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SYNTHESIS, SPECTRAL PROPERTIES AND REDOX BEHAVIOUR OF *CIS*-DIOXO-MOLYBDENUM(VI) COMPLEXES WITH TRIDENTATE ARYLAZO LIGANDS

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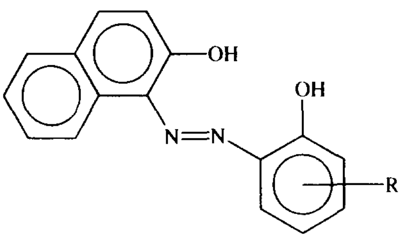
Abstract—Molybdenum complexes of type [MoO_2L] (**2**) [where H_2L = 1-(2-hydroxyphenylazo)-2-hydroxynaphthalene or its substituted derivative] have been isolated. They are deep red coloured, non-electrolytic and diamagnetic in nature and have been characterized by elemental analyses and spectroscopic techniques (electronic, IR, and ^1H NMR). They react with different Lewis bases (B) to yield [$MoO_2L(B)$] (**3**) complexes. The redox activity of complexes **2** were systematically examined by cyclic voltammetry at a glassy carbon electrode in non-aqueous medium. All the complexes show a one-electron reduction of quasi-reversible nature near −0.6 V *vs* SCE.

Molybdenum is an essential element for a number of biological processes.[1] The dinitrogen fixation is believed[2] to occur stepwise through diazene and hydrazine. A number of organohydrazido(2-) molybdenum complexes have been reported.[3–6] Binding of azobenzene or its substituted derivatives with molybdenum is only limited to molybdenum(II) chemistry.[7] In this context we have undertaken a systematic study of synthesis and characterization of molybdenum(VI) complexes derived from tridentate dibasic 2,2′-dihydroxy arylazo ligands (H_2L) having a soft azo donor group.



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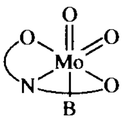
1a: R=4′-CH_3; 1b: R=H



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EXPERIMENTAL

Preparation of compounds

Analytical reagent grade solvents, distilled and dried by standard methods,[8] were used in all cases. All other chemicals were of reagent grade. 1-(Phenylazo)-2-hydroxynaphthalene and its substituted derivative were prepared following usual procedure.[8] 1-(2′-Hydroxy-4′-methylphenylazo)-2-hydroxynaphthalene (H_2L^1, **1a**) and 1-(2′-hydroxyphenylazo)-2-hydroxynaphthalene (H_2L^2, **1b**) were synthesized from the respective monohydroxyazo compounds using the reported method.[9]

[MoO_2L] (**2a,2b**). The complexes were prepared using two different methods. A representative case for each method is given below.

(i) [MoO_2L^1] (**2a**). A solution of 1-(2′-hydroxy-4′-methylphenylazo)-2-hydroxynaphthalene (H_2L^1) (0.135 g, 0.48 mmol) in methanol (20 cm^3) was

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added dropwise to a solution of $Na_2MoO_4 \cdot 2H_2O$ (0.115 g, 0.47 mmol) in water (10 cm^3). The pH of the solution was then reduced to *ca* 3 by dropwise addition of dilute HCl and the solution was stirred for 12 h at room temperature. Deep red coloured precipitate was collected and washed with hexane followed by water. Dried *in vacuo* over P_4O_{10}. Yield: *ca* 64%.

(ii) $[MoO_2L^1]$ (**2a**). Bis(acetylacetonato)dioxomolybdenum(VI) (0.148 g, 0.45 mmol) was taken in dry methanol (10 cm^3) and cooled in an ice-bath. To it a solution of 1-(2′-hydroxy-4′-methylphenylazo)-2-hydroxynaphthalene (H_2L^1) (0.135 g, 0.48 mmol) in dry methanol (20 cm^3) was added with stirring and the stirring was continued for 1 h. The volume of reaction mixture was reduced to about 15 cm^3 by slow evaporation and kept overnight at 278 K. A black crystalline product was collected by filtration and washed with a small volume of dichloromethane. The product was dried *in vacuo* over anhydrous $CaCl_2$. Yield: *ca* 25%.

$[MoO_2L^1(DMSO)]$ (**3a**). To a well stirred solution of $[MoO_2L^1]$ (0.13 g, 0.32 mmol) in dry ethanol (25 cm^3), DMSO (0.1 g, 1.28 mmol) was added and the mixture was refluxed for 2 h. The solution was cooled and the volume of the solution was reduced to *ca* 5 cm^3. The solution was kept overnight at 278 K and shiny microcrystals were deposited. The crystalline product was filtered off and was washed with hexane, dried over fused $CaCl_2$. Yield: *ca* 64%.

Physical measurements

Infrared spectra were recorded as KBr discs using a Perkin–Elmer 783 spectrophotometer from RSIC, NEHU. Electronic spectra of the compounds were recorded on a Shimadzu UV 240 spectrophotometer. Proton resonance measurements were obtained by using Bruker WP-80 and GE NMR QE 300 MHz spectrometers. Carbon, nitrogen and hydrogen analyses were made by RSIC, Chandigarh, India. Cyclic voltammetry measurements were done at 298 K using a CV-27 Bioanalytical system. All experiments were carried out under dry nitrogen in a three-electrode configuration. The working electrode was a glassy carbon electrode and the auxillary electrode was a platinum wire. All potentials are referenced to a saturated calomel electrode (SCE) and the reported potentials are uncorrected for junction potential.

RESULTS AND DISCUSSION

Ligands and complexes

The dibasic 2,2′-dihydroxy arylazo compounds (H_2L; **1a** and **1b**) were used as tridentate ligands. The ligands were synthesized using the reported method.[9] The elemental analyses and spectral properties of the prepared ligands were done. Strong intramolecular hydrogen bonding in the free ligands is evident from the two down-field signals[10,11] at *ca* 12.4 δ and 14.4 δ for two non-equivalent OH protons in ^1H NMR spectra and absence of any OH stretch in IR spectra[12,13] of H_2L.

The complexes $[MoO_2L]$, **2**, were prepared by stirring an aqueous methanolic solution of H_2L and $Na_2MoO_4 \cdot 2H_2O$ (1 : 1 mole ratio) at pH *ca* 3.0 for a few hours at room temperature. Complexes **2** were collected as deep red coloured crystalline solids.

All the complexes are soluble in oxo donor solvents but insoluble or sparingly soluble in chloroform, dichloromethane, benzene and other hydrocarbons. The complexes are non-electrolytes in non-aqueous solvents. The results of elemental analyses (Table 1) are in good agreement with assigned formulation. The complexes **2** are diamagnetic as expected for a $4d^0$ configuration and the absence of OH signals in the ^1H NMR spectra of complexes **2** suggests the binding of azo ligands (**1**) with metal centres via phenolic oxygen atoms. The tridentate behaviour of 2,2′-dihydroxy arylazo ligands (H_2L) via an O, N, O set of donor atoms is well established[14] in palladium(II) chemistry. The IR spectra of complexes **2** exhibit two absorption bands in the range 900–950 cm^{-1} suggesting the presence of a *cis*-MoO_2 moiety, and also a strong vibration at ~ 815 cm^{-1} assignable to $Mo{=}O \cdots Mo$ bridging[15–18] in the solid state. Each of the complexes **2** in donor solvents shows an intense LMCT [$\pi^*(azo) \rightarrow d(Mo)$] band in the visible region with high molar extinction coefficient (Table 1).

$[MoO_2(L)(B)]$ *species*

With *cis*-MoO_2^{2+} group planar tridentate azo ligands spanning three coordination positions generate $[MoO_2L]$ (**2**) and leave the sixth position as a labile site for substrate binding.[16] In this direction different monodentate ligands (B) have been used for substrate binding.

Complexes **3** were synthesized by treating $[MoO_2L]$ (**2**) with an excess of monodentate ligands (B) in non-aqueous media in reflux conditions for a few hours. Picoline, dimethyl sulphoxide, dimethylformamide and hexamethylphosphoramide have been used as monodentate ligands. Significantly, monodentate benzaldehyde also binds the molybdenum centre of complex **2** and the solubility, IR and electronic spectra of the product are very similar to those of other complexes **3**, but the analytically pure compound is yet to be isolated.

Table 1. Analytical and spectral data for selected complexes

	Analytical data[a] (%)			IR data[b]		^{1}H NMR data[c]	Electronic spectra[d]
Complex	C	N	H	$\nu_{Mo=O}$	Selected B vibrations	δ(Me)	$\lambda(\varepsilon)$
2a [MoO_2L^1]	(50.5)	(6.9)	(3.0)	920, 942, 815[e]		2.4	525(13,200)
	50.6	6.9	3.0				
2b [MoO_2L^2]	(49.2)	(7.2)	(2.6)	913, 936, 815[e]			525(11,300)
	48.9	6.8	2.6				
3a [MoO_2L^1 (DMSO)]	(47.3)	(5.8)	(3.7)	900, 920	1030(s)[f]	2.5, 2.25(L^1)[g]	530(13,200)[h]
	46.8	5.8	3.6				
3b [MoO_2L^1 (γ-pic)]	(55.5)	(8.4)	(3.8)	905, 925	1612(s), 1230(m),	2.2(γ-pic)	530(14,100)[h]
	55.2	7.8	3.7		1070(m), 1012(s)	2.16(L^1)[g]	
3c [MoO_2L^1 (DMF)]	(50.3)	(8.8)	(4.0)	905, 930	1630(s)[i], 670(m)[j]	2.03(L^1)	530(13,700)[h]
	50.5	8.3	3.8			2.83, 2.71[g]	
3d [MoO_2L^1 (HMPA)]	(47.3)	(12.0)	(5.1)	903, 923	1175[k]	2.19(L^1)	535(11,300)[h]
	46.6	11.5	4.8			2.33, 2.41[g]	

[a] Calculated values in parenthesis.

[b] As KBr disks.

[c] Values are in ppm from $SiMe_4$ in DMSO-d_6.

[d] λ = Absorption maxima in nm and ε = molar extinction coefficient in MeOH.

[e] Strong and broad band due to Mo=O— > Mo bridging.

[f] ν_{SO}.

[g] In $CDCl_3$.

[h] In CH_2Cl_2.

[i] $\nu_{C=O}$.

[j] δ_{NCO}.

[k] $\nu_{P=O}$.

The characteristic strong vibration at ~815 cm^{-1} of complexes **2** is uniformly absent in complexes **3**. Furthermore complexes **3** show two sharp and strong absorptions in the range 900–950 cm^{-1} due to the *cis*-MoO_2 moiety.[15,17,19] Selected vibrations of molybdenum(VI) bound **B** are given in Table 1. The shifts of ν_{S-O}, $\nu_{C=O}$ and $\nu_{P=O}$ to lower frequencies (Table 1) compared with that of free values suggest[15] that DMSO, DMF and hexamethylphosphoramide preferably bind hard acid molybdenum(VI) through their oxygen atoms.

The electronic spectra of complexes **3** display a strong LMCT band (Fig. 1) around 530 nm in dichloromethane. The influence of different **B** on the electronic spectra of complexes **3** is negligible (Table 1). ^{1}H NMR spectra of complexes **3** unambiguously prove the attachment of the monodentate molecules (**B**) with [MoO_2L] system even in solution (Table 1).

Redox behaviour

The voltammetric studies of complexes **2** and the ligands were done at the glassy carbon electrode in DMF (Table 2). Effectively the complexes **2** in DMF generate corresponding [$MoO_2(L)(DMF)$] species. Both the complexes exhibit a quasi-reversible one-electron couple near −0.57 V (Fig. 2). The peak potentials of the couple near −0.6 V are nearly invariant with scan rates and peak currents are proportional to (scan rate)$^{1/2}$. These facts taken in conjunction with current height settle the nearly or exactly reversible one-electron character of the couple. The one-electron reduction near −0.57 V is believed to be ligand based[20] and the shift is around 350 mV in comparison with the E_{pc} values of the free ligands. Therefore the participation of

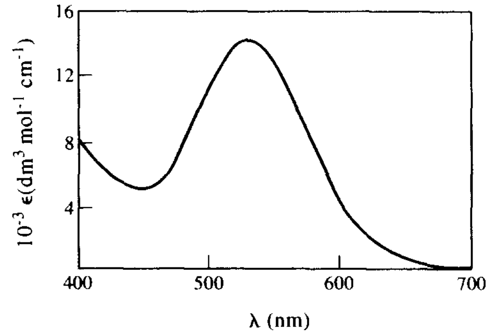

Fig. 1. Visible spectrum of complex **3b** in dichloromethane.

Table 2. Cyclic voltammetric data[a] of free ligands and complexes (**2**)

Compound	Scan rate ($mV\ s^{-1}$)	E_{pc} (V)	E_{pa} (V)	ΔE_p (mV)
1. H_2L^1	50	−0.990	—	
		−1.420	—	
2. H_2L^2	50	−0.960	—	
		−1.335	—	
3. $[MoO_2L^1]$	50	−0.610	−0.540	70
	100	−0.615	−0.535	80
4. $[MoO_2L^2]$	50	−0.625	−0.565	60
	100	−0.630	−0.560	70

[a] At glassy carbon electrode in DMF at 298 K; supporting electrolyte: 0.1 M TEAP; solute concentration $\sim 10^{-3}$ M.

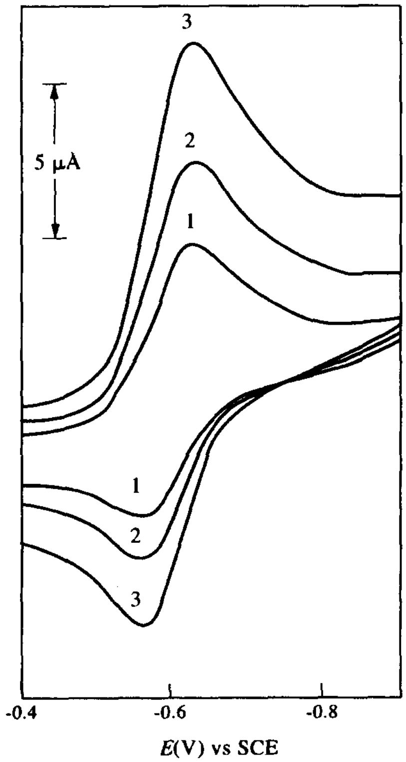

Fig. 2. Cyclic voltammograms of complex **2b** in DMF (0.1 M in TEAP, 298 K) at the glassy carbon electrode; scan rates ($mV\ s^{-1}$): (1) 50, (2) 100, (3) 200.

the azo group in metal binding makes it more reducible and the electron transfer process at solid electrode becomes more reversible.

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