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A series of new oxomolybdenum(IV) complexes involving some NSO donors as the main ligand frame; the first use of diacetyldihydrazones to stabilize the MoO^{+2} acceptor centre

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Abstract

An array of neutral oxomolybdenum(IV) complexes with potentially pentadentate ONSNO donor Schiff bases in the form of thiocarbodihydrazone of salicylaldehyde and substituted salicylaldehydes actually acting as tridentate ONS donor ligands (H_3L) were synthesized through oxo abstraction of the corresponding *cis*-dioxomolybdenum(VI) complexes. Oxomolybdenum(IV) complexes with similar ONS main ligands but different N–N donor coligands were also obtained by one-pot synthesis from the corresponding *cis*-dioxomolybdenum(VI) precursors. The complexes are found to be of the form $[MoO(LH)]_n$ and [MoO(LH)(N–N)], where N–N = bipy (2,2′-bipyridine), ophen (1,10-phenanthroline) and diacetyldihydrazones. In this work diacetyldihydrazones were used as N–N coligands for the first time in molybdenum chemistry. The complexes were characterized by elemental analyses, UV–Vis and IR spectroscopy, magnetic susceptibility measurement at room temperature in the solid state, molar conductivity in solution and by cyclic voltammetry. One of the complexes, [MoO(LH)(*o*-phen)] is structurally characterized by X-ray crystallography. The structure reveals that the molybdenum acceptor centre is present in a distorted octahedral N_3O_2S donor environment. The N–N coligand was found to occupy a plane perpendicular to that taken up by the ONS ligand. It is to be noted that structurally characterized oxomolybdenum(IV) complexes are quite scarce.

Keywords: Oxomolybdenum(IV) complexes; Thiocarbodihydrazone and diacetyldihydrazones ligands; X-ray crystal structure; Oxotransfer property

1. Introduction

Spectroscopic and EXAFS studies have indicated that in the biological functions of certain molybdoenzymes, the oxidation state of Mo cycles between the VI and IV states during substrate binding and reactivation [1,2]. Fairly stable oxomolybdenum(VI) complexes are comparatively scarce than their dioxomolybdenum(VI) counterparts and structurally characterized oxomolybdenum(IV) complexes are extremely rare. As a part of our studies on dioxomolybdenum(VI) and oxomolybdenum(IV) complexes [3–9], we present here synthesis, characterization and reactivity of fifteen new oxomolybdenum(IV) complexes with some potentially pentadentate but functionally dianionic tridentate thiocarbodihydrazone-type Schiff base ligands containing oxygen, nitrogen and sulfur as the donor atoms. Electrochemical behavior of these complexes has been investigated in order to have an insight into the redox behavior of the Mo^{IV} centers of these complexes. We also report here the first use of the diacetyldihydrazones as bidentate chelating N–N donor ligands to stabilize the $Mo^{IV}O^{2+}$-core. We have already reported the $[Mo^{VI}O_2LH]$ and $[Mo^{VI}O_2(LH)(Q)]$ complexes (where Q = a neutral monodentate Lewis base) [7]. Since octahedral complexes of the $[Mo^{IV}O]^{2+}$ core can accommodate five other donor points around itself, the corresponding 1:1 complexes with planar tridentate ONS ligands are coordinatively unsaturated and the two

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vacant sites of the $[Mo^{IV}O(LH)]_n$ moiety can be utilized for binding a neutral chelating bidentate ligand which can play a very important role in the stabilization of the Mo(IV) as well as the Mo(V) oxidation states [10].

The general strategy of synthesis of Mo(IV) complexes with a $[MoO]^{2+}$-core from the corresponding $[MoO_2]^{2+}$ complexes through oxo-abstraction by triphenyl or trialkylphosphine in the absence/presence of N–N bidentate donors in a purified, dry dinitrogen atmosphere has been followed here. Apart from characterisation by various spectroscopic (UV–Vis, IR), electrochemical and chemical techniques, the crystal and molecular structure of compound **6** was solved by single crystal X-ray diffraction analysis. The data revealed a good correlation with the crystal structure of the parent dioxomiolybdenum(VI) complex [7].

2. Results and discussion

2.1. Synthesis and characterization of the ligands and their oxomolybdenum complexes

Preparation of the Schiff base ligands (H_3L^1, H_3L^2, H_3L^3 and H_3L^4) along with their ligand skeletons exhibiting the donor points and the corresponding oxomolybdenum(VI) complexes were reported in one of our previous works [7]. Diacetylihydrazones were synthesized by a slight modification of a reported procedure [11]. [Diacetyl was condensed with the appropriate hydrazine in 1:2 molar proportions in very high yield (90%) from dehydrated ethanol medium and the diacetylihydrazones were precipitated as pale yellow solids by adding a little glacial acetic acid.] These N–N donor ligands were satisfactorily characterized by elemental analysis and IR spectra.

Oxomolybdenum (IV) complexes of the formula $[MoO(LH)]_n$ (**1–4**) were prepared by a general method [5] of refluxing the appropriate $[Mo^{VI}O_2(LH)(R\text{-}OH)]$ complexes with PPh_3 in 1:1.5 molar proportions in dry degassed CH_3CN under dry dinitrogen atmosphere.

The oxomolybdenum (IV) complexes **5–15** of the type [MoO(LH)(N–N)] were prepared by the same general method [5] of refluxing the appropriate $[Mo^{VI}O_2(LH)(R\text{-}OH)]$ complex with PPh_3 in the presence of the N–N donor coligand in 1:1.5:10 molar proportions under dry dinitrogen using dry degassed CH_3CN as the reaction medium. All the $[MoO(LH)]_n$ and [MoO(LH)(N–N)] type compounds are brown, amorphous solids, which are air stable and diamagnetic as is generally found for a species with a d^2 Mo(IV) center [5,7–9]. They are insoluble in water. They have rather low solubility in CH_3CN, CH_2Cl_2, $CHCl_3$ and alcohol but are fairly soluble in polar aprotic coordinating solvents like DMF and DMSO forming brown solutions. The brown color of the DMSO solution is gradually changed to the characteristic orange color of the $[MoO_2(LH)(DMSO)]$ complexes with the simultaneous emission of dimethylsulfide. Also, when the brown solution of a Mo(IV) complex in DMF is reacted with pyridine N-oxide, the brown color is found to become orange indicating oxotransfer from the substrate pyridine N-oxide to the mono-oxo Mo(IV) centre. These observations are indicative of the fact that the Mo(IV) center abstracts the oxo- group from DMSO and pyridine-N-oxide to regenerate the parent dioxomolybdenum(VI) complex. Molar conductivity data in 10^{-3} M DMF solutions of the complexes indicate that all of them are non-electrolytes. All the oxomolybdem(IV) complexes are satisfactorily characterized by elemental analysis (experimental section), IR, electronic spectra (Table 3) and cyclic voltammetric data (Tables 4 and 5).

*2.2. Crystal structure of the complex [MoOL¹H(o-phen)] (**6**)*

The dark green crystals of complex **6** were obtained from the reaction mixture by slow cooling. The crystals exhibited a rhombic habit. Experimental details of the structure determination are given in Table 1. Selected bond lengths and angles are listed in Table 2. The crystal of complex **6** consists of discrete molecules linked into chains by intermolecular H-bonds. The chains run parallel to the crystallographic *c*-axis and alternate molecules are related by the *c*-glide plain. An ellipsoid plot of complex **6** is given in Fig. 1. The tridentate dinegative Schiff base ligand (LH^{2-}) is bonded to the $[Mo^{IV}O]^{2+}$-core on a meridional plane [7,12,13] through S(1), O(2) and the imine nitrogen atom N(4). The other meridional plane, perpendicular to the main ligand frame, is occupied by N(1P) and N(10P) of the ligated 1,10-phenanthroline and with the oxo-oxygen atom O(1) provides a distorted octahedral coordination environment around

Table 1
Crystal data and details of refinement for the complex $[MoO(L^1H)(o\text{-phen})]$ (**6**)

Chemical formula	$C_{27}H_{20}N_6O_3SMo$
Fw	604.49
Crystal system	monoclinic
Space group	$P2_1/c$
a (Å)	18.394 (12)
b (Å)	11.284 (13)
c (Å)	12.064 (7)
β (°)	92.64 (5)
V (Å^3)	2501 (4)
Z	4
T (K)	150.0(2)
λ (Å)	0.71073
D_c (Mg m^{-3})	1.605
μ (Mo Kα) (mm^{-1})	0.651
$F(000)$	1224
R_1, wR_2 $[I > 2\sigma(I)]$	0.0565, 0.1367
Goodness of fit on F^2	1.037

Table 2
Selected bond distances (Å) and bond angles (°) for complex [MoO(L^1H)(*o*-phen)] (**6**)

Bond distances			
Mo–O(1)	1.690(5)	Mo–O(2)	2.076(5)
Mo–N(4)	2.124(7)	Mo–S(1)	2.388(3)
Mo–N(1P)	2.299(6)	Mo–N(10P)	2.178(7)
Bond angles			
O(1)–Mo–O(2)	102.5(2)	O(1)–Mo–N(4)	105.0(3)
O(2)–Mo–N(4)	85.7(2)	O(1)–Mo–N(10P)	86.4(2)
O(2)–Mo–N(10P)	93.5(2)	N(4)–Mo–N(10P)	168.5(2)
O(1)–Mo–N(1P)	158.4(2)	O(2)–Mo–N(1P)	77.7(2)
O(1)–Mo–S(1)	102.2(2)	O(2)–Mo–S(1)	153.93(14)
N(4)–Mo–S(1)	80.0(2)	N(10P)–Mo–S(1)	96.2(2)
N(1P)–Mo–S(1)	82.4(2)		

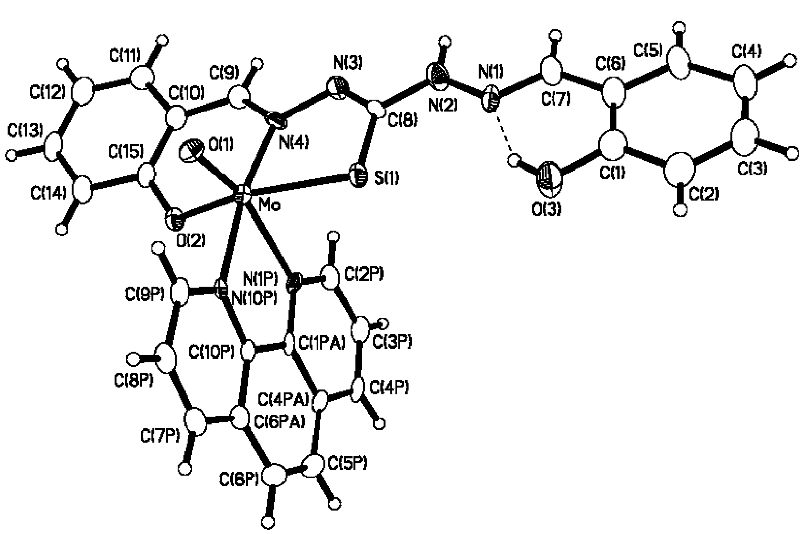

Fig. 1. A view of the structure of [Mo^{IV}O(*o*-phen)(L^1H)] (**6**), showing displacement ellipsoids drawn at the 50% probability level. An intramolecular O–H···N hydrogen bond is indicated by a dotted line.

Mo. The observed Mo–O(1) bond distance is 1.690(5) Å. The Mo–N(1P) bond distance [2.299(6) Å] is somewhat longer than the Mo–N(10P) bond distance [2.178(7) Å], an observation which is consistent with the *trans*-influence of the oxo ligand. The Mo–N(4) distance [2.124(7) Å] is shorter than the corresponding Mo–N(4) distance of 2.265(14) Å in the corresponding parent [$Mo^{VI}O_2$] complex [7]. This suggests a strengthening of the Mo–N(4) bond on removal of the *trans*-effect exerting oxo-oxygen [12–14] of the parent complex containing the $[MoO_2]^{2+}$-core. Comparing with the structure of the parent [$Mo^{VI}O_2$] complex [7], it is observed that the Mo–O(2) (phenolate) bond distance of 2.076(5) Å in MoO(LH)(N–N), is slightly longer than the corresponding Mo–O(4) distance [1.941 Å] in the MoO_2LH complex, which may be an effect of the reduction in the oxidation state and consequent increase in electron density at the metal center. The Mo–S (thiolato) distance is however almost the same in both compounds (~2.4 Å). The 1,10-phenanthroline bite angle of 72.1(2)° at Mo is quite close to the value reported in the literature [14]. The distortion of the coordination shell stems from the incorporation of Mo into the five-membered chelate rings. The *cis*-angles around Mo range from 72.1(2)° to 105.0(3)°, while the three *trans* L–Mo–L angles are 158.4(2)° for O(1)–Mo–N(1P), 153.93(14)° for O(2)–Mo–S(1) and 168.5(2)° for N(4)–Mo–N(10P). All these data reveal a large distortion of MoO(LH)(*o*-phen) from an octahedral ligand environment in which the equatorial plane is occupied by O(1) O(2) N(1P) and S(1), with N(4) and N(10P) occupying the two axial positions. The Mo(IV) centre is slightly displaced from the equatorial plane towards the axially situated N(4) atom. The above-mentioned distortions may be attributed to an optimization of metal–ligand bond distances, as supported by the torsion and dihedral angle data. The lower oxidation state at the metal center in **6**, compared to the parent [$Mo^{VI}O_2$] complex, is also responsible for changes in bond lengths and consequent distortions in the coordination geometry, due to the difference in occupancy of the metal d-orbitals by electrons at two different oxidation states. An intramolecular

0(3)–H(30)···N(1) hydrogen bond (Fig. 1; H···N 1.90 Å, O–H···N 145°) completes a six membered ring and may affect the local conformation of the molecule. Hydrogen bonding also plays an important role in the extended crystal structure. The molecules are linked into chains by intermolecular N(2)–H···O(1) = Mo hydrogen bonds. The chains run parallel to the crystallographic *c* direction and alternate molecules are related by the *c*-glide plane. The O···H bond distance is 1.96 Å with the N–H···O angle of 154°. This structure may be considered as a representative of the whole series.

2.3. IR spectroscopy

Characteristic IR bands of the four ligands and the corresponding dioxomolybdenum(VI) complexes were reported in one of our previous works [7] and the IR spectra of Mo(IV) complexes show that the bonding sites of the ligands remain unaltered. This is confirmed by the crystallographic study of complex **6**. Only a single strong band at ~965 cm^{-1} for the [Mo^{IV}O(LH)]$_n$ complexes, a similar band at ~935 cm^{-1} for the [Mo^{IV}O(N–N)(LH)] complexes (where N–N = 2,2′-bipyridyl; 1,10-phenanthroline) and a band at ~915 cm^{-1} for the [Mo^{IV}O(LH)(N–N)] complexes (where N–N = dihydrazone of diacetyl)] could be located. These bands (Table 3) are attributed to the ν(Mo^{IV} = O) [5,8,9] as opposed to the twin symmetric and antisymmetric stretching bands for the [Mo^{VI}O$_2$]$^{2+}$ moiety in the [Mo^{VI}O$_2$LH] precursors [7]. Coordination of the neutral bidentate N–N donor ligands to the [Mo^{IV}O]$^{2+}$ center lowers the Mo=O stretching frequency considerably [5,8,9]. Comparing the IR spectra of the [Mo^{VI}O$_2$LH], [Mo^{IV}O(LH)]$_n$ and [Mo^{IV}O(N–N)(LH)] complexes it is easily seen that the main ligand framework with all its donor points remains unaltered. The synthetic strategy applied here is known to leave the ligand framework unaffected [5,8,9]. It is likely that the [Mo^{IV}O(LH)]$_n$ complexes are polymeric in nature [5,8,9], the most probable bridging mode being via Mo=O···Mo linkages. This proposal is further supported by the presence of a diagnostic medium intensity band around 815 cm^{-1} which is characteristic of the Mo=O···Mo species [14a] and which is absent in the spectra of [Mo^{IV}O(N–N)LH] complexes.

2.4. Electronic spectra

Electronic spectra of [Mo^{IV}O(LH)]$_n$ and [Mo^{IV}O(N–N)(LH)] complexes were recorded in dry degassed DMF solution and the spectral data are presented in Table 3. A representative spectrum of these Mo(IV) complexes is given in Fig. 2. Spectra of both the [Mo^{IV}O(LH)]$_n$ and

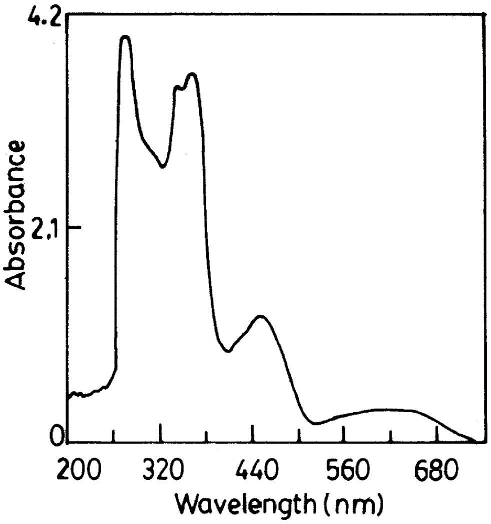

Fig. 2. Representative electronic spectrum of [Mo^{IV}O(N–N)(LH)] compounds **8** in DMF at 298 K.

Table 3
Characteristic IR[a] bands (cm^{-1}) and electronic spectral[b] data [nm (dm^3 mol^{-1} cm^{-1})] for the complexes

Complex	ν(Mo=O)	λ_{max}(ε)
MoOL^{1}H (**1**)	965	428(5865); 358(22613); 309(18939); 274(20564)
MoOL^{2}H (**2**)	967	454(7527); 366(45590); 318(36084); 270(38024)
MoOL^{3}H (**3**)	960	445(9419); 345(40972); 310(34557); 275(39449)
MoOL^{4}H (**4**)	969	426(7350); 363(34201); 316(32902); 282(35472)
MoO(L^{1}H)(bipy) (**5**)	935	655(2037); 437(8237); 350(16703); 318 (20786)
MoO(L^{1}H)(*o*-phen) (**6**)	930	638(3777); 452(8902); 353(16587); 314 (19982)
MoO(L^{2}H)(bipy) (**7**)	939	642(2467); 429(6022); 347(15504); 310 (18689)
MoO(L^{2}H)(*o*-phen) (**8**)	925	647(2134); 443(6418); 341(18092); 316 (20542)
MoO(L^{3}H)(bipy) (**9**)	940	642(2317); 439(7934); 356(17254); 314 (19342)
MoO(L^{3}H)(*o*-phen) (**10**)	943	629(1975); 428(7576); 366(19734); 312 (21893)
MoO(L^{4}H)(*o*-phen) (**11**)	935	640(2189); 446(8119); 351(20249); 320 (23216)
MoO(L^{1}H)(dhz) (**12**)	927	590(2576); 450(7435); 353(21116); 315 (34121)
MoO(L^{2}H)(dhz) (**13**)	929	586(2213); 453(8187); 356(25908); 310 (35745)
MoO(L^{3}H)(dhz) (**14**)	941	578(1996); 451(8194); 345(20352); 316 (33786)
MoO(L^{1}H)(dphz) (**15**)	928	585(2377); 447(8562); 351(19098); 319 (31896)

[a] In KBr pellet.
[b] In DMF.

[$Mo^{IV}O(N–N)(LH)$] complexes exhibit several bands in the 650–270 nm range. The absorption maximum in the 460–400 nm range may be assigned to the thiolato S(pπ) → Mo(dπ) LMCT transition [5,7] caused by the promotion of an electron from the filled HOMO of the ligand with primarily sulfur pπ character, to the empty LUMO of molybdenum with dπ character. The bands located around 350 and 310 nm may be assigned to the nitrogen to molybdenum and oxygen to molybdenum charge transfer transition [7,15], respectively. The bands appearing below 300 nm are due to intra-ligand transitions. In addition to the above bands the complexes exhibit one low energy absorption maxima around 650 nm which is characteristic of the MoO^{2+}-core [5,8,9].

2.5. Electrochemical properties

The cyclic voltammograms of [$Mo^{IV}O(LH)$]$_n$ (Table 4) and [$Mo^{IV}O(N–N)(LH)$] (Table 5) type complexes were characteristic of Mo^{IV} compounds as found previously [5,8,9]. All electrochemical experiments were performed at a Platinum electrode using freshly prepared 10^{-3} M solution of the complexes in dry degassed DMF containing 0.1 M TEAP as the supporting electrolyte and SCE as the reference electrode.

Table 4
Cyclic voltammetric data[a] for [MoO(LH)]$_n$-type oxomolybdenum (IV) complexes (**1**–**4**) at 298 K

Complex	Mo(V)/Mo(IV) E_{pa} (V)	Mo(IV)/Mo(III) E_{pc} (V)
1	+0.59	−0.98
2	+0.58	−1.12
3	+0.61	−1.22
4	+0.51	−1.06

[a] Solvent: DMF; working electrode: Platinum; reference electrode: SCE; E_{pc} and E_{pa} are cathodic and anodic peak potentials, respectively; scan rate: 100 mV s^{-1}; supporting electrolyte: 0.1 M TEAP; solution strength: 10^{-3} M.

In DMF solution the [$Mo^{IV}O(LH)$]$_n$-type complexes **1**–**4** exist as [$MoOLH(DMF)_x$] and an initial positive scan displays an oxidative response at ∼+0.55 V due to the oxidation of [$Mo^{IV}OLH(DMF)_x$] to [$Mo^{V}OLH(DMF)_x$]$^+$. This response retains its position even after repeated scan reversal. An initial negative scan is found to exhibit only one reductive response at ∼−1.5 V which is a two-electron ligand based reduction as observed previously [7]. On scan reversal the previously observed oxidative response remained at ∼+0.55 V and after passing through the positive end of the scan two new reductive responses appeared at ∼−1.0 V and at ∼−1.5 V, the last one being due to the two-electron reduction of the ligand. A representative voltammogram is shown in Fig. 3 and the following arguments may be offered to explain the peak at ∼−1.0 V. The electrogenerated [$Mo^{V}OLH(DMF)_x$]$^+$ is quite unstable and suffers chemical oxidation assisted by a trace of H_2O present in DMF and generates [$Mo^{VI}O_2LH(DMF)_x$] which, in turn, suffers a two electron reduction in the −0.95 to −1.0 V range [15]. On comparison of its current height with an authentic one-electron process [4,5,16] this

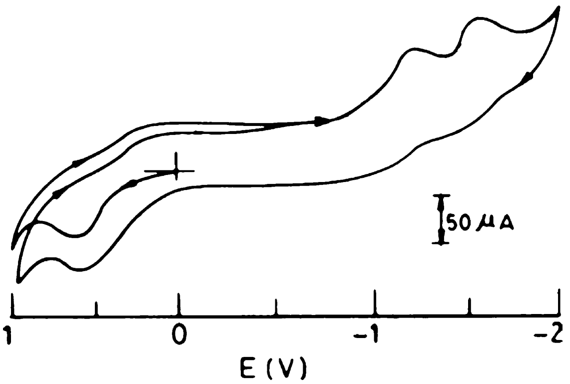

Fig. 3. Representative cyclic voltammogram of [$Mo^{IV}OLH$]$_n$ compounds **1** in DMF at 298 K.

Table 5
Cyclic voltammetric data[a] for [MoO(LH)(N–N)]-type oxomolybdenum (IV) complexes (**5**–**15**) at 298 K

Complex	Mo(V)/Mo(IV)				Mo(IV)/Mo(III)			
	E_{pa} (V)	E_{pc} (V)	ΔE_p (mV)	$(E_{1/2})_1$ (V)	E_{pc} (V)	E_{pa} (V)	ΔE_p (mV)	$(E_{1/2})_1$ (V)
5	+0.25	+0.14	110	+0.195	−1.87	−1.69	180	−1.78
6	+0.21	+0.15	60	+0.180	−1.73	−1.65	80	−1.69
7	+0.26	+0.18	80	+0.220	−1.87	−1.72	150	−1.79
8	+0.26	+0.19	70	+0.225	−1.72	−1.62	100	−1.67
9	+0.25	+0.19	60	+0.220	−1.88	−1.72	160	−1.80
10	+0.26	+0.19	70	+0.225	−1.83	−1.72	110	−1.77
11	+0.24	+0.17	70	+0.205	−1.77	−1.65	120	−0.71
12	+0.27	+0.19	80	+0.230	−1.94	−1.80	140	−1.87
13	+0.27	+0.20	70	+0.235	−1.94	−1.83	110	−1.88
14	+0.34	+0.24	100	+0.290	−1.95	−1.85	100	−1.90
15	+0.29	+0.19	100	+0.240	−1.72	−1.63	90	−1.67

[a] Solvent: DMF; working electrode: Platinum; reference electrode: SCE; $E_{1/2} = 0.5(E_{pa} + E_{pc})$; $E_p = E_{pc} - E_{pa}$; E_{pc} and E_{pa} are cathodic and anodic peak potentials, respectively; scan rate: 100 mV s^{-1}; supporting electrolyte: 0.1 M TEAP; solution strength: 10^{-3} M.

reduction seemed to represent a two-electron process. Such an observation was noted previously in the case of $Mo^{VI}O_2L$-type compounds [5,7].

During an initial positive scan, the $[Mo^{IV}O(N–N)(LH)]$ (**5**–**15**) complexes exhibit a quasi reversible redox couple with an oxidation around +0.25 V and a reduction at ~+0.14 V ($E_{1/2} = \sim 0.19$ V), {for N–N = dihydrazones of diacetyl, the reduction is at ~+0.19 V ($E_{1/2} = \sim 0.22$ V)}, an irreversible reductive response at ~−1.6 V and finally a quasi reversible reductive couple at ~−1.9 V. The corresponding oxidative peak is found at ~−1.7 V. These are assigned to be the Mo^{V}/Mo^{IV} redox couple, the ligand reduction and finally the $Mo^{IV} \rightarrow Mo^{III}$ reduction respectively. The one-electron nature of all these electrode processes is established by a comparison with an authentic one-electron system [4,5,16] under the same conditions. Such observations were reported earlier by our group [5]. The features remain practically unaltered on repeated scans. A representative voltammogram is shown in Fig. 4.

The most probable explanation of these observations is that the compound $[Mo^{IV}O(LH)(N–N)]$ undergoes one-electron oxidation to Mo^{V} at ~+0.25 V, which is reduced back to Mo^{IV} at ~+0.14 V on scan reversal. Then the ligand undergoes a reduction at ~−1.6 V and subsequently Mo^{IV} is reduced to Mo^{III} at ~−1.85 V. This Mo^{III} compound with the reduced form of the ligand undergoes oxidation to Mo^{IV} at ~−1.7 V. It appears from the above discussion that neutral N–N chelating ligands with $M(d\pi)–L(\pi^*)$ mixing ability, (viz., bipyridyl, phenanthroline and the diacetyldihydrazones) play an important role in stabilizing the Mo^{V} oxidation state.

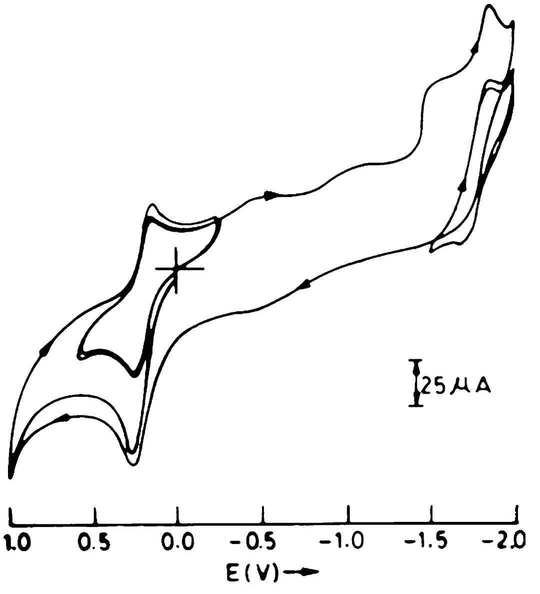

Fig. 4. Representative cyclic voltammogram of $[Mo^{IV}O(N–N)(LH)]$ compounds **5** in DMF at 298 K.

2.6. Oxo-transfer from DMSO

An interesting observation was noted while making an attempt to record the electronic spectra of these compounds in DMSO. As soon as a [MoOLH]/[MoO(LH)(N–N)] complex is dissolved in DMSO a change of color commences: the solution ultimately became yellow–orange and displayed all the characteristic features of the corresponding MoO_2L complex. This change is almost instantaneous for the $[Mo^{IV}O(LH)]_n$ complexes while the solutions of the $[Mo^{IV}O(N–N)(LH)]$ complexes take around 10 min to undergo such a change, the bands at 650 nm gradually disappearing within this time. These changes are accompanied by a distinct smell of Me_2S. Similar changes were also observed with the addition of DMSO, H_2O and pyridine-*N*-oxide to the DMF solutions of the samples. When a concentrated solution (dark brown) of a $[MoO(LH)]_n$ type complex was treated with pyridine N-oxide/DMSO and kept at room temperature it turned orange. On addition of excess alcohol to this solution an orange solid separated. It was filtered, washed with alcohol and dried over fused $CaCl_2$. It was identified as the original molybdenum(VI) compound from which the $[Mo^{IV}O(LH)]_n$ was generated. This oxo-accepting behavior of these complexes with a consequent oxidation at the Mo center from IV to VI may be related to the oxo-transfer behavior of oxidoreductase enzymes, which bring about a two-electron reduction of the substrate by removing an oxo ligand.

3. Experimental

3.1. Materials

$[MoO_2(acac)_2]$ was prepared as described in the literature [17]. Reagent grade solvents were dried and distilled prior to use. All other chemicals were reagent grade, available commercially and used without further purification.

3.2. Physical measurements

Elemental analyses were performed on a Perkin–Elmer 240 C, H, N analyser. The NMR spectra were recorded on a Bruker 300 NMR spectrometer. IR spectra were recorded as KBr pellets on a Perkin–Elmer 783 spectrometer while electronic spectra were recorded in solution using a Shimadzu UV/visible 2100 recording spectrophotometer. Magnetic susceptibility at room temperature was measured with a PAR model 155 vibrating sample magnetometer with Hg $[Co(SCN)_4]$ as calibrant. Electrochemical data were collected with a BAS CV-27 electrochemical analyser and a BAS model X–Y recorder at 298 K, using a three electrode cell, fitted with a purge gas inlet and outlet, consisting of a platinum working electrode, platinum auxiliary electrode and SCE reference electrode, and fitted with a purge gas inlet and outlet. Cyclic voltammograms were recorded in DMF solutions of the metal complexes containing 0.1M tetraethylammonium perchlorate as supporting electrolyte. The value for the ferrocenium–ferrocene couple under the experimental conditions is 0.40 V.

3.3. Synthesis of Schiff base ligands $L^{1-4}H$

All the four ligands were prepared by a method reported previously [7,15].

3.4. Preparation of diacetyldihydrazone(s)

These were synthesised by a slight modification of the reported procedure [11]. A solution of diacetyl (0.5 mmol) in dehydrated alcohol (25 ml) was slowly added to a stirred solution of hydrazine hydrate/phenylhydrazine (1.0 mmol) in the same solvent (25 ml) over a period of 30 min. After an hour of stirring one drop of glacial acetic acid was added to the reaction mixture from which the Schiff base was precipitated in 5–10 min. The mixture was filtered and the resulting pale yellow solid was washed twice with cold dry alcohol and dried over fused $CaCl_2$ before recrystallisation from hot anhydrous ethanol.

Diacetyldihydrazone (dhz): Yield 60%. *Anal.* Calc. for $C_4H_{10}N_4$: C, 42.11; H, 8.77; N, 49.12. Found: C, 42.09; H, 8.75; N, 49.13%; {Diacetyldi(phenylhydrazone)} (dphz): Yield 62%. *Anal.* Calc. for $C_{16}H_{18}N_4$: C, 72.18; H, 6.77; N, 21.05. Found: C, 72.20; H, 6.75; N, 21.04%.

3.5. Synthesis of $[MoO_2LH(MeOH)]$ $[LH = L^1H, L^2H, L^3H, L^4H]$

The precursor molybdenum(VI) compounds were prepared by a method similar to one reported previously [7,15] using the appropriate ligands.

*3.6. Preparation of the $[Mo^{IV}O(LH)]_n$ compounds (**1**–**4**)*

All these $[Mo^{IV}O(LH)]_n$ compounds were prepared under dry N_2 atmosphere by the following general method: the $[Mo^{VI}O_2L]$ compound (1 mmol) was suspended in dry degassed CH_3CN (30 ml) and refluxed under dry N_2. PPh_3 (1.5 mmol) was dissolved in dry, degassed CH_3CN (10 ml) and was added to the $[MoO_2L]$ solution under reflux. Within 10 min a brown compound separated. It was filtered from the hot solution, washed several times with dry degassed CH_3CN and dried in a vacuum desiccator over fused $CaCl_2$. $MoOL^1H$ (**1**): Yield 66%. *Anal.* Calc. for $C_{15}H_{12}N_4O_3SMo$: C, 42.45; H, 2.83; N, 13.21%. Found: C, 42.43; H, 2.75; N, 13.18%; $MoOL^2H$ (**2**): Yield 70%. *Anal.* Calc. for $C_{15}H_{10}N_4O_3SBr_2Mo$: C, 30.93; H, 1.72; N, 9.62. Found: C, 30.90; H, 1.70; N, 9.59%; $MoOL^3H$ (**3**): Yield 69%. *Anal.* Calc. for $C_{15}H_{10}N_6O_7SMo$: C, 35.02; H, 1.96; N, 16.34. Found: C, 34.99; H, 1.95; N, 16.31%; $MoOL^3H$ (**4**): Yield 68%. *Anal.* Calc. for $C_{17}H_{16}N_4O_3SMo$: C, 45.13; H, 3.54; N, 12.39. Found: C, 45.14; H, 3.55; N, 12.37%.

*3.7. Preparation of the $[Mo^{IV}O(N–N)LH]$ (**5**–**11**) compounds where N–N = 2, 2′-bipy and 1,10-phenanthroline*

All these $[Mo^{IV}O(N–N)LH]$ (**5**–**11**) compounds were prepared under dry N_2 atmosphere by the following general method: the $[Mo^{VI}O_2LH]$ compound (1 mmol) was suspended in dry degassed CH_3CN (20 ml) and refluxed under dry N_2. The appropriate N–N donor ligand (1.0 mmol) and PPh_3 (1.5 mmol) were separately dissolved in dry degassed CH_3CN (15 ml). The solution of the appropriate N–N donor ligand was added to the $[MoO_2L]$ solution under reflux immediately followed by the solution of PPh_3. Within half an hour a dark green microcrystalline compound separated out. It was filtered from the hot solution, washed thrice with dry degassed CH_3CN and dried in a vacuum desiccator over fused $CaCl_2$. $MoO(L^1H)$(bipy) (**5**): Yield 62%. *Anal.* Calc. for $C_{25}H_{12}N_6O_3SMo$: C, 49.02; H, 3.27; N, 13.73. Found: C, 49.00; H, 3.25; N, 13.72%; $MoO(L^1H)$(*o*-phen) (**6**): Yield 63%. *Anal.* Calc. for $C_{27}H_{20}N_6O_3SMo$: C, 50.94; H, 3.14; N, 13.21. Found: C, 50.89; H, 3.12; N, 13.19%; $MoO(L^2H)$(bipy) (**7**): Yield 60%. *Anal.* Calc. for $C_{25}H_{18}N_6O_3SBr_2Mo$: C, 38.96; H, 2.34; N, 10.88. Found: C, 38.93; H, 2.35; N, 10.81%; $MoO(L^2H)$(*o*-phen) (**8**): Yield 62%. *Anal.* Calc. for $C_{27}H_{18}N_6O_3SBr_2Mo$: C, 40.81; H, 2.27; N, 10.58. Found: C, 40.79; H, 2.25; N, 10.56%; $MoO(L^3H)$(bipy) (**9**): Yield 61%. *Anal.* Calc. for $C_{25}H_{18}N_8O_7SMo$: C, 42.72; H, 2.56; N, 15.93. Found: C, 42.74; H, 2.55; N, 15.92%; $MoO(L^3H)$(*o*-phen) (**10**): Yield 63%. *Anal.* Calc. for $C_{27}H_{18}N_8O_7SMo$: C, 44.65; H, 2.48; N, 15.43. Found: C, 44.63; H, 2.48; N, 15.32%; $MoO(L^4H)$(*o*-phen) (**11**): Yield 60%. *Anal.* Calc. for $C_{29}H_{24}N_6O_3SMo$: C, 52.41; H, 3.61; N, 12.63. Found: C, 52.40; H, 3.65; N, 12.67%.

*3.8. Preparation of the $[Mo^{IV}O(N–N)(LH)]$ (**12**–**15**) compounds where N–N = diacetyldihydrazone*

All these $[Mo^{IV}O(N–N)(LH)]$ (**12**–**15**) compounds were prepared under dry N_2 atmosphere by the general method [5] adopted for the preparation of the $[Mo^{IV}O(N–N)(LH)]$ (**5**–**11**) compounds described before using the appropriate dihydrazone in place of bipyridyl/orthophenanthroline. $MoO(L^1H)$(dhz) (**12**): Yield 60%.

Anal. Calc. for $C_{19}H_{22}N_8O_3SMo$: C, 42.36; H, 4.05; N, 20.73. Found: C, 42.31; H, 4.15; N, 20.72%; $MoO(L^2H)(dhz)$ (**13**): Yield 64%. *Anal.* Calc. for $C_{19}H_{20}N_8O_3SBr_2Mo$: C, 32.76; H, 2.90; N, 16.03. Found: C, 32.77; H, 2.87; N, 16.09%; $MoO(L^3H)(dhz)$ (**14**): Yield 62%. *Anal.* Calc. for $C_{19}H_{20}N_{10}O_7SMo$: C, 36.30; H, 3.21; N, 22.23. Found: C, 36.31; H, 3.15; N, 22.12%; $MoO(L^1H)(dphz)$ (**15**): Yield 61%. *Anal.* Calc. for $C_{31}H_{30}N_8O_3SMo$: C, 53.93; H, 4.35; N, 16.23. Found: C, 53.89; H, 4.41; N, 16.25%.

3.9. Crystal structure determination

A dark red spheroidal crystal of **6** ($0.28 \times 0.22 \times 0.20$ mm^3) was protected in a film of perfluoropolyether (RS3000) and mounted on a Stoe Stadi-4 four-circle diffractometer, in the cold stream of an Oxford Cryosystems open-flow cryostat [18] operating at 150 K. Data collection employed graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) and $\omega - \theta$ scans. The structure was solved by direct methods [19] followed by iterative cycles of least squares refinement and difference Fourier synthesis, and refined by full-matrix least squares [20]. Crystal data and details of the structure determination appear in Table 2.

4. Concluding remarks

A number of not so familiar oxomolybdenum(IV) complexes of some related multidentate NSO donor ligands are synthesized by oxo-abstraction from their structurally characterized dioxomolybdenum(VI) precursors. This is the first instance of diacetyldihydrazone ligands being used for stabilizing the MoO^{+2} core. Reports on structures of such Mo(IV) complexes are quite rare and in this work the crystal and molecular structure of a representative member of the [MoO(HL)(N–N)]-type complexes is reported. The oxo-abstraction property of these Mo(IV) complexes from substrates like triphenylphosphine oxide and pyridine N-oxide is demonstrated by the formation and the isolation of the precursor Mo(VI) complexes. Such reactions are reminiscent of $Mo^{IV}O^{+2}$ complexes, which mimic the active centers of the reduced forms of oxidoreductase molybdoenzymes. Results of cyclic voltammetric studies (Table 5) indicate that among the [MoO(HL)(N–N)] complexes, the dihydrazones of diacetyl are better stabilizers of the Mo(IV) oxidation state than either bipyridyl or orthophenanthroline.

5. Supplementary data

Crystallographic data have been deposited with the CCDC. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union road, Cambridge CB2 1EZ, UK (fax +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk, quoting the deposition number CCDC 200937 for complex **6**.

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