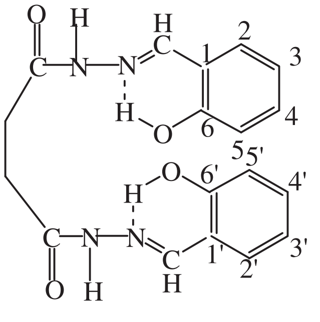


Fig. 1. Disalicyldehyde Succinoyldihydrazone.

3. Synthesis of complex $[(MoO_2)_2(L)(H_2O)_2]$ ($H_4L = H_4$slsh (1))

A typical procedure for the preparation of this complex is given below.

$MoO_2(acac)_2$ (2.80 g, 8.59 mmol) in ethanol (85 mL) was dissolved by gentle heating. Dihydrazone (H_4slsh) (1.00 g, 2.94 mmol) in (80 mL) ethanol was taken and stirred for about 15 min to give a homogeneous suspension which was added to $MoO_2(acac)_2$ solution drop by drop over a period of 15 min accompanied by refluxing of the reaction mixture for $1^{1/2}$ h at 65 °C. This yielded a yellow coloured precipitate which was filtered off and washed with EtOH, ether and dried over anhydrous $CaCl_2$. Yield: 0.81 g.

Synthesis of complex $[(MoO_2)_2(L)(A)_2]\cdot H_2O$ (where $H_4L = H_4$slsh, A = pyridine (py, 2), 2-picoline (2-pic, 3), 3-picoline (3-pic, 4), 4-picoline (4-pic, 5):

A typical procedure for the preparation of these complexes is given below.

$MoO_2(acac)_2$ (2.56 g, 7.85 mmol) was dissolved in (50 mL) ethanol by gentle heating and stirring. A suspension of H_4slsh (1 g, 2.82 mmol) in ethanol (50 mL) was added to the above solution accompanied by stirring for a period of 15 min. To this solution, pyridine (2.01 g, 2.54 mmol) was added accompanied by vigorous stirring for about $1^{1/2}$ h maintaining $MoO_2(acac)_2$, H_4slsh and pyridine in the molar ratio 3:1:10. This precipitated the complexes which was filtered in hot condition, washed three times with 10 mL ethanol each time and finally with ether and dried over anhydrous $CaCl_2$.

The remaining complexes were also obtained by following essentially the above procedure by adding simultaneously pyridine bases to the suspension obtained by mixing $MoO_2(acac)_2$ and H_4L maintaining $MoO_2(acac)_2$: H_4L and pyridine bases molar ratio at 3:1:10. The complexes were isolated in the same way. Yield: (0.69–7.8) g.

4. Results and discussion

All of the complexes have been prepared by the same general method carrying out reaction between $MoO_2(acac)_2$ and dihydrazone in 3:1 molar ratio in ethanol either as such or in the presence of monodentate pyridine bases maintaining $MoO_2(acac)_2$, H_4L and pyridine base molar ratio at 3:1:10. Accordingly, the complexes have the same general composition $[(MoO_2)_2(H_4L)(H_2O)_2]$ and $[(MoO_2)_2(H_4L)(A)_2]\cdot H_2O$ where ($H_4L = H_4$slsh; A = py, 2-pic, 3-pic and 4-pic). These compounds are light yellow, yellow, orange and yellowish orange, respectively. All of the complexes are air-stable and decompose above 300 °C without melting. All of the complexes are insoluble in water and common organic solvents such as EtOH, MeOH, acetone, CCl_4, $CHCl_3$, benzene and ether while they are completely soluble in highly coordinating solvents such as DMSO and DMF. A consistent effort to crystallize the complexes either from saturated solution or by diffusing into saturated solution in

CH_3CN, DMSO and DMF in a closed system led to the precipitation of amorphous products. Such behaviour of the complexes with regard to their crystallization prevented their analyses by X-ray crystallography.

All complexes except (1), show weight loss corresponding to one water molecule at 110 °C indicating the presence of one water molecules in their lattice structure and while the complex (1) shows weight loss corresponding to two water molecules at 180 °C, only suggesting that these water molecules are present in the first coordination sphere around the metal centre. The remaining complexes do not show any weight loss at this temperature ruling out the possibilities of presence of coordinated water molecules to the metal centre [15]. However, the complexes (2–5), showed weight loss at 220 °C corresponding to two py/2-pic/3-pic/4-pic molecules. The expulsion of these donor molecules at this temperature indicates that they are coordinated to the metal centre.

4.1. Mass spectra

The complex (1) has been studied with the help of mass spectral study as representative examples to assess the molecular complexity of the complexes in general. The mass spectrum of the complex (1) is shown in Fig. 2. The mass spectrum of the complex shows a peak at m/z value of 607.1. This m/z value of 607.1 matches with the mass of the molecular fragment $[(MoO_2)_2(slshH)]^+$ (607.26). This ion results from the loss of both the water molecules from the first coordination sphere of the complex [16]. The mass spectrum of the complex (1) clearly demonstrates the presence of $[(MoO_2)_2(slshH)]^+$ (607.26) molecular ion as the major species in solution in the form of single charged monoprotonated species [17]. Such mass spectral behaviour of the complex suggests that it is bimetallic monomeric and does not undergo dimerization even under the conditions of study by mass spectrometry.

4.2. Molar conductance

All of the complexes have molar conductance value in the region 1.3–2.9 Ω^{-1} cm^2 mol^{-1} in DMSO solution at 10^{-3} M dilution. These values are consistent with the non-electrolytic nature in this solvent [18].

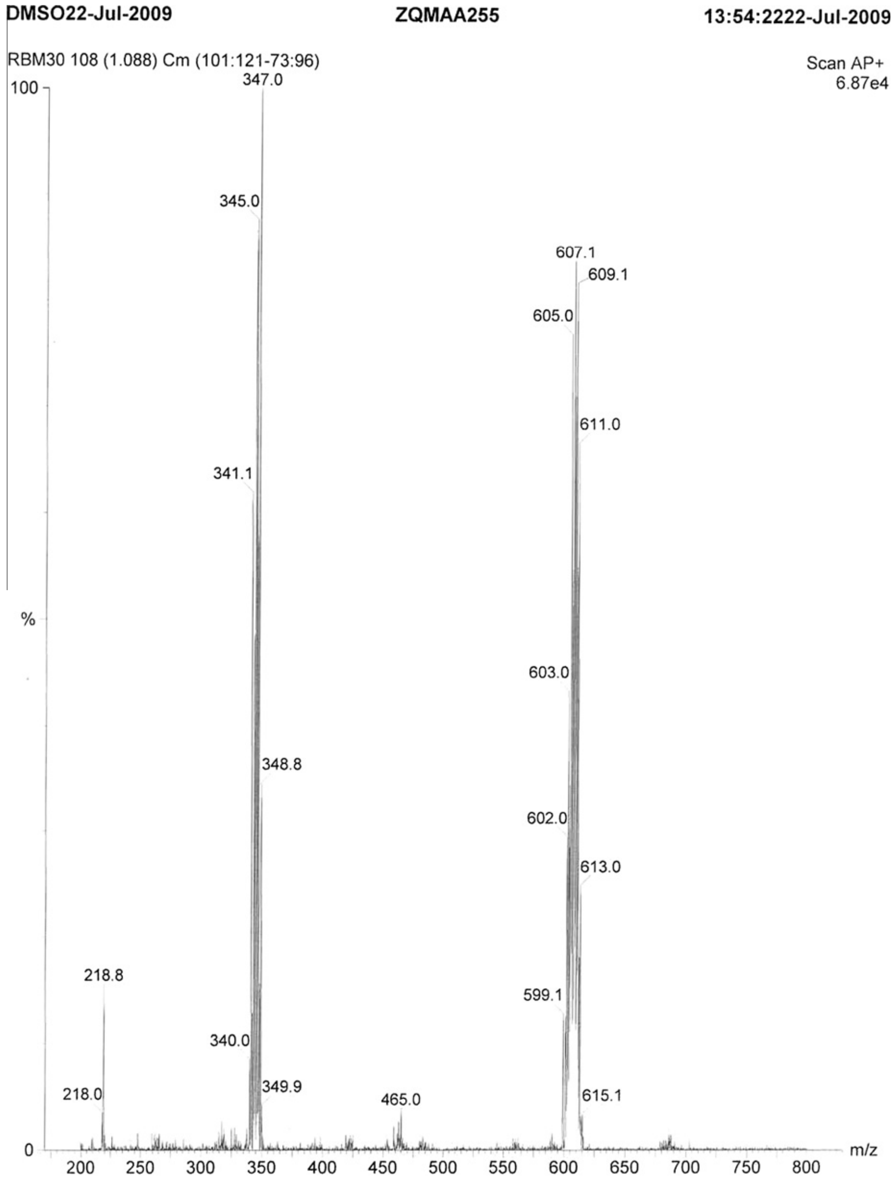


Fig. 2. Mass spectrum of [(MoO2)2(slsh)(H2O)2] (**1**) in DMSO.

Table 1
Complexes, colour, decomposition point, elemental analysis, molar conductance and Electronic spectral data for homobimetallic molybdenum(VI) complexes derived from disalicylaldehyde succinoyldihydrazone.

Sl. No.	Complex/ligand and colour	D.P (°C)	Yield (%)	Elemental analysis: found (cal)%				Molar conductance (Ω^{-1} cm^2 mol^{-1})	Electronic spectral bands λ_{max} (nm) ε_{max} (dm^{-3} mol^{-1} cm^{-1})
				Mo	C	H	N		
L	H_4slsh	250	80	–	61.23 61.01	5.15 5.12	15.69 15.81	–	283(33333), 322(11700)
1	$[(MoO_2)_2(slsh)(H_2O)_2]$ Orange	>300	67	29.65 (29.88)	33.13 (33.66)	2.80 (2.83)	8.79 (8.72)	1.8	282(74000), 293(73600), 309(61200), 403(6400)
2	$[(MoO_2)_2(slsh)(py)_2]\cdot H_2O$ Orange Yellow	>300	70	24.23 (24.52)	42.59 (42.98)	3.39 (3.36)	10.92 (10.74)	2.3	282(49140), 292(48510), 313(39255), 403(3520)
3	$[(MoO_2)_2(slsh)(2\text{-pic})_2]\cdot H_2O$ Orange	>300	71	23.59 (23.67)	44.81 (44.45)	3.53 (3.49)	10.98 (10.36)	1.8	282(44897), 292(43877), 321(33673), 403(2040)
4	$[(MoO_2)_2(slsh)(3\text{-pic})_2]\cdot H_2O$ Yellowish Orange	>300	64	23.86 (23.67)	44.02 (44.45)	3.44 (3.49)	10.09 (10.36)	2.7	282(66630), 292(65650), 312 (55410), 403(6470)
5	$[(MoO_2)_2(slsh)(4\text{-pic})_2]\cdot H_2O$ Yellow	>300	67	23.49 (23.67)	45.00 (44.45)	3.44 (3.49)	10.79 (10.36)	2.4	282(82653), 292(80612), 316(64285), 403(5010)

Table 2
Structurally significant ^{1}H NMR spectral data (in ppm) for homobimetallic Molybdenum(VI) complexes derived from disalicylaldehyde succinoyldihydrazone.

Sl. No.	Ligand/complex	ó-CH_2	ó-phenyl	ó-CH=N	ó-(NH)	ó-(OH)	ó (py/α/β/γ)
L	H_4slsh	2.07(s) 2.50(s) 2.93(s)	6.63–7.50(m)	8.81(s) 8.26(s)	10.15(s)	11.27(s) 11.64(s)	–
1	$[(MoO_2)_2(slsh)(H_2O)_2]$	2.06(s) 2.71(s)	6.84–7.43(m)	7.91(s)	–	–	–
2	$[(MoO_2)_2(slsh)(py)_2]\cdot H_2O$	2.07(s) 2.72(s)	6.82–7.60(m)	8.09(s)	–	–	8.64 (8.61)[a]
3	$[(MoO_2)_2(slsh)(2\text{-pic})_2]\cdot H_2O$	2.07(s) 2.71(s)	6.82–7.54(m)	7.95(s)	–	–	8.59(8.48)[a] 2.72(2.55)[b]
4	$[(MoO_2)_2(slsh)(3\text{-pic})_2]\cdot H_2O$	2.07(s) 2.71(s)	6.80–7.56(m)	7.98(s)	–	–	8.58(8.43)[a] 2.38(2.32)[b]
5	$[(MoO_2)_2(slsh)(4\text{-pic})_2]\cdot H_2O$	2.07(s) 2.71(s)	6.65–7.70(m)	8.37(s)	–	–	8.62(8.60)[a] (2.32)

[a] *o*-Proton signal of py/2-pic/3-pic/4-pic.

[b] Methyl proton signal of 2-pic/3-pic/4-pic.

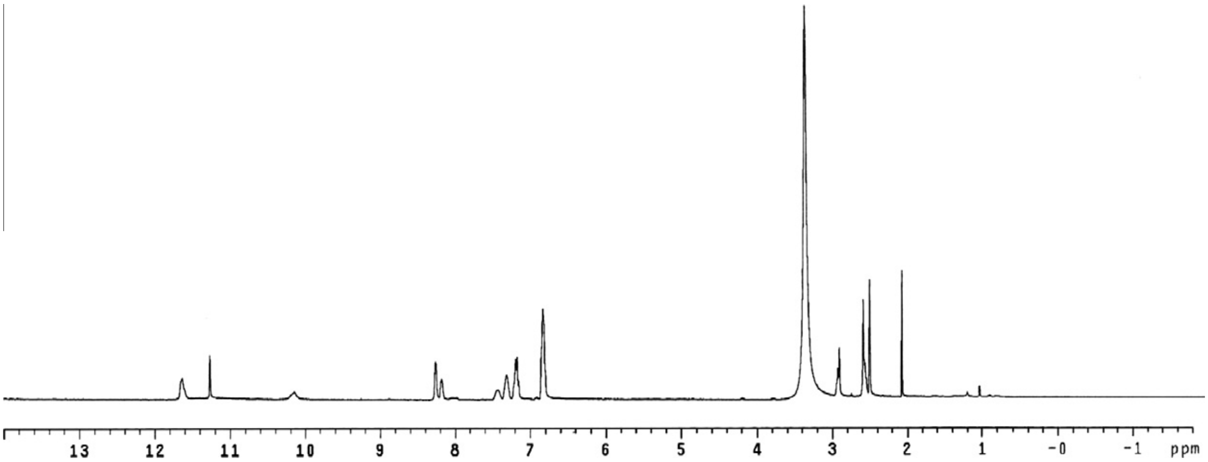


Fig. 3. ^{1}H NMR spectrum of Disalicylaldehyde succinoyldihydrazone (H_4slsh) in DMSO-d_6.

4.3. Electronic spectra

UV–Vis spectra of the ligand and the complexes were recorded in DMSO solution and the relevant data are given in Table 1. The ligand band at 283 nm is split into two bands in the electronic spectra of the complexes. One component remains almost unshifted in position while the other component shows red shift by 9 nm and appears at 292 nm. The free ligand appearing at 322 nm shows blue shift on complexation and appears in the region 309–321 nm. The splitting of ligand band and its red as well as blue shift is a good evidences of chelation of the ligand to the metal centre. The complexes show a new strong broad band centred at ~ 403 nm on the UV–visible border region. Since the ligand is not expected to be chromophoric in the visible region and all the complexes are diamagnetic, these bands have been assigned as the ligand–metal charge transfer (LMCT) transition on the basis of their high intensity. They may be associated, most probably, with the ligand-to-metal charge transfer originating from an electronic

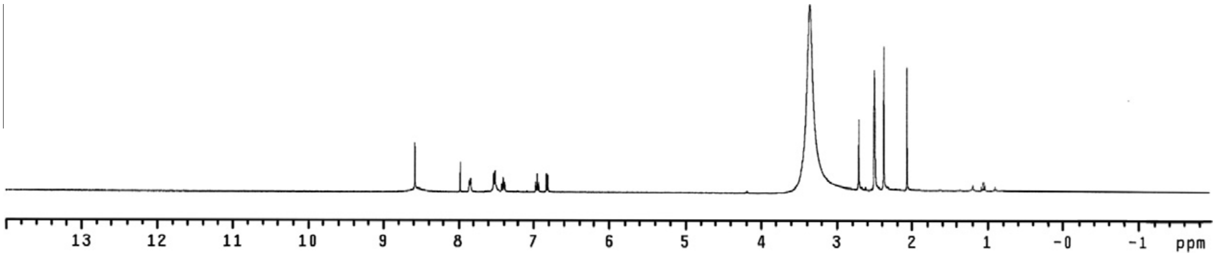


Fig. 4. ^{1}H NMR spectrum of $[(MoO_2)_2(slsh)(3\text{-}pic)_2]\cdot H_2O$ (**4**) in DMSO-d_6.

Table 3
Structurally significant IR spectral data (in cm^{-1}) for homobimetallic Molybdenum(VI) complexes derived from disalicylaldehyde succinoyldihydrazone.

Sl No.	Ligand/complex	υOH + NH	υC=O	υC=N	Amide II + υC-O phenolic	υNCO	υC—O	υN—N	υM=O	υM—O phenolic	υM—O carbonyl
L	H_4slsh	3449s 3204m 3065m	1666vs	1626m	1566m	–	1281s	1049w	–	–	–
1	$[(MoO_2)_2(slsh)(H_2O)_2]$	3416s	–	1613vs	1560s	1516w	1268s	1036w	956s 910s 857vs	–	–
2	$[(MoO_2)_2(slsh)(py)_2]\cdot H_2O$	3443m	–	1613vs	1553s	1508w	1268s	1036w	990w 903vs 817m	–	–
3	$[(MoO_2)_2(slsh)(2\text{-}pic)_2]\cdot H_2O$	3292w 3363w	–	1613vs	1560m	1523w	1268s	1035w	950s 917m 857vs	–	–
4	$[(MoO_2)_2(slsh)(3\text{-}pic)_2]\cdot H_2O$	–	–	1613vs	1560m	1516w	1268m	1078w	956s 910s 857vs	592m	472w
5	$[(MoO_2)_2(slsh)(4\text{-}pic)_2]\cdot H_2O$	3443m 3031m	–	1613vs	1554s	1519w	1261s	1029w	943s 910vs 840w	592m	472w

Table 4
Low frequency IR data.

Sl No.	Complexes	ν(M—O) (phenol)	ν(M—O) (carbonyl)	ν(M—N) (hydrazine)	ν(M—N) (pyridyl)
1	$[(MoO_2)(slsh)(H_2O)_2]$	590s	435w	343s 313s	–
2	$[(MoO_2)(slsh)(py)_2]\cdot H_2O$	582s	435m	344m 301s	–

Table 5
The electrochemical parameters for the homobimetallic Mo(VI) complexes of disalicylaldehyde succinoyldihydrazone.

Sl. No	Complex	Epa/V	Epc/V
1	$[(MoO_2)_2(slsh)(H_2O)_2]$	+0.82 −0.60 −1.28	+0.92 −0.67 −1.40
2	$[(MoO_2)_2(slsh)(py)_2]\cdot H_2O$	+0.73 −0.50	−0.58 −1.52
3	$[(MoO_2)_2(slsh)(2\text{-}pic)_2]\cdot H_2O$	+0.70 −0.26	−0.42 −1.56
4	$[(MoO_2)_2(slsh)(3\text{-}pic)_2]\cdot H_2O$	+0.55 −0.09	−0.20 −1.62
5	$[(MoO_2)_2(slsh)(4\text{-}pic)_2]\cdot H_2O$	+0.65 −0.25	−0.35 −1.23

excitation from the HOMO of phenolate oxygen to the LUMO of molybdenum [19].

4.4. ^{1}H NMR spectra

All of the complexes were characterised by ^{1}H NMR spectroscopy Table 2. The ^{1}H NMR spectra of the ligand (H_4slsh) and complex (4) are shown in Figs. 3 and 4. The ^{1}H NMR spectra of the complexes show conclusive evidence regarding the involvement of dihydrazone in coordination to the metal centre in enol form. The two proton signals observed at δ 11.20 and 11.64 ppm assigned to δ-OH protons in the free dihydrazone disappears in the complexes. This suggests involvement of phenolate oxygen atoms in coordination via deprotonation. The δ-NH proton signal which appear at δ 10.15 ppm in the ^{1}H NMR spectrum of the free dihydrazone disappears in the complexes. The disappearance of δ-NH proton signals indicates the collapse of the amide structure of the dihydrazone and its coordination to the metal centre through carbonyl oxygen atoms in the enol form. The azomethine proton signals, on an average, show a upfield shift of about δ 0.13–0.62 ppm in all of the complexes. The upfield shift of these signals is attributed to drainage of electron density from nitrogen atoms of

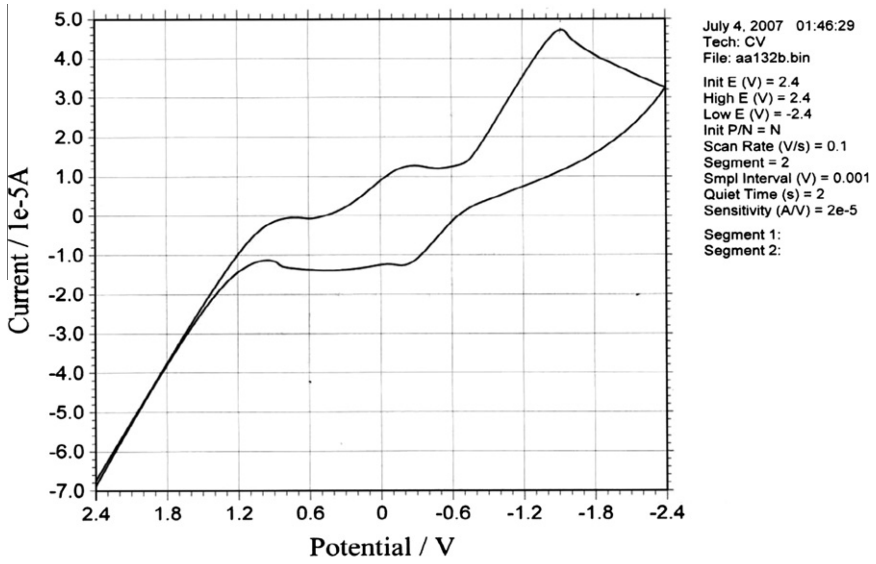
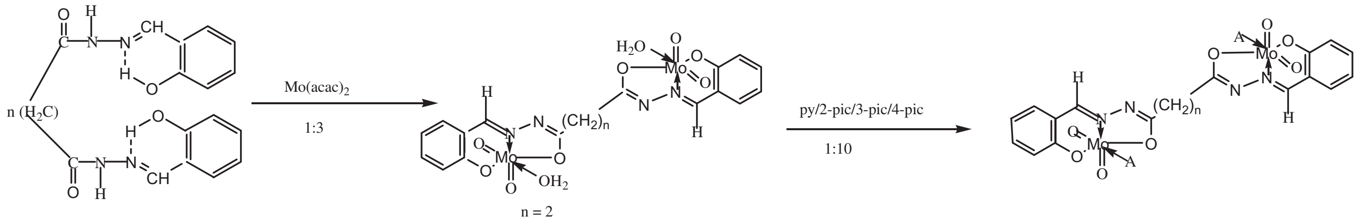


Fig. 5. Cyclic voltammogram of [(MoO2)2(slsh)(py)2]·H2O (**2**) in DMSO.



Scheme 1. Tentative structure of the complexes (**1**–**5**) where A = py, 2-pic, 3-pic, 4-pic.

azomethine group to the metal centre [20,21]. The phenyl proton multiplet appears in the δ 6.63–δ 7.70 ppm region in all of the complexes.

In addition to azomethine protons signals, some new signals in the region δ 8.62–8.64 ppm are also observed in the ^1H NMR spectra of the complexes. These signals are attributed to arise due to *o*-protons of pyridyl ring of pyridine, 2-picoline, 3-picoline and 4-picoline molecules, respectively. These signals are downfield shifted as compared to their positions in free pyridine, 2-picoline, 3-picoline and 4-picoline molecules in the complexes which suggests that the pyridine ring nitrogen atom is coordinated to the metal centre [22]. Further, the ^1H NMR spectra of the complexes show new signals appearing at δ 2.38 and 2.72 ppm. These signals are assigned to methyl protons of 2-picoline, 3-picoline molecules, respectively. These signals appear at δ 2.55, 2.32 and δ 2.37 ppm in the free 2-picoline, 3-picoline and 4-picoline molecules, respectively [23]. Thus the methyl protons are also downfield shifted in these complexes indicating coordination through nitrogen atoms of pyridine, 2-picoline, 3-picoline and 4-picoline molecules to the metal centre.

The most crucial point of importance in the ^1H NMR spectra of the complexes is the collapse of the two resonances corresponding to δ CH=N-signal in the free ligand into a single resonance. This ^1H NMR spectral evidence suggests that **the dihydrazone which exists** in the *anti-cis* configuration in the uncoordinated state isomerizes to attain *staggered* configuration in the complexes. Similar coordination mode of malonoyldihydrazone to the metal centres has been established by Gopinath and co-workers [24] on the basis of X-ray crystallographic study.

4.5. IR spectra

The structurally significant IR spectral bands for the free dihydrazone and its homobimetallic complexes have been set out in Table 3. The complexes show essentially different features in the region 3100–3500 cm^{-1} as compared to those of the uncoordinated dihydrazone. Corresponding to υ-NH band in the IR spectrum of the, a medium broad signal at around δ10 ppm should have been observed in the ^1H NMR spectra of the complexes but this signal is not observed in the DMSO solution. This may be either due to very broad nature of the corresponding signal or due to conversion of secondary amine group into azomethine group. In the complexes, the strong band 3204 cm^{-1} in the free dihydrazone is invariably absent in IR spectra indicating coordination of dihydrazone to the metal centres in the enol form. Further, the complexes do show medium to weak band in the region 3100–3500 cm^{-1} except the complex (1) which shows strong band at 3416 cm^{-1}, may be attributed to coordinated H_2O molecules. In the remaining complexes, the medium to weak band in the same region may be attributed to arise due to H_2O molecules absorbed by KBr during the pellet preparation.

The strong amide I band observed at 1666 cm^{-1} in the free dihydrazone is absent in the IR spectra of the complexes. This confirms the enolization of the ligand in the complexes [25]. The υC=N band appears as a strong single band in all of the complexes at 1613 cm^{-1}. The band registers a lower shift by 13 cm^{-1} compared to free ligand indicating coordination of dihydrazone through azomethine nitrogen atoms to the metal centre. The free dihydrazone shows a medium to strong intensity band at 1566 cm^{-1}. This band is assigned to have composite character due to mixed contribution of the amide (II) and υ(C—O)(phenolate) bands. This band shifts to lower frequency by 6–13 cm^{-1} in all the complexes. Such a feature associated with this band shows weak bonding between phenolate oxygen atom and metal centre. Further, the new band observed in the region 1508–1523 cm^{-1} in all of the complexes is assigned to υNCO vibrations of the newly formed NCO^- group [26]. The IR of the complexes (4) and (5) show new bands at 592 cm^{-1} and 472 cm^{-1}. These bands have tentatively been assigned to υ(M—O)(phenolic) and υ(M—O)(carbonyl) [27,28], respectively. However, the possibility of coupling of these vibrations with some ligand bands cannot be ruled out. The dioxo groups exhibit strong bands in the region 850–1000 cm^{-1} due to *anti*-symmetric and symmetric stretching vibrations, *cis*-dioxo groups show two such strong bands while the *trans*-dioxo groups show only one band. All of the complexes show two strong bands in the region 910–956 cm^{-1} respectively of almost equal intensity indicating the presence of *cis*-MoO_2^{2+} grouping in these complexes [29]. In addition, the complexes show a medium to strong band in the region 817–857 cm^{-1}. The first two bands are assigned to υ_s and υ_{as} stretching vibrations of *cis*-MoO_2^{2+} group. The bands observed in the region 817–857 cm^{-1} in **the complexes are similar to those** observed by Chakravarty and Rajan [30] and Holm et al [31] and other workers [32] and **are assigned** to υMo═O···Mo vibrations. The appearance of two bands in the region 857–956 cm^{-1} coupled with the typical band in the region 817–857 cm^{-1} in the complexes **suggests** that the bridging Mo═O···**Mo bands** in these complexes are weak and that the molybdenyl group maintains its identity as *cis*-MoO_2^{2+} group.

4.6. Low frequency IR

The free ligand H_4slsh shows absorption bands at 573 m, 538s, 522s, 520s, 497s, 465s, 450s, 405s, 373 m, 357 m cm^{-1}, in low frequency infrared spectra. The low frequency IR of the complexes $[(MoO_2)(slsh)(H_2O)_2]$ (1), $[(MoO_2)(slsh)(py)_2]{\cdot}H_2O$ (2), have been studied as representative examples to make assignment of bands due to coordinated pyridine molecules as shown in Table 4. Ligand bands have been excluded and the new bands appearing in the 582–590 cm^{-1} region have been assigned to ν(M—O)(phenolate). On the other hand, a new band observed at 435 cm^{-1} is assigned to ν(M—O)(carbonyl). The appearance of these two bands in the complexes suggests the involvement of phenolate and enolate oxygen atoms in bonding to the metal. The complexes show new bands in the region 301–344 cm^{-1}. These new bands occur in almost in the same region in which the ν(M—N) bands have seen reported to occur in metal complexes of hydrazine derivatives. Hence, these bands are assigned to ν(M—N) stretching vibration due to coordinated > C═N group.

4.7. Cyclic voltammetry

The cyclic voltammograms of a 2 mM solution of the complexes have been recorded at a scan rate of 100 mV/s by cyclic voltammetry in DMSO solution due to their insolubility in non-coordinating organic solvents (CH_3CN and CH_2Cl_2) with a 0.1 M tetra-n-butyl ammonium perchlorate (TBAP) as a supporting electrolyte. The data have been set out in Table 5. The ligand in the present study does not exhibit any redox activity in the potential range −2.4 to + 2.4. Hence, these reductive and oxidative waves observed in the complexes in the present study may be attributed to electron transfer reactions centred on metal centre.

The cyclic voltammogram of the complex $[(MoO_2)_2(slsh)(H_2O)_2]$ (1) is characterised by a reductive wave at +0.92, −0.67 and −1.40 V in the cathodic scan. Corresponding to this, there is oxidative wave in the anodic scan at + 0.82, −0.60 and −1.28 V. **This redox** behaviour arises due to electron transfer reaction centred on metal. The redox couples are assigned to the following electron transfer reactions.

$$[O_2Mo^{VI}(L)Mo^{VI}O_2(H_2O)_2] + e \leftrightharpoons [O_2Mo^{VI} \cdot (L)Mo^{V}O_2(H_2O)_2]^- \quad (1)$$

$$[O_2Mo^{VI}(L)Mo^{V}O_2(H_2O))_2]^- + e \leftrightharpoons [O_2Mo^{V}(L)Mo^{V}O_2(H_2O)_2]^{2-} \quad (2)$$

$$[O_2Mo^{V}(L)Mo^{V}O_2(H_2O)]^{2-} + e \leftrightharpoons [O_2Mo^{V}(L)Mo^{IV}O_2(H_2O)_2]^{3-} \quad (3)$$

The complex $[(MoO_2)_2(slsh)(py)_2]{\cdot}H_2O$ (2) shows two reductive waves at −0.58, −1.52 V and corresponding oxidative waves appear at +0.73, −0.50 V, respectively is shown in Fig. 5. The difference between these waves is 131 and 102 mV, respectively, the waves are quasi-reversible in nature. In view of the absence of any wave in the range +2.4 to −2.4 in the free ligand, these redox couples are assigned to Mo(VI)/Mo(V)/Mo(IV) redox reactions as shown below.

$$[O_2Mo^{VI}(L)Mo^{VI}O_2(py)_2] + e \leftrightharpoons [O_2Mo^{VI}(L)Mo^{V}O_2(py)_2]^- \quad (4)$$

$$[O_2Mo^{VI}(L)Mo^{V}O_2(py)_2]^- + e \leftrightharpoons [O_2Mo^{VI}(L)Mo^{IV}O_2(py)_2]^{2-} \quad (5)$$

The complexes (3) and (4) show two reductive waves at −0.42, −1.56; −0.20, −1.62 V and two corresponding oxidative waves at +0.70, −0.26;+0.55, −0.09, respectively. These waves are quasi-reversible because the separation between the corresponding reductive and oxidative waves falls in the region 75–153 mV which is more than the values of 60 mV required for one electron transfer reversible reactions. The complex (5) also shows essentially similar electrochemical behaviour (reductive waves at −0.35, −1.23 V; oxidative waves at + 0.65, −0.25 V) as the complexes (3) and (4). These two waves may be assigned to $Mo^{VI}Mo^{VI}/Mo^{VI}Mo^{V}$ and $Mo^{VI}Mo^{V}/Mo^{VI}Mo^{IV}$ redox couples as in the case of the complexes (3) and (4). Electrochemical studies on several *cis*-dioxomolybdenum(VI) complexes derived from multidentate nitrogen and oxygen donor ligands have generally shown irreversible or quasi-reversible behaviour. The high peak separation, most probably, results from a slow heterogeneous electron exchange rate rather than from intervening homogeneous reactions [33].

5. Conclusion

The stoichiometry and physico-chemical studies reveal the formation of homobimetallic Mo(VI) complexes. The appearance of azomethine proton signal in the ^1H NMR spectra of the molybdenum(VI) complexes (1–5) in the form of singlet suggests that the dihydrazone is coordinated to the metal centres in *staggered*-configuration. In this configuration, in all of the complexes, the different parts of the dihydrazone molecules are coordinated to the different metal centres ruling out the possibility of any steric crowding in the molecule. As a result, both the hydrazone parts of the coordinator dihydrazone molecule remain in the same plane giving rise to a singlet corresponding to azomethine protons. The dihydrazone coordinates to the metal centres as tetrabasic hexadentate tridentate ligand in the enol form. In this form the metal centres are bonded to NOO coordination centres. The mass spectral behaviour suggests that these complexes are monomeric in nature. An octahedral stereochemistry around the metal ions has been proposed on the basis of above-mentioned studies as shown in Scheme 1.

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