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Journal of Coordination Chemistry

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713455674>

Chemical, electrochemical and structural studies of some *cis*-dioxomolybdenum(VI) complexes of two tridentate ONS chelating ligands

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To cite this Article Pramanik, Nikhil Ranjan , Ghosh, Saktiprosad , Raychaudhuri, Tapas Kumar , Chaudhuri, Siddhartha , Drew, Mike G. B. and Mandal, Sudhanshu Sekhar(2007) 'Chemical, electrochemical and structural studies of some *cis*-dioxomolybdenum(VI) complexes of two tridentate ONS chelating ligands', Journal of Coordination Chemistry, 60: 20, 2177 – 2190

To link to this Article: DOI: 10.1080/00958970701258192

URL: <http://dx.doi.org/10.1080/00958970701258192>

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Chemical, electrochemical and structural studies of some *cis*-dioxomolybdenum(VI) complexes of two tridentate ONS chelating ligands

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(Received 21 September 2006; revised 26 October 2006; in final form 28 October 2006)

Several *cis*-dioxomolybdenum complexes of two tridentate ONS chelating ligands H_2L^1 and H_2L^2 (obtained by condensation of S-benzyl and S-methyl dithiocarbazates with 2-hydroxyacetophenone) have been prepared and characterized. Complexes **1** and **2** are found to be of the form $MoO_2(CH_3OH)L^1 \cdot CH_3OH$ and MoO_2L , respectively, (where L^{2-} = dianion of H_2L^1 and H_2L^2). The sixth coordination site of the complexes acts as a binding site for various neutral monodentate Lewis bases, B, forming complexes **3–10** of the type MoO_2LB (where B = γ -picoline, imidazole, thiophene, THF). The complexes were characterized by elemental analyses, various spectroscopic techniques, (UV-Vis, IR and 1H NMR), measurement of magnetic susceptibility at room temperature, molar conductivity in solution and by cyclic voltammetry. Two of the complexes $MoO_2(CH_3OH)L^1 \cdot CH_3OH$ (**1**) and $MoO_2L^1(imz)$ (**5**) were structurally characterized by single crystal X-ray diffraction. Oxo abstraction reactions of **1** and **5** led to formation of oxomolybdenum(IV) complex of the MoOL type.

Keywords: Dioxomolybdenum(VI) complexes; Dithiocarbazate; Schiff bases; X-ray structures

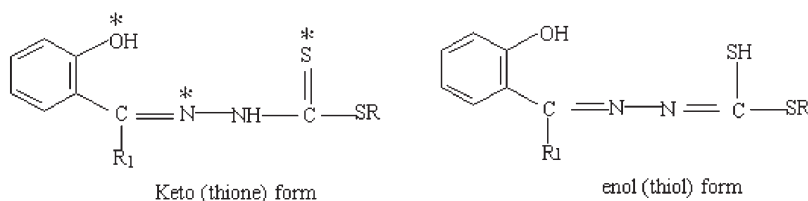
1. Introduction

Coordination chemistry of molybdenum in higher oxidation states ligated to mixed hard-soft ONS donor ligands has attracted attention because of the possible relationship of these species to the active sites of redox active molybdoenzymes [1, 2]. For many years it has been assumed that the presence of sulfur atoms coordinated to molybdenum is essential for molybdenum complexes to have oxotransfer activity and

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many model compounds that mimic such oxotransferases have been studied [3–9]. However, a number of complexes have been reported where the presence of sulfur atoms coordinated to molybdenum is not mandatory for oxotransfer activity [10]. Catalytic reactions of molybdoenzymes are known to involve oxidation states Mo(VI) and Mo(IV) [11, 12] but recent EPR studies show that Mo(V) is also involved during electron transfer to or from the redox centers.

In this study synthesis, characterization, chemical and electrochemical activity of some Mo(VI) complexes are reported which are found to resemble some properties of the active sites of molybdoenzymes [13–17]. The ligand frame used in this study consists of Schiff bases derived from condensation of 2-hydroxyacetophenone with S-benzyl and S-methyl dithiocarbazates. Such ligands (H_2L^1 and H_2L^2) are binegative tridentate ONS donor systems [18], coordinating through their thioenol form.



R	R ₁	Ligand
CH ₂ C ₆ H ₅	CH ₃	H ₂ L ¹
CH ₃	CH ₃	H ₂ L ²

Tautomeric thione and thiol forms of the Schiff-base ligands

In this work we report synthesis and characterization of mononuclear dioxo Mo(VI) complexes of the type $MoO_2(CH_3OH)L^1 \cdot CH_3OH/MoO_2L^2$ and MoO_2LB (where B is a neutral monodentate Lewis base). All complexes have been characterized by elemental analyses, electrochemical and various spectroscopic (UV-Vis, IR, 1H NMR) techniques. Crystal and molecular structures of $MoO_2(CH_3OH)L^1CH_3OH$ (**1**) and $MoO_2L^1(imz)$ (**5**) have been determined by single crystal X-ray diffraction.

2. Experimental

2.1. Materials

$[MoO_2(acac)_2]$ was prepared as described in the literature [19]. Reagent grade solvents were dried and distilled prior to use. All other chemicals used for preparative work were of reagent grade, available commercially and used without further purification.

2.2. Synthesis of ligands

The Schiff-base ligands S-benzyl- β -N-(2-hydroxyphenylethylidene) dithiocarbazate (H_2L^1) and S-methyl- β -N-(2-hydroxyphenylethylidene) dithiocarbazate (H_2L^2)

were prepared by condensing S-benzyl and S-methyl dithiocarbazates [20] with 2-hydroxyacetophenone in ethanol. The ligands have been satisfactorily characterized by elemental analysis, IR and ^1H NMR data.

S-benzyl- β -N-(2-hydroxyphenylethylidene) dithiocarbazate (H_2L^1). Yield $\sim 80\%$, m.p. $\sim 148^\circ\text{C}$. Anal. Calcd for $\text{C}_{16}\text{H}_{16}\text{N}_2\text{S}_2\text{O}$ (%): C, 60.76; H, 5.06; N, 8.86, Found: C, 60.26; H, 4.65; N, 8.73. IR (KBr Pellet), cm^{-1} : $\nu_{(\text{N-H})}$ 3171 (m), $\nu_{(\text{O-H})}$ 3436 (sh), $\nu_{(\text{C=N})}$ 1600 (s), $\nu_{(\text{C=S})}$ 1309 (m), ^1H NMR (dmso d_6): ($\text{H}_3\text{C}-\text{C}=\text{N}^-$) 2.47 s (3), ($-\text{CH}_2-$) 4.51 s (2), ($\text{NH}-$) 11.25 s (1), (aromatic-OH) 11.26 s (1), (aromatic proton) 6.84–6.90 m (2), 7.24–7.41 m (7).

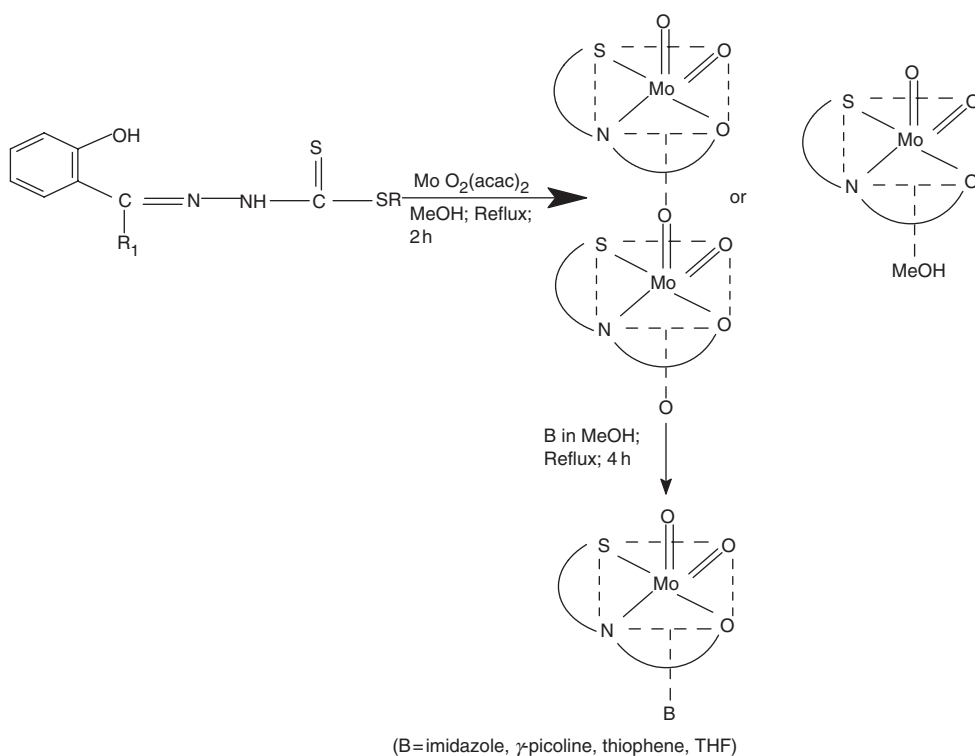
S-methyl- β -N-(2-hydroxyphenylethylidene) dithiocarbazate (H_2L^2). Yield $\sim 75\%$, m.p. $\sim 160^\circ\text{C}$. Anal. Calcd for $\text{C}_{10}\text{H}_{12}\text{N}_2\text{S}_2\text{O}$ (%): C, 50.00; H, 5.00; N, 11.66, Found: C, 49.80; H, 4.98; N, 11.71. IR (KBr Pellet), cm^{-1} : $\nu_{(\text{N-H})}$ 3173 (m), $\nu_{(\text{O-H})}$ 3432 (sh), $\nu_{(\text{C=N})}$ 1600 (s), $\nu_{(\text{C=S})}$ 1344 (m), ^1H NMR (dmso- d_6): ($\text{H}_3\text{C}-\text{C}=\text{N}^-$) 2.46 s (3), ($-\text{NH}-$) 11.42 s (1), ($-\text{CH}_3$) 2.55 s (3), (aromatic-OH) 12.68 s (1), (aromatic proton) 6.86–6.99 m (2), 7.3 t (1), 7.6 d (1).

2.3. Synthesis of complexes

$\text{MoO}_2(\text{CH}_3\text{OH}) \text{L}^1 \cdot \text{CH}_3\text{OH}$ (1). To a filtered solution of 0.33 g (1.0 mmol) of $\text{MoO}_2(\text{acac})_2$ in dry methanol (20 mL), 0.316 g (1.0 mmol) H_2L^1 in 15 mL of dry methanol was added and the resulting orange solution was refluxed for 2 h. The volume of the solution was then reduced to about 10 mL on a water bath. On cooling the orange-yellow compound that separated, was filtered, washed with cold methanol and dried *in vacuo* over anhydrous CaCl_2 , yield $\sim 80\%$. The compound was recrystallized from dry methanol. Anal. Calcd for $\text{C}_{18}\text{H}_{22}\text{N}_2\text{S}_2\text{O}_5\text{Mo}$ (%): C, 42.69; H, 4.35; N, 5.53, Mo, 18.97, Found: C, 42.51; H, 4.26; N, 5.52, Mo, 18.68. IR (KBr Pellet), cm^{-1} : $\nu_{(\text{C=N})}$ 1579 (vs), $\nu_{(\text{Mo=O})}$ 939 (s), 914 (s), $\nu_{(\text{Mo-S})}$ 391 (s), $\nu_{(\text{Mo-N})}$ 573 (m), UV-Vis (CH_2Cl_2) [$\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$): 298 (24067), 370 (9752); ^1H NMR (dmso- d_6): ($\text{H}_3\text{C}-\text{C}=\text{N}^-$) 2.76 s (3), ($-\text{CH}_2-$) 4.43 s (2), (aromatic proton) 6.86–6.90 m (2), 7.24–7.49 m (7).

MoO_2L^2 (2) was prepared similarly using 0.240 g (1.0 mmol) of H_2L^2 with a yield of 75%. Anal. Calcd for $\text{C}_{10}\text{H}_{10}\text{N}_2\text{S}_2\text{O}_3\text{Mo}$ (%): C, 32.78; H, 2.73; N, 7.65, Mo, 26.22, Found: C, 32.75; H, 3.21; N, 7.99, Mo, 25.92. IR (KBr Pellet), cm^{-1} : $\nu_{(\text{C=N})}$ 1597 (s), $\nu_{(\text{Mo=O})}$ 950 (s), 900 (s), $\nu_{(\text{Mo-S})}$ 380 (m), $\nu_{(\text{Mo-N})}$ 565 (s), UV-Vis (CH_2Cl_2) [$\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$): 242 (13817), 296 (11518) 373 (4565); ^1H NMR (dmso- d_6): ($\text{H}_3\text{C}-\text{C}=\text{N}^-$) 2.77 s (3), ($-\text{CH}_3$) 2.55 s (3), (aromatic proton) 6.86–6.89 dd (1), 7.00–7.06 m (1), 7.43–7.48 m (1), 7.84–7.88 dd (1).

Complexes 3–10. These are of the general formula MoO_2LB and were prepared [18] by refluxing the parent compounds **1** and **2** in methanol with the appropriate monodentate Lewis base (such as γ -picoline, imidazole, thiophene or THF) in 1 : 2 mole ratio for ~ 4 h [scheme 1]. The orange-yellow crystalline solids so formed were filtered, washed



Scheme 1. Reaction diagram for the isolation of Mo(VI) complexes.

with dry methanol and dried in vacuo over anhydrous CaCl_2 , Yield ~ 70 – 75% . All are air stable, insoluble in water and diamagnetic as expected for a species with a d^0 Mo(VI) [21]. All the compounds are quite soluble in polar aprotic solvents like CH_2Cl_2 , CH_3CN , DMF and DMSO. Molar conductivity data in 10^{-3}M CH_2Cl_2 solution indicates their non-electrolyte character. Electronic spectra of all the complexes were recorded in CH_2Cl_2 and cyclic voltammograms were recorded in DMF (table 3).

MoO₂L¹(γ -pic) (3). Anal. Calcd for $\text{C}_{22}\text{H}_{21}\text{N}_3\text{S}_2\text{O}_3\text{Mo}$ (%): C, 49.34; H, 3.92; N, 7.85, Mo, 17.94, Found: C, 49.20; H, 3.75; N, 7.68, Mo, 18.00. IR (KBr Pellet), cm^{-1} : $\nu_{(\text{C}=\text{N})}$ 1543 (s), $\nu_{(\text{Mo}=\text{O})}$ 998 (vs), 912 (vs), $\nu_{(\text{Mo}-\text{S})}$ 389 (m), $\nu_{(\text{Mo}-\text{N})}$ 622 (s), UV-Vis (CH_2Cl_2) [$\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$): 297 (20726), 373 (8398).

MoO₂L²(γ -pic) (4). Anal. Calcd for $\text{C}_{16}\text{H}_{17}\text{N}_3\text{S}_2\text{O}_3\text{Mo}$ (%): C, 41.83; H, 3.70; N, 9.15, Mo, 20.91, Found: C, 41.75; H, 3.62; N, 9.20, Mo, 20.79. IR (KBr Pellet), cm^{-1} : $\nu_{(\text{C}=\text{N})}$ 1585 (s), $\nu_{(\text{Mo}=\text{O})}$ 945 (s), 900 (S), $\nu_{(\text{Mo}-\text{S})}$ 395 (m), $\nu_{(\text{Mo}-\text{N})}$ 660 (m); UV-Vis (CH_2Cl_2) [$\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$): 243 (19115), 299 (14468), 370 (5062).

MoO₂L¹(imz) (5). Anal. Calcd for $\text{C}_{19}\text{H}_{18}\text{N}_4\text{S}_2\text{O}_3\text{Mo}$ (%): C, 44.70; H, 3.53; N, 10.98, Mo, 18.82, Found: C, 45.00; H, 3.34; N, 10.85, Mo, 18.76. IR (KBr Pellet),

cm^{-1} : $\nu_{(\text{C}=\text{N})}$ 1581 (vs), $\nu_{(\text{Mo}=\text{O})}$ 939 (s), 885 (s), $\nu_{(\text{Mo}-\text{S})}$ 385 (m), $\nu_{(\text{Mo}-\text{N})}$ 640 (m); UV-Vis (CH_2Cl_2) [$\lambda_{\text{max/nm}}$ ($\epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$): 302 (22096), 379 (7817).

MoO₂L²(imz) (6). Anal. Calcd for $\text{C}_{13}\text{H}_{14}\text{N}_4\text{S}_2\text{O}_3\text{Mo}$ (%): C, 35.94; H, 3.22; N, 12.90, Mo, 22.72, Found: C, 36.10; H, 3.13; N, 12.87, Mo, 21.98. IR (KBr Pellet), cm^{-1} : $\nu_{(\text{C}=\text{N})}$ 1599 (vs), $\nu_{(\text{Mo}=\text{O})}$ 925 (s), 900 (s), $\nu_{(\text{Mo}-\text{S})}$ 385 (m), $\nu_{(\text{Mo}-\text{N})}$ 660 (s); UV-Vis (CH_2Cl_2) [$\lambda_{\text{max/nm}}$ ($\epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$): 299 (8590), 345 (6652).

MoO₂L¹(thiophene) (7). Anal. Calcd for $\text{C}_{20}\text{H}_{18}\text{N}_2\text{S}_3\text{O}_3\text{Mo}$ (%): C, 45.62; H, 3.42; N, 5.32, Mo, 18.23, Found: C, 45.32; H, 3.22; N, 5.30, Mo, 18.11. IR (KBr Pellet), cm^{-1} : $\nu_{(\text{C}=\text{N})}$ 1573 (s), $\nu_{(\text{Mo}=\text{O})}$ 991 (vs), 925 (s), $\nu_{(\text{Mo}-\text{S})}$ 389 (s), $\nu_{(\text{Mo}-\text{N})}$ 570 (s); UV-Vis (CH_2Cl_2) [$\lambda_{\text{max/nm}}$ ($\epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$): 298 (23369), 373 (9436).

MoO₂L²(thiophene) (8). Anal. Calcd for $\text{C}_{14}\text{H}_{14}\text{N}_2\text{S}_3\text{O}_3\text{Mo}$ (%): C, 37.33; H, 3.11; N, 6.22, Mo, 21.33, Found: C, 36.90; H, 3.00; N, 6.31, Mo, 21.00. IR (KBr Pellet), cm^{-1} : $\nu_{(\text{C}=\text{N})}$ 1579 (m), $\nu_{(\text{Mo}=\text{O})}$ 1000 (s), 928 (vs), $\nu_{(\text{Mo}-\text{S})}$ 390 (m), $\nu_{(\text{Mo}-\text{N})}$ 570 (m); UV-Vis (CH_2Cl_2) [$\lambda_{\text{max/nm}}$ ($\epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$): 242 (14894), 296 (12598), 367 (5097).

MoO₂L¹(THF) (9). Anal. Calcd for $\text{C}_{20}\text{H}_{22}\text{N}_2\text{S}_2\text{O}_4\text{Mo}$ (%): C, 46.63; H, 4.28; N, 5.45, Mo, 18.67, Found: C, 45.87; H, 4.20; N, 5.36, Mo, 18.34. IR (KBr Pellet), cm^{-1} : $\nu_{(\text{C}=\text{N})}$ 1573 (s), $\nu_{(\text{Mo}=\text{O})}$ 989 (vs), 925 (s), $\nu_{(\text{Mo}-\text{S})}$ 387 (m), $\nu_{(\text{Mo}-\text{N})}$ 589 (s); UV-Vis (CH_2Cl_2) [$\lambda_{\text{max/nm}}$ ($\epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$): 299 (25923), 371 (10491).

MoO₂L²(THF) (10). Anal. Calcd for $\text{C}_{14}\text{H}_{18}\text{N}_2\text{S}_2\text{O}_4\text{Mo}$ (%): C, 38.36; H, 4.11; N, 6.39, Mo, 21.92, Found: C, 38.22; H, 4.00; N, 6.21, Mo, 22.00. IR (KBr Pellet), cm^{-1} : $\nu_{(\text{C}=\text{N})}$ 1595 (s), $\nu_{(\text{Mo}=\text{O})}$ 945(vs), 900 (s), $\nu_{(\text{Mo}-\text{S})}$ 370 (w), $\nu_{(\text{Mo}-\text{N})}$ 590 (m); UV-Vis (CH_2Cl_2) [$\lambda_{\text{max/nm}}$ ($\epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$): 242 (18836), 296 (15756), 369 (6303).

2.4. Physical measurements

Elemental analyses were performed on a Perkin–Elmer 240 C, H, N analyzer. NMR spectra were recorded on a Bruker 300 L NMR spectrometer operating at 300 MHz with TMS as internal standard. IR spectra were recorded as KBr pellets on a Perkin–Elmer model 883 infrared spectrophotometer. Electronic spectra were recorded on a HITACHI U-3501 UV-Vis recording spectrophotometer. Magnetic susceptibility was measured with a PAR model 155 vibrating sample magnetometer with Hg [Co(SCN)₄] as calibrant. Electrochemical data were collected on a Sycopel model AEW2 1820 F/S instrument at 298 K using a Pt working electrode, Pt auxiliary electrode and SCE reference electrode. Cyclic voltammograms were recorded in DMF containing 0.1 M TEAP as supporting electrolyte.

Table 1. Crystal data and details of refinement for **1** and **5**.

	Complex 1	Complex 5
Chemical formula	C ₁₈ H ₂₂ MoN ₂ O ₅ S ₂	C ₁₉ H ₁₈ MoN ₄ O ₃ S ₂
Formula weight (M)	506.46	510.45
Crystal system	Monoclinic	Triclinic
Space group	<i>P</i> 2 ₁ / <i>C</i>	<i>P</i> $\bar{1}$
<i>a</i> (Å)	7.739 (9)	9.0075 (13)
<i>b</i> (Å)	21.56 (2)	10.7920 (7)
<i>c</i> (Å)	13.222 (15)	11.1851 (14)
α (°)	91.736 (8)	
β (°)	100.394 (10)	110.599 (11)
γ (°)	92.825 (7)	
<i>V</i> (Å ³)	2170 (4)	1015.2 (2)
<i>Z</i>	4	2
Temperature (K)	293 (2)	293 (2)
<i>D</i> _C (g cm ⁻³)	1.550	1.670
μ (Mo-K α) (mm ⁻¹)	0.8	0.881
<i>F</i> (000)	1032	516
Goodness of fit on <i>F</i> ²	1.153	1.166
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0464, <i>wR</i> ₂ = 0.093	<i>R</i> ₁ = 0.0642, <i>wR</i> ₂ = 0.1464

2.5. Crystallographic measurements

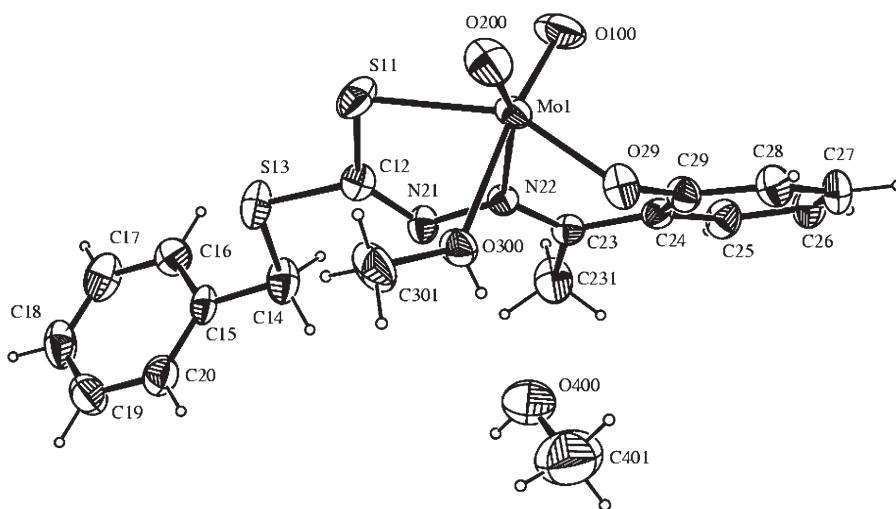
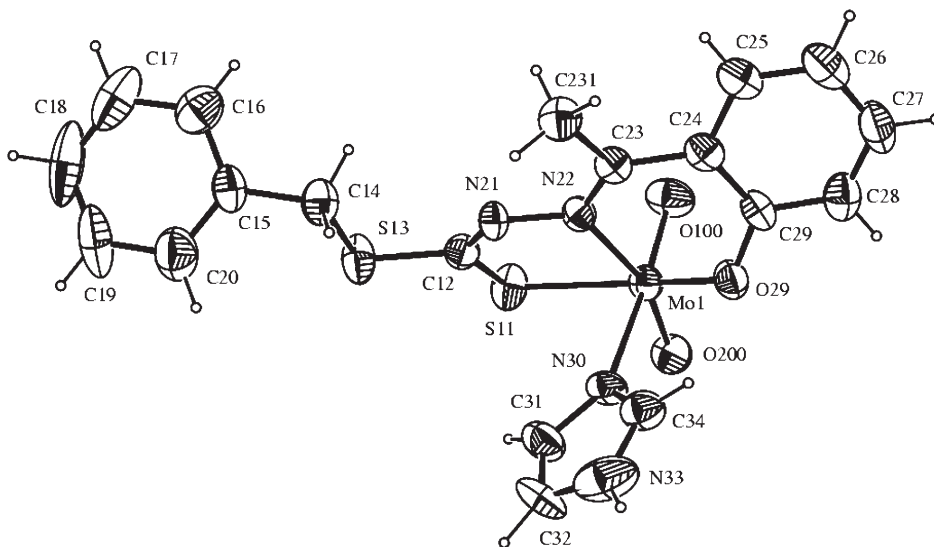
The X-ray diffraction data for **1** were collected on a MAR research Image Plate diffractometer using Mo-K α ($\lambda = 0.71013$ Å) radiation and processed for Lorentz, polarisation and absorption effects using the XDS package [22]. The crystal structure was solved by direct methods using SHELXS-86 [23] and refined on *F*² by the full matrix least squares method using SHELXL-93 [24] with anisotropic thermal parameters for the non-hydrogen atoms. The position of the hydrogen atoms were determined geometrically and refined using the 'riding' model.

The data for complex **5** were collected on a Bruker-Nonius MACH3 diffractometer using Mo-K α radiation and processed using the XCAD4 program [25]. They were corrected for absorption effects using the empirical method of North, Phillips and Mathews [26]. The structure was solved by direct methods using the program SIR-92 [27] and refined using SHELXL-97 [28]. The refinement of this structure was similar to that in complex **1**. All crystallographic data are summarized in table 1.

3. Results and discussion

3.1. Description of the crystal structure of the complexes MoO₂(CH₃OH)*L*¹ · CH₃OH (**1**) and MoO₂*L*¹(imz) (**5**)

The molecular structure and atom-numbering scheme of **1** and **5** are shown in the figures 1 and 2. Crystallographic data are given in table 1 and selected bond lengths and angles are presented in table 2. In **1**, three donor atoms O(29), N(22) and S(11) from the ligand and one terminal oxo atom O(200), occupy the meridional plane [29, 30] and N(22) is situated trans to the oxo-oxygen O (200). The dianionic tridentate ligand forms one five-membered and one six-membered metallocycle involving the [MoO₂]²⁺ core,

Figure 1. ORTEP diagram of **1** [MoO₂ (CH₃OH) L¹ · CH₃OH].Figure 2. ORTEP diagram of **5** [MoO₂L¹(imz)].

the bite angles N(22)–Mo(1)–S(11) and N(22)–Mo(1)–O(29) being 76.23(9)° and 79.64(13)°, respectively.

Complex **1** has the NO₄S donor set around the Mo(VI) center in a distorted octahedron. The Schiff-base ligand is bonded to the [MoO₂]²⁺ core through the phenolate oxygen O(29), the thioenolate sulfur S(11) and the azomethine nitrogen N(22). Both O(100) and O(300), the latter from coordinated methanol molecule, occupy axial positions generating an O(100)–Mo(1)–O(300) angle of 167.59(13)° confirming the distorted octahedral nature of the donor environment around the Mo(VI), the

Table 2. Selected bond lengths (Å) and angles (°) for **1** and **5**.

	Complex 1	Complex 5
Mo(1)–O(29)	1.938 (3)	1.942 (5)
Mo(1)–O(100)	1.688 (3)	1.703 (6)
Mo(1)–S(11)	2.461 (2)	2.439 (2)
S(11)–C(12)	1.749 (4)	1.750 (8)
Mo(1)–O(200)	1.717 (3)	1.687 (5)
S(13)–C(12)	1.759 (4)	1.737 (8)
Mo(1)–O(300)	2.301 (3)	
N(21)–N(22)	1.405 (4)	1.409 (9)
Mo(1)–N(30)		2.373 (7)
O(29)–C(29)	1.360 (5)	1.343 (9)
Mo(1)–N(22)	2.284 (4)	2.296 (6)
O (100)–Mo (1)–O (200)	105.9 (2)	106.2 (3)
O (100)–Mo (1)–O (300)	167.59 (13)	
O (100)–Mo (1)–N (30)		166.6 (2)
O (200)–Mo (1)–O (300)	86.19 (15)	
O (200)–Mo (1)–N (30)		86.9 (2)
O (100)–Mo (1)–O (29)	97.8 (2)	95.9 (3)
O (200)–Mo (1)–O (29)	107.0 (2)	106.0 (2)
O (100)–Mo (1)–N (22)	90.93 (15)	90.6 (2)
O (200)–Mo (1)–N (22)	160.49 (12)	161.2 (3)
O (29)–Mo (1)–N (22)	79.64 (13)	79.9 (2)
O (29)–Mo (1)–O (300)	75.64 (13)	
O (29)–Mo (1)–N (30)		77.3 (2)
N (22)–Mo (1)–O (300)	77.64 (12)	
N (22)–Mo (1)–N (30)		76.8 (2)
O (100)–Mo (1)–S (11)	100.32 (15)	97.9 (2)
O (200)–Mo (1)–S (11)	90.85 (13)	92.98 (19)
O (29)–Mo (1)–S (11)	149.90 (9)	152.28 (17)
N (22)–Mo (1)–S (11)	76.23 (9)	76.09 (17)
O (300)–Mo (1)–S (11)	81.80 (10)	
N (30)–Mo (1)–S (11)		83.92 (16)

Table 3. Cyclic voltammetric peak potential data ^a (V vs. SCE) in DMF solution at 298 K.

Complexes	<i>E</i> _{pc} (V)	<i>E</i> _{pa} (V)
MoO ₂ L ¹ · CH ₃ OH	−1.03	0.09
MoO ₂ L ²	−1.00	−0.14
MoO ₂ L ¹ (imz)	−1.07	−0.12
MoO ₂ L ² (imz)	−1.06	−0.11
MoO ₂ L ¹ (γ-pic)	−1.05	−0.12
MoO ₂ L ² (γ-pic)	−1.04	−0.10
MoO ₂ L ¹ (thiophene)	−1.11	−0.12
MoO ₂ L ² (thiophene)	−1.01	−0.12

^aSolvent: DMF (dry, degassed); supporting electrolyte: 0.1 M TEAP; solution strength: 10^{−3} M; electrode: platinum; reference electrode: SCE; scan rate: 50 mV s^{−1}.

Mo center is slightly displaced by 0.3334 (3) Å from the least squares plane described by N(22), O(29), S(11) and O(200) towards the apical oxo-oxygen O(100). The [MoO₂]²⁺ core has a *cis* configuration with conventional [31] average value for the Mo(1)–O(100)/O(200) distance [1.7025(3) Å] and O(100)–Mo(1)–O(200) bond angle 105.9(2)°, which is close to the energy minimum value estimated from MO theory [32]. Unequal bond distances involving the donor points and the Mo(VI) acceptor clearly

exhibit the extent of distortion of the coordination octahedron. The Mo(1)–O(300) bond *trans* to the terminal oxygen atom O(100) is longer [2.301(3) Å] compared to the length of the other Mo–O bond [Mo(1)–O(29)=1.938(3) Å] and indicates weaker binding of the coordinated methanol which can act as a substrate binding site. This expectation is realized in the facile formation of MoO₂LB (where B is a neutral monodentate Lewis base like γ -picoline, imidazole, thiophene or THF).

The Mo=O bond lengths Mo(1)–O(100)=1.688(3) Å, Mo(1)–O(200)=1.717(3) Å are unexceptional [33–36]. The azomethine nitrogen N(22) is *trans* to the oxo-oxygen O(200) and the Mo(1)–N(22) bond length of 2.284(4) Å is rather long due to *trans* effect. The C(12)–N(21) bond length [1.289(5) Å] is close to usual C=N bond length [37, 38]. The Mo(1)–S(11) distance of 2.461(2) Å is very near to the values observed in similar molybdenum complexes [30, 39, 40]

In complex **5** the molybdenum(VI) center is a distorted octahedral donor environment consisting of two *cis* oxo atoms O(100) and O(200), phenolate oxygen O(29), thioenolate sulfur S(11), an azomethine nitrogen N(22) and the tertiary nitrogen N(30) of imidazole. In fact, the structure of **5** can be derived from the structure of **1**, MoO₂(CH₃OH)L¹·CH₃OH by replacing the coordinated methanol molecule with an imidazole which occupies the axial position *trans* to the oxo atom O(100) generating a O(100)–Mo(1)–N(30) angle of 166.6(2)°. This also points to the distortion of the octahedron around Mo(VI), with the Mo center slightly displaced by 0.2947(8) Å from the least squares plane described by N(22), O(29), S(11) and O(200) towards the apical oxo-oxygen O(100). A remarkable feature of the structure of **5** is that, the values of the bond lengths and bond angles of **1** involving the Mo(VI) center remain mostly unchanged in **5**. Even the length of the metal oxygen double bond (Mo=O) axial to the coordinated imidazole (which is known to be highly influenced by axial coordination in many oxo-metal complexes and is thought to be a measure of σ -donor capacity of the coordinated ligand) stands practically unchanged [33, 37, 41].

That the length of the Mo(1)–N(30) bond is longer [2.373(7) Å] than the other Mo–N (azomethine) bond Mo(1)–N(22) [2.296(6) Å] reveals rather weak attachment of imidazole to the [MoO₂]²⁺. This is confirmed by the TG and DTA study of **5**, which exhibited easy loss of imidazole on controlled heating. As evidenced from the packing diagram (figure 3) of **5**, the structure is stabilized by hydrogen bonding involving the hydrogen atom attached to N(33) and the oxo-oxygen O(200) of the [MoO₂]²⁺ acceptor.

3.2. IR and ¹H NMR spectra

Both ligands exhibit two broad IR bands of medium intensity in the 3436–3171 cm^{−1} region, the higher frequency one due to the ν (O–H) mode while the lower one assigned to the ν (N–H) vibration [42]. Strong ν (C=N) bands around 1600 cm^{−1} of the free ligands are red shifted to 1543–1579 and 1579–1598 cm^{−1}, respectively, in the corresponding complexes indicating coordination from the azomethine nitrogen [43, 44] to the metal ion. The ν (C=S) band observed in the 1309–1344 cm^{−1} region for the ligands, disappeared upon complex formation. A new band in the 570–640 cm^{−1} region was observed in the spectra of complexes and is assigned to ν (Mo–N) [42]. The complexes exhibit a medium intensity band around 370–395 cm^{−1} which may be assigned to ν (Mo–S) [45]. Like most *cis*-dioxomolybdenum(VI) complexes, two IR

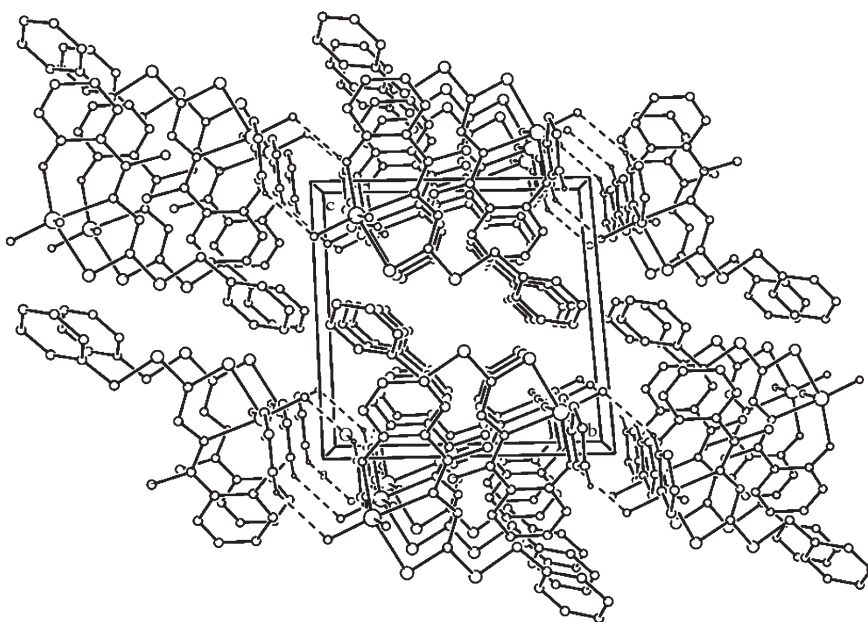


Figure 3. Packing diagram of **5** [MoO₂L¹(imz)].

bands are observed in the 1000–885 cm^{−1} region, the higher and the lower frequency bands originating from the anti-symmetric and the symmetric stretching modes of the [MoO₂]²⁺ moiety [37, 46, 47].

¹H NMR data for the ligands and **1** and **2** are summarized in sections 2.2 and 2.3. The signals in the ¹H NMR spectra corresponding to N–H and O–H, i.e. those at δ 11.25 and δ 11.26 of H₂L¹ and those at δ 11.42 and δ 12.68 of H₂L² disappear in **1** and **2** as a result of complexation. In the complexes, involvement of the azomethine nitrogen is indicated by the shift of the –CH₃ proton signal from δ 2.46 to δ 2.77. Resonance due to the methylene protons of the ligand (H₂L¹) at δ 4.51 remains practically unaffected in **1** indicating the non-involvement of the S-benzyl sulfur in coordination.

Similar observation for all types of protons is noted in case of (H₂L²) and its corresponding complex **2**.

3.3. Electrochemical properties

Cyclic voltammograms of the ligands and their Mo(VI) complexes at a platinum electrode were recorded in dry degassed DMF containing 0.1 M TEAP as the supporting electrolyte over a potential range of 0.0 to −1.5 V. The numerical data are listed in Table 3 and representative voltammograms are shown in figure 4. For Mo^{VI}O₂ (CH₃OH) L¹ · CH₃OH and Mo^{VI}O₂L² only one irreversible reductive response could be located in the potential range 0.0 to −1.11 V. This response is assigned to a metal centered 2e[−] process [48, 37, 49–51]. Two-electron involvement is established by comparison of the current height with authentic 2e[−] species under identical experimental conditions. On scan reversal an irreversible oxidative response is located

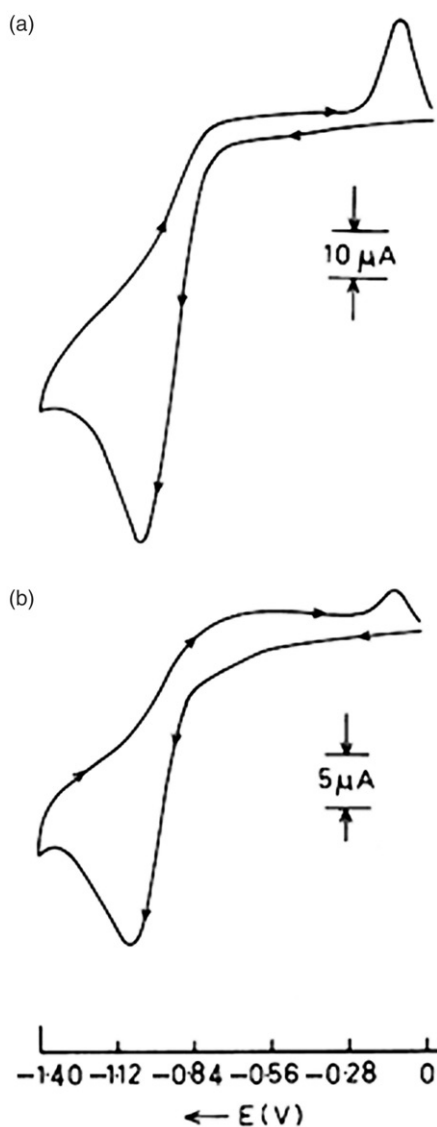


Figure 4. Cyclic voltammograms for **1** (a) and **5** (b) in DMF solution.

in the -0.09 to -0.14 V range, probably due to oxidation of the species produced (in the range -1.00 to -1.11 V) by previous cathodic reduction followed by chemical reaction with the medium. Cyclic voltammograms of the ligands and their zinc complexes did not exhibit any reductive response within the potential window scanned. The cyclic voltammograms of $\text{Mo}^{\text{VI}}\text{O}_2\text{LB}$ (where B = γ -picoline, imidazole, thiophene, THF.) exhibit little difference from those of the parent complexes and therefore the actual species in the solution is $\text{MoO}_2\text{L}^1/\text{L}^2(\text{DMF})$. This is confirmed by recording the electronic spectra of the Mo(VI) complexes and their adducts $\text{Mo}^{\text{VI}}\text{O}_2\text{LB}$ in DMF which exhibit identical spectral features. It is to be noted that reduction of dioxo Mo(VI) complexes in aprotic solvents are generally irreversible [52].

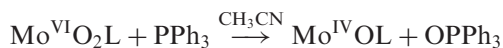
3.4. Electronic Spectra

The lowest energy absorption maxima located in the 350–380 nm range may be assigned [17] to a $S(p\pi) \rightarrow Mo(d\pi)$ LMCT transition caused by promotion of an electron from the filled HOMO of the ligand of primarily sulfur $p\pi$ character to the empty LUMO of molybdenum $d\pi$ character. Other LMCT bands are observed in the region 350–294 nm [30, 38, 48, 50]. These bands may be assigned as nitrogen to molybdenum and oxygen to molybdenum charge transfer transitions [17], respectively. The bands appearing below 294 nm are due to intra-ligand transitions.

3.5. Study of reactivity of dioxomolybdenum(VI) complexes

Substrate binding. The dioxomolybdenum(VI) complexes **1** and **2** have been synthesized and isolated from CH_3OH ; complex **1** has a coordinated CH_3OH molecule as well as a CH_3OH of crystallization while **2** appears to be oligomeric in the solid state. Weak coordination of CH_3OH is manifested in the longer $Mo(1) \rightarrow O(300)$ distance of 2.301(3) Å compared to the other $Mo(1) \rightarrow O(200)$ distance of 1.717(3) Å. This is further substantiated by facile replacement of the coordinated methanol by a monodentate Lewis bases (B) such as γ -picoline, imidazole, thiophene or THF (which are stronger nucleophiles than CH_3OH) yielding the corresponding MoO_2L^1B and MoO_2L^2B compounds. Again, when these compounds are dissolved in coordinating solvents such as DMF/DMSO, the monodentate ligand B is readily replaced by the solvent molecule, evident from the colour change of the solutions, electronic spectra and electrochemical results. So the sixth coordination position of the distorted octahedral $MoO_2L \cdot CH_3OH$ moiety may be considered as the substrate binding site.

Oxo transfer to substrate. Complexes **1** and **2** exhibit oxotransfer to PPh_3 when reacted with PPh_3 in CH_3OH/CH_3CN medium. The band around 380 nm due to $S(p\pi) \rightarrow Mo(d\pi)$ LMCT transition in the parent complex shifts to lower energy (~ 465 nm) and a new band appears around 625 nm. The isolated complexes $MoOL^1$ and $MoOL^2$ exhibit the same spectral features. The oxotransfer reaction may be represented as



which may be considered as a two-electron-redox/oxygen atom transfer process.

4. Conclusion

Several dioxomolybdenum(VI) complexes of the type MoO_2L and MoO_2LB have been synthesized and characterized by various physicochemical techniques and two by X-ray crystallographic analysis. Resemblances of these compounds with the active center of some known oxo-transfer molybdoenzymes containing a ONS donor environment has been demonstrated through oxo abstraction from dioxo $Mo(VI)$ complexes by PPh_3 leading to formation of the corresponding mono oxo $Mo(IV)$ species and reoxidation of the resultant mono oxo $Mo(IV)$ complexes to the parent $Mo(VI)$ species by use of

DMSO/Pyridine N-oxide. The one-step two-electron reduction is supported by electrochemical studies. Substrate binding characteristic of model complexes is demonstrated by the formation of adducts MoO₂LB involving neutral monodentate Lewis bases such as γ -picoline, imidazole, thiophene and THF.

Supplementary data

Crystallographic data have been deposited with the CCDC, 12, Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-366033; Email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk) and are available on request, quoting the deposition number 267353 and 267354 for the complex **1** and complex **5**, respectively.

Acknowledgments

We are grateful to Prof. C. Sinha, Department of Chemistry, Jadavpur University, for electrochemical measurements and Dr R. Chakraborty, Department of Chemistry, Hooghly Mohsin College for constant support and interest in this work.

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