

# A family of mononuclear molybdenum-(VI), and -(IV) oxo complexes with a tridentate (ONO) ligand

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The salicylhydrazone of anthranilhydrazide ( $H_2L$ ) reacted with  $MoO_2(acac)_2$  in refluxing alcohols to yield compounds of the general formula  $MoO_2L(ROH)$  (where  $R = CH_3, C_2H_5, n-C_3H_7, n-C_4H_9$ ). The complex  $MoO_2L(C_2H_5OH)$  is found to undergo facile reaction with heterocyclic bases to form  $MoO_2L(Q)$ -type complexes where  $Q =$  pyridine, 4-picoline, imidazole and substituted imidazoles. Single crystal X-ray structural studies on the ligand  $H_2L$  (**1**) and the complexes  $MoO_2L(C_2H_5OH)$  (**2**) and  $MoO_2L(Imz)$  (**3**) indicate that the free ligand exists in its keto form, but in the two complexes **2** and **3** the ligand coordinates to the  $MoO_2^{2+}$  core through the enolate oxygen, the phenolate oxygen and the azomethine nitrogen. Reaction of  $MoO_2L(C_2H_5OH)$  with  $PPh_3$  in  $CH_3CN$  under dry dinitrogen, in the absence and presence of bipy, produced  $Mo^{IV}OL$  (**2a**) (brown) and  $Mo^{IV}OL(bipy)$  (**2b**) (green) respectively along with  $Ph_3PO$ . This reaction is reminiscent of the oxotransfer reaction from the  $MoO_2^{2+}$  core of a molybdoenzyme to the substrate  $PPh_3$ . Complexes **2** and **3** crystallized in the  $P2_1/n$  and  $P2_1/c$  space groups respectively and for both of them  $Z = 4$ . The structures clearly show that **2** and **3** have distorted octahedral coordination environments in which the  $Mo-O$ (ethanol) bond of **2** and the  $Mo-N$ (imidazole) bond of **3** are significantly longer than is usually observed. This is indicative of the weak bonding of ethanol and imidazole to the  $MoO_2^{2+}$  core and points to the inherent weakness of the sixth coordination position of the coordination polyhedron of the  $MoO_2^{2+}$  core in  $MoO_2L(C_2H_5OH)$  and  $MoO_2L(Imz)$ .

## Introduction

The coordination chemistry of molybdenum(VI) has assumed special importance due to its recently discovered biochemical significance<sup>1-3</sup> as well as for the involvement of Mo(VI) compounds as catalysts in several industrial processes such as amoxidation of propene,<sup>4</sup> epoxidation of olefins,<sup>5</sup> olefin metathesis<sup>6</sup> and isomerization of allylic alcohols.<sup>7</sup> The discovery of the presence of NSO donor points around the Mo(VI) centre of oxotransferase enzymes like xanthine oxidase, DMSO reductase<sup>8,9</sup> etc. led to the synthesis and exploration of the oxotransfer ability of a number of such model complexes that mimic the oxotransferase molybdoenzymes.<sup>10-13</sup> These studies also led to the belief that the presence of one or more sulfur donor point(s) is essential for the oxotransfer activity of such complexes. The first report of a Mo(VI) complex without the presence of sulfur donor point(s) appeared in 1990.<sup>14</sup> Since then quite a number of Mo(VI) complexes of multidentate ONO donor systems have been reported.<sup>15-20</sup>

Schiff bases derived from salicylaldehyde and amino alcohols which contain both phenolic and alcoholic groups along with a neutral nitrogen donor in the form of an imine nitrogen atom have been used as polydentate diacidic chelating ligands to prepare complexes containing the  $MoO_2^{2+}$ -core.<sup>21-23</sup> However, Schiff bases obtained by condensing ring substituted aromatic acidhydrazides with *o*-hydroxycarbonyl compounds like salicylaldehyde and *o*-hydroxyacetophenone have rarely been used in molybdenum chemistry. These ligands are of particular interest because their complexes of the type  $MoO_2L$  or  $MoOL$  possess one or two "open" coordination sites that can be utilized for substrate binding. In one of our previous works we used a few thiosemicarbazone (ONS) ligands and reported a number of Mo-(VI), -(V), and -(IV) oxo complexes. That was the first instance of the use of thiosemicarbazone ligands in the

modeling of the molybdenum binding site of the molybdenum cofactor of an oxotransferase enzyme.<sup>24</sup> In the present work we report the synthesis of a few dioxomolybdenum(VI) complexes of the general formula  $MoO_2L(ROH)$  (where  $R = CH_3, C_2H_5, C_3H_7$ , and  $n-C_4H_9$ ). As only the complex  $MoO_2L(EtOH)$  yielded good crystals, it is taken as a representative member and the detailed characterisation and exploration of chemical and electrochemical reactivity of  $MoO_2L(EtOH)$  (where  $H_2L =$  the 2-aminobenzoylhydrazone of salicylaldehyde) is reported here. During the study of the reactivity of  $MoO_2L(EtOH)$  we isolated  $MoO_2L(Q)$ -type complexes (where  $Q =$  neutral monodentate Lewis bases), and also succeeded in isolating and characterising complexes of the formula  $Mo^{IV}OL$ , and  $Mo^{IV}OL(N-N)$  (where  $N-N$  is a neutral bidentate donor). Structural characterisation of the ligand  $H_2L$ , and the complexes  $MoO_2L(EtOH)$  and  $MoO_2L(Imz)$  by single crystal X-ray diffraction techniques is also reported.

## Results and discussion

### A. Dioxomolybdenum(VI) complexes

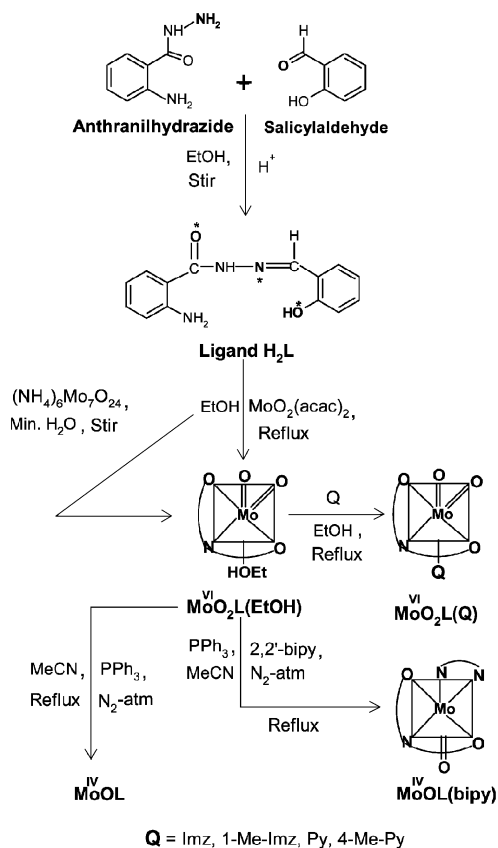
**Synthesis.** The anthranilhydrazone of salicylaldehyde,  $H_2L$  (**1**), was used as the ligand. It is found to act as a dianionic tridentate ONO donor in this work. Reaction (Scheme 1) of this ligand with bis(acetylacetonato)dioxomolybdenum(VI) in ethyl alcohol under refluxing conditions produced the orange colored complex  $MoO_2L(EtOH)$  (**2**) in excellent yield. When  $MoO_2L(EtOH)$  was reacted with different heterocyclic bases ( $Q$ ) in ethanol, complexes of general formula  $MoO_2L(Q)$  (**3-6**) (where  $Q =$  pyridine,  $\gamma$ -picoline, imidazole and substituted imidazoles) were obtained in good yield.

All complexes are air stable in the solid state and are moderately soluble in ethanol and acetonitrile but highly soluble in

**Table 1** Characteristic IR <sup>a</sup> bands and electronic spectral data <sup>b</sup> for the studied complexes

Complex	$\nu(\text{Mo}=\text{O})/\text{cm}^{-1}$	$\lambda_{\text{max}}/\text{nm}$ ( $\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ )
MoO <sub>2</sub> L(EtOH) ( <b>2</b> )	912, 900	430 (8277), 319 (17019), 290 (16939)
MoO <sub>2</sub> L(Imz) ( <b>3</b> )	914, 898	436 (8732), 324 (16937), 290 (15693)
MoO <sub>2</sub> L(1-Me-Imz) ( <b>4</b> )	920, 906	428 (9129), 321 (17108), 287 (16352)
MoO <sub>2</sub> L(Py) ( <b>5</b> )	925, 914	432 (8081), 319 (16482), 292 (15685)
MoO <sub>2</sub> L(4-Me-Py) ( <b>6</b> )	929, 908	435 (8237), 317 (16703), 288 (15711)
MoOL ( <b>2a</b> )	921	722 (242), 432 (910), 321 (1817), 297 (1814)
MoOL(bipy) ( <b>2b</b> )	950	672 (81), 429 (2022), 321 (5254), 281 (13089)

<sup>a</sup> Recorded as KBr pellets. <sup>b</sup> In DMF.

**Scheme 1** Reaction scheme for the isolation of dioxomolybdenum(VI) and oxomolybdenum(IV) complexes.

DMF and DMSO. Magnetic susceptibility and molar conductivity data indicate that these MoO<sub>2</sub><sup>2+</sup> complexes are diamagnetic and electrically non-conducting in solution.

**Spectral characteristics.** Selected spectral data of the complexes are summarized in Table 1. IR spectra of the complexes do not exhibit the ligand bands at 3451 [ $\nu(\text{OH})$ ], 3193 [ $\nu(\text{NH})$ ] and 1643  $\text{cm}^{-1}$  [ $\nu(\text{C}=\text{O})$ ].<sup>25,26</sup> Characteristic strong bands in the spectra of both the ligand and the complexes are located at 1610–1616 and 1540–1554  $\text{cm}^{-1}$  due to  $\nu(\text{C}=\text{N})$  and  $\nu(\text{C}=\text{C}/\text{aromatic})$  stretching modes of the ligand.<sup>26,27</sup> All complexes (**2–6**) exhibit two bands at *ca.* 898–914 and 912–929  $\text{cm}^{-1}$ , assigned to symmetric and antisymmetric vibrations respectively, of the *cis*-MoO<sub>2</sub> core.<sup>3,13,24,28</sup>

The electronic absorption spectra (in DMF) of all the complexes (**2–6**) display a shoulder in the 436–428 nm region and two strong absorptions are located in the 325–315 and 300–280 nm range, which are assignable to L–Mo( $d\pi$ ) LMCT and intraligand transitions respectively.<sup>24,28–30</sup> All such data are included in Table 1.

The <sup>1</sup>H NMR (DMSO *d*<sub>6</sub>) spectral data of the free ligand and its dioxomolybdenum(VI) complex, **2**, are given in the Experimental section. The spectrum of the free ligand exhibits an OH

**Table 2** Cyclic voltammetric results<sup>a</sup> for dioxomolybdenum(VI) complexes at 298 K

Complex	$E_{\text{pc}}/\text{V}$
<b>2</b>	–0.91, –1.32
<b>3</b>	–0.90, –1.24
<b>4</b>	–0.91, –1.36
<b>5</b>	–0.93, –1.28
<b>6</b>	–0.88, –1.42

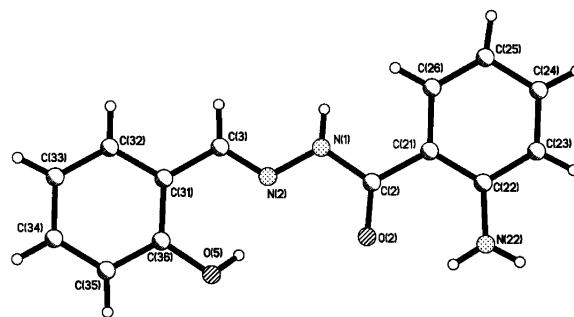
<sup>a</sup> Solvent: acetonitrile; working electrode: platinum; reference electrode: SCE; supporting electrolyte: 0.1 M TEAP; scan rate: 100  $\text{mV s}^{-1}$ .

(phenolic) proton resonance at 10.01 ppm, an imine carbon proton resonance at 8.31 ppm and aromatic proton resonances at 7.44–6.70 ppm, respectively.<sup>31</sup> On coordination, the signal for the OH proton disappears, indicating deprotonation of the phenolic OH and subsequent coordination of the phenoxide-oxygen to the MoO<sub>2</sub><sup>2+</sup> core in MoO<sub>2</sub>L(EtOH). Involvement of the imine nitrogen in coordination shifted the resonance signal of the imine carbon proton about 0.6 ppm downfield.<sup>3</sup>

**Redox properties.** The electrochemical behavior of all Mo<sup>VI</sup>O<sub>2</sub> complexes has been examined in MeCN solution using cyclic voltammetry at a platinum electrode with TEAP as supporting electrolyte. The corresponding data for all the Mo<sup>VI</sup>O<sub>2</sub> complexes are included in Table 2. When only the reduction pathway is scanned the CV trace of all the complexes display two irreversible reductive responses<sup>24,28,29</sup> within the potential window –0.8 to –1.5 V which are assigned to Mo(VI)/Mo(V)<sup>32,33</sup> and Mo(V)/Mo(IV) processes, respectively. The ligand **1** is redox inactive within this potential window. On scanning the oxidation half an irreversible oxidation wave for all the complexes is located in the +1.50 to +1.70 V range. As the Mo(VI) complex cannot undergo a metal-centered oxidation, this is attributed to a ligand-centered process.

### Description of the structure of ligand **1** and complexes **2** and **3**.

The molecular structure and the atom numbering schemes for ligand **1** (H<sub>2</sub>L) and the complexes **2** [MoO<sub>2</sub>L(EtOH)] and **3** [MoO<sub>2</sub>L(Imz)] are shown in Figs. 1–3, respectively with the relevant bond distances and angles collected in Tables 3–5. The ligand behaves in a tridentate manner in which the donor

**Fig. 1** Ball-and-stick plot of H<sub>2</sub>L (**1**) with atom labeling scheme.

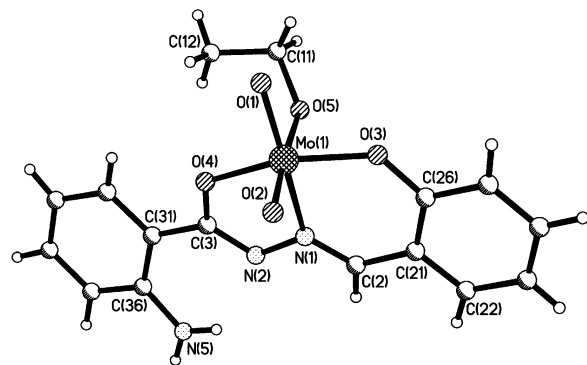


Fig. 2 Ball-and-stick plot of  $\text{MoO}_2\text{L}(\text{EtOH})$  (**2**) with atom labeling scheme.

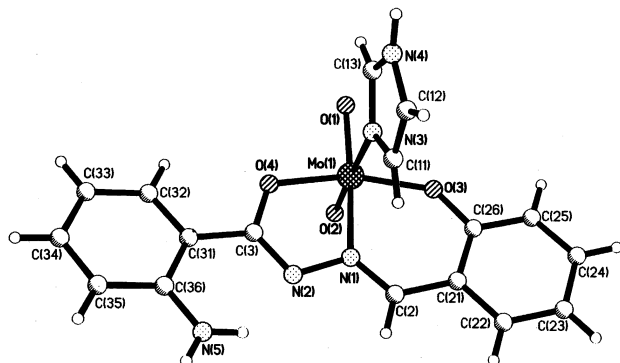


Fig. 3 Ball-and-stick plot of  $\text{MoO}_2\text{L}(\text{Imz})$  (**3**) with atom labeling scheme.

points, O(5), N(2) and O(2) occupy a meridional plane.<sup>34,35</sup> The free ligand is found to exist in the keto form as the C(2)–O(2) distance of 1.223(6) Å, corresponds to a carbon–oxygen double bond.<sup>36</sup>

The coordination geometry around molybdenum can be described as distorted octahedral in the two Mo(vi) complexes (**2** and **3**), the ligand dianion acting in a planar tridentate manner forming one five-membered and another six-membered metalocycle involving the  $\text{MoO}_2^{2+}$  moiety. As expected from its structure, the Schiff base ligand is bonded to the *cis*- $\text{MoO}_2^{2+}$  ion in a planar fashion involving the *xy*-plane, coordinating through the phenolate oxygen O(3), the enolate oxygen O(4) and the imine nitrogen atom N(1) and an oxo group O(1) lying *trans* to N(1). In complex **2** [ $\text{MoO}_2\text{L}(\text{EtOH})$ ] an ethanol molecule completes the distorted octahedral coordination sphere which lies *trans* to the other oxo group O(2). The Mo–O(alcohol) bond [2.343(2) Å] is significantly longer than the other Mo–O bonds [1.693(3)–1.997(2) Å] indicating that the alcohol molecule is weakly bonded to the  $\text{MoO}_2^{2+}$ -core and this position holds the possibility of functioning as a substrate-binding site. This possibility is realized in the facile formation of adducts of the general formula  $\text{MoO}_2\text{L}(\text{Q})$ . In complex **3** [ $\text{MoO}_2\text{L}(\text{Imz})$ ] the position of the alcohol molecule is taken up by the Lewis base imidazole coordinating through its tertiary nitrogen N(3). The rather large Mo–N(3) distance [2.377(2) Å] reveals that the imidazole moiety is also rather weakly coordinated to the  $\text{MoO}_2^{2+}$  core. The Mo–O(1) and Mo–O(2) bond distances of the  $\text{MoO}_2^{2+}$  group are unexceptional<sup>3,37,38</sup> and almost equal [1.693(3)–1.707(2) Å] for complexes **2** and **3**. These observations raise an interesting point about the suspected inherent weakness of the sixth position in the coordination octahedron of the  $\text{MoO}_2^{+2}$  core, *trans* to the Mo=O(2) bond.

From comparison of the bond distances and angles of ligand **1** and complexes **2** and **3** it is clear that the ligand coordinates to the  $\text{MoO}_2^{2+}$ -core in the deprotonated enolate form because in

Table 3 Selected bond lengths (Å) and angles (°) for ligand **1**

C(3)–N(2)	1.276(7)	C(2)–O(2)	1.223(6)
N(2)–N(1)	1.374(5)	C(22)–N(22)	1.377(6)
C(2)–N(1)	1.385(7)	C(36)–O(5)	1.360(6)
C(31)–C(36)–O(5)	121.2(4)	N(1)–C(2)–O(2)	119.3(4)
C(31)–C(3)–N(2)	118.2(4)	C(21)–C(2)–O(2)	123.8(5)
N(2)–N(1)–C(2)	116.1(4)	C(21)–C(22)–N(22)	122.9(4)

Table 4 Selected bond lengths (Å) and angles (°) for complex **2**

Mo(1)–O(2)	1.693(3)	Mo(1)–O(4)	1.997(2)
Mo(1)–O(1)	1.704(2)	Mo(1)–N(1)	2.237(3)
Mo(1)–O(3)	1.925(2)	Mo(1)–O(5)	2.343(2)
O(2)–Mo(1)–O(1)	105.97(13)	O(3)–Mo(1)–N(1)	80.67(10)
O(2)–Mo(1)–O(3)	98.52(13)	O(4)–Mo(1)–N(1)	71.69(9)
O(1)–Mo(1)–O(3)	102.79(11)	O(2)–Mo(1)–O(5)	170.38(11)
O(2)–Mo(1)–O(4)	97.85(12)	O(1)–Mo(1)–O(5)	83.54(10)
O(1)–Mo(1)–O(4)	98.09(11)	O(3)–Mo(1)–O(5)	80.45(10)
O(3)–Mo(1)–O(4)	148.68(10)	O(4)–Mo(1)–O(5)	78.98(9)
O(2)–Mo(1)–N(1)	94.04(12)	N(1)–Mo(1)–O(5)	76.35(9)
O(1)–Mo(1)–N(1)	158.78(11)		

Table 5 Selected bond lengths (Å) and angles (°) for complex **3**

Mo(1)–O(2)	1.702(2)	Mo(1)–O(4)	2.010(2)
Mo(1)–O(1)	1.707(2)	Mo(1)–N(1)	2.235(2)
Mo(1)–O(3)	1.920(2)	Mo(1)–N(3)	2.377(2)
O(2)–Mo(1)–O(1)	105.21(11)	O(3)–Mo(1)–N(1)	81.66(9)
O(2)–Mo(1)–O(3)	98.55(12)	O(4)–Mo(1)–N(1)	72.01(8)
O(1)–Mo(1)–O(3)	103.16(10)	O(2)–Mo(1)–N(3)	171.38(10)
O(2)–Mo(1)–O(4)	95.07(11)	O(1)–Mo(1)–N(3)	83.11(9)
O(1)–Mo(1)–O(4)	97.80(10)	O(3)–Mo(1)–N(3)	81.42(9)
O(3)–Mo(1)–O(4)	150.94(9)	O(4)–Mo(1)–N(3)	81.35(8)
O(2)–Mo(1)–N(1)	93.23(10)	N(1)–Mo(1)–N(3)	78.22(8)
O(1)–Mo(1)–N(1)	159.83(9)		

complexes **2** and **3** the C–O bond distances [C(3)–O(4)] exhibit values of 1.318(4) and 1.324(4) Å and are nearer to a C–O single bond than to a C–O double bond distance. However, it falls short of the pure C–O single bond distance of 1.42 Å. The reason for such shortening may be attributed to electron delocalisation in the coordinated ligand.<sup>39,40</sup> The adjacent C(3)–N(2) bonds now display a typical double bond distance [1.306(4) and 1.299(4) vs. 1.385(7) Å in **1**] and a concomitant lengthening of the N(2)–N(1) bond [1.401(4) and 1.402(3) vs. 1.374(5) Å in **1**] is also apparent for complexes **2** and **3**. The C(2)–N(1) bond distances in **2** and **3** are almost the same [1.288(4) and 1.285(4) Å, respectively] and are pretty close to the usual C=N length.<sup>41,42</sup> The N–N–C bond angle of the ligand **1** [N(2)–N(1)–C(2), 116.1(4)°] is reduced by a few degrees [N(1)–N(2)–C(3), 109.1(3) and 110.1(2)° for **2** and **3**, respectively] on complex formation. These changes are directly due to coordination of the ligand to the  $\text{MoO}_2^{2+}$  moiety when it becomes a delocalised system.<sup>39,40</sup> Thus, the structures of **1** and **2** along with the facile formation of  $\text{MoO}_2\text{L}(\text{Q})$ -type complexes from  $\text{MoO}_2\text{L}(\text{EtOH})$  is a signature of the substrate binding character of the sixth coordination site lying *trans* to the oxo oxygen O(2). The rather long Mo–N distance and consequent weak binding of the Lewis base to the sixth coordination position lying *trans* to the oxo-oxygen O(2) may be a consequence of displacement of the Mo atom from the equatorial mean plane towards the apical oxo-oxygen O(2). This displacement, naturally, makes the Mo(vi) acceptor centre rather inaccessible to the donor approaching from the appropriate direction.

## B. Oxomolybdenum(IV) complexes

**Synthesis and spectral characteristics.** The oxomolybdenum(IV) complexes were synthesized by two different methods (described later). The complex  $\text{MoOL}$  (**2a**) is air stable in the solid state whereas  $\text{MoOL}(\text{bipy})$  (**2b**) is not very stable in

**Table 6** Cyclic voltammetric results<sup>a</sup> for oxomolybdenum(IV) complexes at 298 K

Complex	Mo(VI)/Mo(IV) $E_{pa}/V$	Mo(V)/Mo(IV) $E_{pa}/V$	Mo(IV)/Mo(III)			
			$E_{pa}/V$	$E_{pc}/V$	$\Delta E_p/mV$	$(E_{1/2})/V$
<b>2a</b>	—	+0.08	-1.12	-0.80	320	-0.96
<b>2b</b>	+1.16	—	—	—	—	—

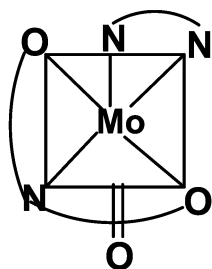
<sup>a</sup> Solvent: DMF for **2a** and CH<sub>3</sub>CN for **2b**; working electrode: platinum; reference electrode: SCE;  $E_{1/2} = 0.5(E_{pa} + E_{pc})$ ;  $\Delta E_p = E_{pa} - E_{pc}$ ;  $E_{pc}$  and  $E_{pa}$  are cathodic and anodic peak potentials, respectively; scan rate: 100 mV s<sup>-1</sup>.

moist air. Complexes **2a** and **2b** have poor solubility in organic solvents like CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub> and CH<sub>3</sub>CN, but are highly soluble in DMF and DMSO and on exposure to moist air they are slowly transformed to the parent MoO<sub>2</sub>L complex. Such a conversion may be attributed to the abstraction of an oxo-oxygen from the solvent DMSO by the [MoO]<sup>2+</sup> complexes. As four-coordinate Mo(IV)-oxo complexes are rather unlikely, they are probably polymeric species in the solid state. All the complexes are non-electrolytes in DMF and are diamagnetic at room temperature.<sup>24,43,44</sup>

Some spectral characteristics of compounds **2a** and **2b** are listed in Table 1. As in the case of the MoO<sub>2</sub><sup>2+</sup> complexes, the ligand H<sub>2</sub>L functions in a dianionic tridentate manner in MoOL and MoOL(bipy). IR spectral features of these MoO(IV) complexes clearly reveal coordination from the deprotonated phenolic and enolic oxygens and the azomethine nitrogen. These complexes exhibit a single strong, sharp band in the 950–920 cm<sup>-1</sup> region, representing the  $\nu(\text{Mo}=\text{O})_t$ <sup>24</sup> mode.

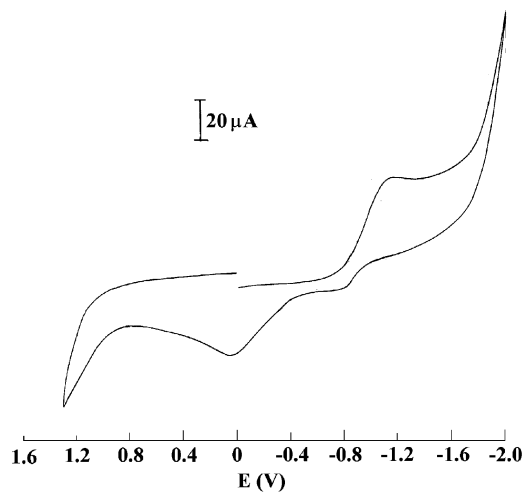
Electronic spectra of the Mo(IV)-oxo compounds were recorded in dry DMF solution, and the compounds are found to display (Table 1) several absorption maxima in the 280–730 nm range. The spectra of the Mo(IV)-oxo compounds exhibit a new band of moderate intensity in the low energy 670–730 nm region. Absorption in this region is a characteristic feature of the [MoO]<sup>2+</sup> core.<sup>24,45,46</sup>

The proposed structure of **2b** is shown in Fig. 4.

**Fig. 4** The proposed structure of **2b**.

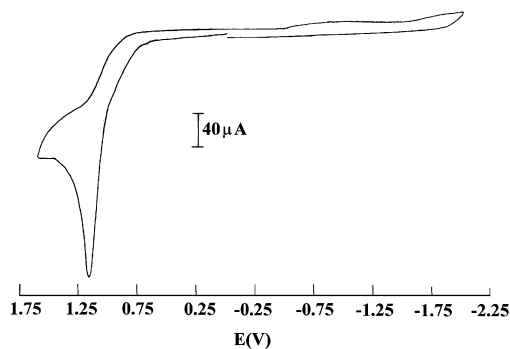
**Electrochemistry.** The electron-transfer behavior of complexes **2a** and **2b** (Table 6) has been examined in DMF and CH<sub>3</sub>CN respectively using conditions described earlier. The Mo(IV)-oxo complex **2a** is found to undergo an irreversible one-electron reduction to the corresponding Mo(III) complex and a one-electron irreversible oxidation to a Mo(V) complex. Similar observations were noted by Boyd and Spence<sup>45</sup> as well as our own group<sup>24</sup> for other Mo(IV)-oxo complexes with dianionic tridentate ligands having ONO and SNO donor sites. By contrast, the cyclic voltammograms for complex **2b** display only an oxidation wave, which is irreversible in nature.

**Mo<sup>IV</sup>OL.** Because of its poor solubility in MeCN, cyclic voltammograms of Mo<sup>IV</sup>OL (Fig. 5) were recorded in DMF. In an initial scan at a rate of 100 mV s<sup>-1</sup> a reductive response was located around -1.12 V. Reversal of the scan produced two anodic waves at -0.80 and +0.08 V, respectively. The oxidation wave around -0.8 V may be assigned to reoxidation of the species previously reduced at -1.12 V to the initial Mo(IV)-oxo complex. The reductive couple at -1.12 V ( $E_{1/2} = -0.96$  V) is

**Fig. 5** Cyclic voltammograms of MoOL (**2a**) in DMF (0.1 M TEAP) at a platinum electrode; scan rate 100 mV s<sup>-1</sup> and potentials recorded vs. SCE.

assigned to the Mo(IV)/Mo(III)<sup>24</sup> process. The irreversible anodic process at +0.08 V is assigned to the Mo(V)/Mo(IV)<sup>24</sup> process. The one electron nature of both these processes was confirmed by coulometry.

**Mo<sup>IV</sup>OL(bipy).** The electrochemical behavior of Mo<sup>IV</sup>OL-(bipy) (Fig. 6) has been examined in MeCN solution. The CV

**Fig. 6** Cyclic voltammograms of MoOL(bipy) (**2b**) in CH<sub>3</sub>CN (0.1 M TEAP) at a platinum electrode; scan rate 100 mV s<sup>-1</sup> and potentials recorded vs. SCE.

trace of this complex exhibits no reduction wave up to -1.8 V and shows only one irreversible oxidation process at a quite high positive potential of +1.16 V. As neither the free ligand nor the parent Mo(VI) complex (**2**) of the same ligand show any oxidation wave in this region, this oxidation wave may be assigned to the Mo(VI)/Mo(IV) process. The two-electron nature of this process was confirmed by coulometry.

**Reactivity of the complexes. Substrate binding.** The dioxomolybdenum(VI) complex **2** [MoO<sub>2</sub>L(EtOH)] has been synthesised and isolated from C<sub>2</sub>H<sub>5</sub>OH media. When **2** is reacted with monodentate heterocyclic bases (Q) like pyridine,  $\gamma$ -picoline, imidazole, substituted imidazoles *etc.* in ethanol, the corresponding MoO<sub>2</sub>L(Q) compounds are obtained. These

reactions can be considered as substrate binding reactions of the MoO<sub>2</sub>L-core when the heterocyclic base substrate binds itself to the MoO<sub>2</sub>L moiety by replacing the weakly coordinated C<sub>2</sub>H<sub>5</sub>OH. But, when these compounds are dissolved in coordinating solvents such as DMF/DMSO, the monodentate ligand Q is replaced by a solvent molecule, as is evident from the color change of the resultant solutions, and their electronic spectra. The Mo(IV)-oxo complex MoOL (**2a**) has been isolated from CH<sub>3</sub>CN solution but it does not contain solvent molecules. **2a** is found to react readily with 2,2'-bipyridyl to produce the six-coordinate complex MoOL(bipy) (**2b**).

*Oxo transfer to substrate.* The tendency of the Mo(VI) complex MoO<sub>2</sub>L(EtOH) to transfer an oxygen atom to the substrate has been examined in CH<sub>3</sub>CN using PPh<sub>3</sub> as the substrate. The parent complex **2** has a band at 430 nm due to a L(O) → M(Mo) LMCT transition. When the complex is reacted with PPh<sub>3</sub>, this band is found to be shifted towards lower energy and a new band appears at 722 nm. The oxo transfer reaction may be represented as



PPh<sub>3</sub>O has been isolated and identified. This oxo-transfer reaction may be visualised<sup>47</sup> as a simple bimolecular reaction.<sup>24</sup>

## Conclusions

Use of tridentate ONO donor acid hydrazone ligands for the preparation of dioxomolybdenum(VI) and oxomolybdenum(IV) complexes has been achieved. Model complexes, which are found to mimic the active site of some oxotransferase molybdoenzymes, are known to contain at least one sulfur donor point around the MoO<sub>2</sub><sup>+2</sup> or MoO<sup>+2</sup> moieties along with other N/O donor centres. In this study the donor environment consists exclusively of N- and O-donor points and no S-donor centre is present. In spite of that the MoO<sub>2</sub>L complex is found to exhibit oxotransfer to a substrate. Also, no indication of μ-oxo Mo(V) dimer formation is noted during oxo-transfer reactions.

## Experimental

### Materials

[MoO<sub>2</sub>(acac)<sub>2</sub>] was prepared as described in the literature.<sup>48</sup> Reagent grade solvents were dried and distilled prior to use. All other chemicals were reagent grade, available commercially and used as received. Tetraethylammonium perchlorate (TEAP) used for electrochemical work was prepared as reported in the literature.<sup>49</sup>

### Physical measurements

Elemental analyses were performed on a Perkin-Elmer 240 C, H, N analyser. IR spectra were recorded on a Perkin-Elmer 783 spectrometer. <sup>1</sup>H NMR spectra were recorded with a Bruker AVANCE DPX 300 MHz spectrometer using SiMe<sub>4</sub> as an internal standard. Electronic spectra were recorded on a Shimadzu UV/VIS recording spectrophotometer. Magnetic susceptibility was measured with a PAR model 155 vibrating sample magnetometer with Hg[Co(SCN)<sub>4</sub>] as the calibrant. Electrochemical data were collected using an EG&G PARC electrochemical analyser (model 250/5/0) and a PC-controlled EG&G/PARC-VERSASTAT2 potentiostat at 298 K in a dry nitrogen atmosphere. Cyclic voltammetry experiments were carried out with a platinum working electrode, platinum auxiliary electrode and SCE as reference electrode and TEAP as supporting electrolyte.

### Crystallography

Crystal data for ligand **1** and compounds **2** and **3**, along with other experimental details, are summarized in Table 7 with

selected bond lengths and angles in Tables 3–5. Single-crystal data collection were performed at 293(2) K on a Siemens P4 four circle diffractometer using graphite monochromated Mo-Kα radiation (λ = 0.71073 Å). The ligand H<sub>2</sub>L (**1**) crystallizes in the monoclinic space group *P2<sub>1</sub>/c*, complex MoO<sub>2</sub>L(EtOH) (**2**) in the monoclinic space group *P2<sub>1</sub>/n*, and complex MoO<sub>2</sub>L(Imz) (**3**) in the monoclinic space group *P2<sub>1</sub>/c*. The intensities were corrected for Lorentz and polarization effects and semi-empirical absorption corrections were performed on the basis of  $\Psi$  scans for nine chosen reflections with high  $\chi$  values. Following structure solution, positional parameters and temperature factors were refined by full matrix least squares against  $F_o^2$  with SHELX-97.<sup>50</sup> All non-hydrogen atoms were refined anisotropically and a riding model with isotropic temperature factors was employed for hydrogen atoms.

CCDC reference numbers 182101–182103.

See <http://www.rsc.org/suppdata/dt/b2/b207129k/> for crystallographic data in CIF or other electronic format.

### Synthesis

Syntheses of the ligand H<sub>2</sub>L and all the Mo(VI) and Mo(IV) complexes are summarized in Scheme 1 and the individual details are given below.

**H<sub>2</sub>L, 1.** The 2-aminobenzoylhydrazone of salicylaldehyde (H<sub>2</sub>L, **1**) was prepared by reacting anthranilhydrazide (7.6 g, 50.33 mmol) and salicylaldehyde (6.1 g, 50.00 mmol) in stirring ethanol (25 ml) for 2 h. The resulting yellowish-white compound was filtered, washed thrice with ethanol and dried over fused CaCl<sub>2</sub>. Mp 165°C. Yield 8.91 g (70%). Anal. calc. for C<sub>14</sub>H<sub>13</sub>N<sub>3</sub>O<sub>2</sub>: C, 65.81; H, 5.13; N, 16.45. Found: C, 65.26; H, 5.09; N, 16.76%. <sup>1</sup>H NMR (DMSO d<sub>6</sub>): δ 7.44–6.70 (m, 8H, C<sub>6</sub>H<sub>4</sub>), 8.31 (s, 1H, CH), 10.01 (s, OH).

**[MoO<sub>2</sub>L(EtOH)], 2.** 0.28 g (1.09 mmol) of H<sub>2</sub>L was dissolved in 30 ml ethanol by refluxing on a water bath and 0.33 g (1.01 mmol) of solid MoO<sub>2</sub>(acac)<sub>2</sub> was added to the resultant solution and the mixture refluxed for 3 h and then filtered. Slow evaporation of the orange filtrate over 3 days produced dark orange crystals. Yield 0.35 g (80%). Anal. calc. for C<sub>16</sub>H<sub>16</sub>N<sub>3</sub>O<sub>5</sub>Mo: C, 45.04; H, 3.78; N, 9.85. Found: C, 44.84; H, 3.90; N, 9.91%. <sup>1</sup>H NMR (DMSO d<sub>6</sub>): δ 7.68–6.54 (m, 16H, C<sub>6</sub>H<sub>4</sub>), 8.98 (s, 1H, CH).

**[MoOL], 2a.** To a refluxing solution of MoO<sub>2</sub>L(EtOH) (0.22 g, 0.51 mmol) in 25 ml of degassed acetonitrile 0.393 g (1.5 mmol) of PPh<sub>3</sub> in 5 ml of acetonitrile was added. The reddish orange solution turned dark brown and a brown compound separated within 1 h. The brown compound was collected by rapid filtration of the hot mixture, washed well with hot acetonitrile and dried *in vacuo*. Yield 0.13 g (70%). Anal. calc. for C<sub>14</sub>H<sub>11</sub>N<sub>3</sub>O<sub>3</sub>Mo: C, 45.99; H, 3.03; N, 11.49. Found: C, 45.84; H, 3.12; N, 11.23%.

**[MoOL(bipy)], 2b (bipy = 2,2'-bipyridine).** To a refluxing solution of MoO<sub>2</sub>L(EtOH) (0.22 g, 0.51 mmol) in 25 ml of degassed acetonitrile 0.78 g (5.0 mmol) of 2,2'-bipyridine (bipy), followed by a solution of PPh<sub>3</sub> (0.393 g, 1.5 mmol) in 5 ml of degassed acetonitrile was added. The orange-red solution turned green after 1 h and refluxing was continued for another 4 h. The green compound **2b** was precipitated by adding excess dichloromethane followed by excess n-hexane. It was rapidly filtered and washed well with n-hexane and dried *in vacuo*. Yield 0.19 g (70%). Anal. calc. for C<sub>24</sub>H<sub>19</sub>N<sub>5</sub>O<sub>3</sub>Mo: C, 55.24; H, 3.67; N, 13.42. Found: C, 55.01; H, 3.90; N, 13.51%.

**[MoO<sub>2</sub>L(Imz)], 3 (Imz = imidazole).** To a clear orange solution (obtained by refluxing) of **2** (0.22 g, 0.52 mmol) in ethanol (50 ml) was added imidazole (0.05 g, 0.75 mmol) and the mixture was left to reflux for 3 h. The volume of this dark orange solution was then reduced to 20 ml using a rotary evaporator. On standing at room temperature, the solution

**Table 7** Crystal and refinement data for ligand **1** and complexes **2** and **3**

	<b>1</b>	<b>2</b>	<b>3</b>
Formula	C <sub>14</sub> H <sub>13</sub> N <sub>3</sub> O <sub>2</sub>	C <sub>16</sub> H <sub>16</sub> MoN <sub>3</sub> O <sub>5</sub>	C <sub>17</sub> H <sub>15</sub> MoN <sub>5</sub> O <sub>4</sub>
<i>M</i>	255.3	426.3	449.3
Crystal symmetry	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P2</i> / <i>c</i>	<i>P2</i> <sub>1</sub> / <i>n</i>	<i>P2</i> <sub>1</sub> / <i>c</i>
<i>a</i> /Å	13.181(3)	12.019(2)	11.340(3)
<i>b</i> /Å	6.500(13)	9.804(2)	6.742(11)
<i>c</i> /Å	14.432(3)	15.004(3)	22.902(4)
<i>V</i> /Å <sup>3</sup>	1225.5(4)	1665.4(6)	1727.7(7)
<i>Z</i>	4	4	4
<i>F</i> (000)	536	860	904
$\mu$ (Mo-K $\alpha$ )(mm <sup>-1</sup> )	0.096	0.820	0.795
Collected reflections	1330	3072	4118
Independent reflections	1330	2926	3938
<i>R</i> <sub>1</sub> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	0.062	0.032	0.033
<i>wR</i> <sub>2</sub> (all data)	0.140	0.072	0.075

deposited shiny brown crystals. Yield 0.19 g (80%). Anal. calc. for C<sub>17</sub>H<sub>15</sub>N<sub>5</sub>O<sub>4</sub>Mo: C, 45.40; H, 3.36; N, 15.58. Found: C, 45.31; H, 3.49; N, 15.87%.

**[MoO<sub>2</sub>L(1-Me-Imz)], 4.** This compound was prepared using same procedure as in the case of compound **3**. Yield 0.19 g (80%). Anal. calc. for C<sub>18</sub>H<sub>17</sub>N<sub>5</sub>O<sub>4</sub>Mo: C, 46.62; H, 3.70; N, 15.10. Found: C, 46.61; H, 3.75; N, 14.99%.

**[MoO<sub>2</sub>L(Py)], 5 (Py = pyridine).** Complex **2** (0.22 g, 0.52 mmol) was treated with 2 ml pyridine and the mixture heated until a clear deep yellow solution was produced. 20 ml of dry ethanol was then added and the solution refluxed for 3 h. Slow evaporation of the reaction mixture over 5 days produced yellow crystals. Yield 0.18 g (75%). Anal. calc. for C<sub>19</sub>H<sub>16</sub>N<sub>4</sub>O<sub>4</sub>Mo: C, 49.64; H, 3.51; N, 12.19. Found: C, 49.24; H, 3.45; N, 12.09%.

**[MoO<sub>2</sub>L(4-Me-Py)], 6.** This compound was prepared using same procedure as above (compound **5**). Yield 0.18 g (75%). Anal. calc. for C<sub>20</sub>H<sub>18</sub>N<sub>4</sub>O<sub>4</sub>Mo: C, 50.71; H, 3.83; N, 11.83. Found: C, 50.84; H, 3.90; N, 11.51%.

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