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Synthesis, characterization, crystal structure and density functional theory (DFT) calculations of dioxomolybdenum (VI) complexes of an ONS donor ligand derived from benzoylacetone and S-benzyl dithiocarbazate

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ABSTRACT

A few dioxomolybdenum complexes of the type MoO_2L and MoO_2L ·B of a new diprotic tridentate ONS chelating ligand, H_2L , have been synthesized with the aim to examine their potential to behave as models for the active site of an oxidoreductase molybdoenzyme like xanthineoxidase. The MoO_2L complex produces MoO_2L B on treatment with neutral monodentate Lewis bases such as γ -picoline, 2-methylimidazole or 1-allylimidazole, utilizing the vacant sixth coordination site. They have been characterized by spectroscopic and electrochemical techniques. The complexes MoO_2L (1), $MoO_2L(\gamma$ -pic) (2) and MoO_2L (1-allylimiz) (4) were structurally characterized by single crystal X-ray diffraction. The complex $Mo^{VI}O_2L$ exhibits oxotransfer to PPh₃ in acetonitrile medium leading to the formation of $Mo^{IV}OL$, which is reoxidized to $Mo^{VI}O_2L$ on treatment with DMSO or pyridine N-oxide. DFT calculations on the ligand and complexes 1, 2 and 4 were also carried out.

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1. Introduction

Apart from their versatile behavior in relation to numerous oxidation states (-2 to +6), variable stereochemical and electronic properties [1], and catalytic activity toward some industrially important chemical processes [2,3] in the higher oxidation states, complexes of Mo(V) and Mo(VI) ligated to some NS/ONS donor ligands [4–7] have still retained the attention of coordination chemists and bio-inorganic chemists, especially because of their deep involvement in some important bio-chemical processes occurring in several forms of plants and some lower order animals [8,9].

Attempts to design and synthesize model complexes that contain characteristic features which hold the possibility of forming complexes that may mimic the active center of a molybdoenzyme are still actively being pursued. In this backdrop, we have undertaken the present work. It may be mentioned that for several years we have continuously been involved in this area of molybdenum chemistry [10–15]. In this paper, we report the synthesis of the complexes MoO_2L and MoO_2L ·B (where B is a neutral monodentate Lewis base) of a tridentate ONS chelating ligand derived from benzoylacetone and S-benzyldithiocarbazate. Characterization by elemental analyses and various spectroscopic (IR, UV–Vis and ¹H NMR) methods are also reported. The crystal and molecular structures of three complexes, MoO_2L (1), $MoO_2L(\gamma-pic)$ (2) and MoO_2 -L(1-allyl imz) (4), have been determined by single crystal X-ray crystallography. The chemical activity and the electro-chemical behavior of these complexes have been examined.

2. Experimental

2.1. Materials

Reagent grade solvents were dried and distilled prior to use. All other chemicals used for the preparative work were of reagent grade, available commercially and used without further purification.

2.2. Synthesis

2.2.1. Synthesis of the ligand (H_2L)

A mixture of 10 ml (0.2 mol) hydrazine hydrate and 11.2 g (0.2 mol) KOH in 70 ml of 90% ethanol was cooled down to



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-10 °C, then 15 ml (0.25 mol) of CS₂ was added dropwise with constant stirring. The yellow oil which formed was separated and dissolved in 60 ml of previously cooled 40% ethanol. To this, 23 ml (0.2 mol) of benzyl chloride was added slowly with vigorous stirring. The white product which formed was collected and after recrystallization from benzene was dissolved in 50 ml of absolute ethanol. To this solution, 32.4 g (0.2 mol) of benzoylacetone in 50 ml ethanol was added. The resulting mixture was stirred for 1 h at room temperature. The crystals which settled down were filtered off, washed with ethanol and dried in vacuo (Scheme 1). Yield: ~80%; M.p.: ~120 °C. Anal. Calcd. for C₁₈H₁₈N₂S₂O: C, 63.16; H, 5.26; N, 8.19. Found: C, 62.19; H, 5.53; N, 7.89%. IR (KBr pellet), cm⁻¹: $v_{(N-H)}$ 3025 (w), $v_{(O-H)}$ 3357 (s), $v_{(C=N)}$ 1627 (s), $v_{(C=S)}$ 1315 (s); ¹H NMR (dmso-d₆): (H₃C-C=N-) 2.46 (s, 3H), (-CH₂-) 4.36 (s, 2H), (-CH) 6.48 (s, 1H), (-NH-) 12.1 (s, 1H), (-OH) 12.26 (s, 1H), (aromatic protons) 7.20-7.33 (m, 10H).

2.2.2. Synthesis of the complexes

2.2.2.1. MoO_2L (1). To a filtered solution of 0.33 g (1.0 mmol) of $MoO_2(acac)_2$ in 20 ml of dry CH₃OH was added 0.342 g (1.0 mmol) of the ligand H₂L in 15 ml of dry CH₃OH. The resulting red solution was stirred at room temperature for 2 h. The crystalline red compound that separated out was filtered, washed with cold CH₃OH and dried in vacuo over anhydrous CaCl₂, in a yield of ~80%. The compound was recrystallized from dry CH₃OH. *Anal.* Calcd. for C₁₈₋H₁₆N₂S₂O₃Mo: C, 46.15; H, 3.42; N, 5.98; Mo, 20.51. Found: C, 46.01; H, 3.39; N, 5.25; Mo, 20.02%. IR (KBr pellet), cm⁻¹: $v_{(C=N)}$

1598 (s), $\nu_{(Mo=O)}$ 905 (vs), 840 (vs), $\nu_{(Mo-N)}$ 583 (m), $\nu_{(Mo-S)}$ 471 (w); UV–Vis (CH₂Cl₂) [λ_{max} /nm (ϵ /dm³ mol⁻¹ cm⁻¹)]: 258 (5550), 342 (4030), 406 (2750); ¹H NMR (dmso-d₆): (H₃C–C=N–) 2.49 (s, 3H), (–CH₂–) 4.43 (s, 2H), (–CH) 6.42 (s, 1H), (aromatic protons) 7.27–7.37 (m, 5H), 7.42–7.50 (m, 5H).

Compounds **2–4**, of the general formula MoO₂L·B, were prepared by refluxing the parent complex **1** in CH₃OH with the appropriate monodentate Lewis base (such as γ -picoline, 2-methylimidazole or 1-allylimidazole) in a 1:2 molar ratio for ~4 h (Scheme 2). Red crystalline solids so formed were filtered, washed with dry CH₃OH and dried in vacuo over anhydrous CaCl₂, in yields of ~70–75%.

2.2.2.2. $MoO_2L(\gamma - pic)$ (**2**). Anal. Calcd. for $C_{24}H_{23}N_3S_2O_3Mo$: C, 51.33; H, 4.09; N, 7.48; Mo, 17.11. Found: C, 51.05; H, 3.95; N, 7.48; Mo, 16.97%. IR (KBr pellet) cm⁻¹: $v_{(C=N)}$ 1598 (s), $v_{(Mo=O)}$ 940 (vs), 840 (vs), $v_{(Mo-N)}$ 581 (m), $v_{(Mo-S)}$, 471 (w); UV–Vis (CH₂-Cl₂) [λ_{max}/nm ($\epsilon/dm^3 mol^{-1} cm^{-1}$)]: 256 (22 000), 341 (12 630), 414 (10 330); ¹H NMR (dmso-d₆): (H₃C-C=N-) 2.46 (s, 3H), (-CH₂-) 4.39 (s, 2H), (-CH) 6.38 (s, 1H), (-CH₃) 2.42 (s, 3H), (aromatic protons) 7.17–7.33 and 7.38–7.46 (m, 14H).

2.2.2.3. $MoO_2L(2-meth imz)$ (**3**). Anal. Calcd. for $C_{22}H_{22}N_4S_2O_3Mo: C$, 48.00; H, 4.00; N, 10.18; Mo, 17.12. Found: C, 47.82; H, 3.90; N, 10.02; Mo, 16.85%. IR (KBr pellet) cm⁻¹: $v_{(C=N)}$ 1521 (vs), $v_{(Mo=O)}$ 967 (s), 904 (s), $v_{(Mo-N)}$ 562 (m), $v_{(Mo-S)}$ 480 (w); UV–Vis (CH₂Cl₂) [λ_{max}/nm ($\epsilon/dm^3 mol^{-1} cm^{-1}$)]: 265 (3570), 311 (2090), 416



Scheme 1. Reaction diagram for the isolation of the ligand ($R = -CH_2C_6H_5$).



 $(B = \gamma - picoline, 2 - methylimidazole or 1 - allylimidazole)$

Scheme 2. Reaction diagram for the isolation of the Mo (VI) complexes.

(3730); ¹H NMR (dmso-d₆): ($H_3C-C=N-$) 2.46 (s, 3H), (-CH₂-) 4.38 (s, 2H), (-CH) 6.37 (s, 1H), (-CH₃) 2.43 (s, 3H), (aromatic protons) 7.20–7.35 and 7.37–7.46 (m, 12H).

2.2.2.4. $MoO_2L(1-allyl imz)$ (**4**). Anal. Calcd. for $C_{24}H_{24}N_4S_2O_3Mo: C$, 50.00; H, 4.17; N, 9.72; Mo, 16.67. Found: C, 49.82; H, 4.00; N, 9.53; Mo, 16.32%. IR (KBr pellet) cm⁻¹: $v_{(C=N)}$ 1572 (vs), $v_{(Mo=O)}$ 924 (s), 894 (vs), $v_{(Mo-N)}$ 565 (m), $v_{(Mo-S)}$ 475 (m); UV–Vis (CH₂Cl₂) [λ_{max} /nm (ϵ /dm³ mol⁻¹ cm⁻¹)]: 263 (5730), 307 (3060), 416 (4810); ¹H NMR (dmso-d₆): (H₃C-C=N-) 2.46 (s, 3H), (-CH₂-) 4.38 (s, 2H), (-CH) 6.37 (s, 1H), (-CH₂-CH=CH₂) 5.97 (m, 2H), 4.61 (d, 1H), 5.17 (d, 1H cis), 5.64 (d, 1H trans), (aromatic protons) 7.20–7.32 and 7.37–7.46 (m, 13H).

2.3. 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 an internal standard. IR spectra were recorded as KBr pellets on a Perkin-Elmer model 883 infrared spectrophotometer. Electronic spectra were recorded using 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 the 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 TBAP as a supporting electrolyte. Thermal analyses were carried out in a Mettler Toledo TGA/SDTA 851 Thermal Analyzer in a dynamic atmosphere of dinitrogen (flow rate = 30 cm³ min⁻¹).

2.4. Computational details

Full geometry optimization of different tautomeric forms of the ligand H₂L and complexes **1**. **2** and **4** were carried out in the singlet state using the DFT method at the B3LYP level of theory [16,17] with a net charge = 0 for the complexes. The 6-31+G(d) basis set was assigned for all elements except molybdenum. The SDD basis set with an effective core potential was employed for the molybdenum atom [18,19]. Vibrational frequency calculations were performed to ensure that the optimized geometries represent the local minima of the potential energy surface and there are only positive eigen-values used. The electronic stabilities of the optimized geometries have been checked. The lowest 40 singlet-singlet vertical electronic excitations based on B3LYP optimized geometries were computed using the time-dependent density functional theory (TD-DFT) formalism [20-22] in CH₂Cl₂ with a conductor-like polarizable continuum model (CPCM) [23-25], using the same B3LYP level and basis sets. All computations were performed using the GAUSSIAN03 (G03) program [26]. GaussSum [27] was used to calculate the fractional contributions of various groups to each molecular orbital.

2.5. Crystallographic measurements

Crystallographic data for complexes **1** and **2** were collected on a MAR research Image Plate diffractometer and for complex **4** on a Bruker-Nonius APEX-II diffractometer with a CCD-area detector equipped with graphite-monochromated Mo K α (λ = 0.71013 Å) radiation. Unit-cell dimensions and intensity data were measured at 150 and 296 K. The crystal structures were solved by direct methods using SHELXS-97 and refined by full-matrix least-squares based on F^2 with anisotropic displacement parameters for non-hydrogen atoms using SHELXL-97. The hydrogen atoms were included in calculated positions.

3. Results and discussion

3.1. Synthesis

The Schiff base ligand was prepared by condensing S-ben-zyldithiocarbazate with benzoylacetone in ethanol. The ligand was satisfactorily characterized by elemental analysis, IR and 1 H NMR data.

Dioxomolybdenum complex 1, of the formula MoO₂L, was prepared by stirring at room temperature with the appropriate ligand in a 1:1 molar proportion using methanol as the solvent. Mo(VI) complexes (2–4) of the general formula MoO₂L·B (where B = γ -picoline, 2-methylimidazole or 1-allylimidazole) were also prepared by refluxing **1** with the corresponding neutral monodentate Lewis base in methanol medium. The base (B) is coordinated in the sixth coordination position. All the complexes are red crystalline solids. All the complexes have been formulated on the basis of elemental analyses, are stable in the solid state and are diamagnetic, as expected for a species with d⁰ Mo(VI). All the compounds are quite soluble in polar aprotic solvents, like CH₂Cl₂, CH₃CN, DMF and DMSO, but are insoluble in water. The molar conductivity data in 10^{-3} (M) CH₂Cl₂ solution indicates their non-electrolytic character. Electronic spectra of all the complexes were recorded in CH₂Cl₂ and cyclic voltammograms were recorded in DMF. Complexes 1. **2** and **4** have been structurally characterized by the single crystal X-ray diffraction technique.

3.2. Spectral characteristics

Characteristic IR bands of the ligand and the Mo(VI) complexes are given in Section 2.2.2. The ligand exhibits two broad IR bands of medium intensity in the 3357–3025 cm⁻¹ region, the higher frequency one being due to the $v_{(O-H)}$ mode, while the lower one is assigned to the $v_{(N-H)}$ vibration [28]. Strong $v_{(C=N)}$ bands around 1627 cm⁻¹ for the free ligand are red shifted to 1521–1598 cm⁻¹ in the corresponding complexes, indicating coordination by the azomethine [29,30] nitrogen to the metal ion. The $v_{(C=S)}$ band, observed in the 1315 cm⁻¹ region for the ligand, disappeared upon complex formation. A new band in the 562–583 cm⁻¹ region was observed in the spectra of the complexes and is assigned to $v_{(MQ-N)}$ [28]. The complexes exhibit a medium intensity band around 471–480 cm⁻¹, which may be assigned to $v_{(Mo-S)}$ [31]. Like most cis-dioxo Mo(VI) complexes, two IR bands are observed in the 967–840 cm⁻¹ region, the higher and the lower frequency bands originating from the anti-symmetric and the symmetric stretching frequencies of the $[MoO_2]^{2+}$ moiety [32–34].

Electronic spectra of the Mo(VI) complexes **1–4** were recorded in dry CH_2Cl_2 and the spectral data are presented in Section 2.2.2. The lowest energy absorption maxima, located in the 307–342 nm range, may be assigned [35] to an $S(p\pi)$ -Mo($d\pi$) LMCT transition caused by the promotion of an electron from the full 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 307–265 nm [36–38]. These bands may be assigned to nitrogen to molybdenum and oxygen to molybdenum charge transfer transitions [35] respectively. The bands appearing below 265 nm are due to intra-ligand transitions.

¹H NMR data for the ligand and the corresponding complexes are summarized in Section 2.2.2. The signals at δ 12.26 and 12.10 ppm in the ¹H NMR spectrum of the ligand H₂L, corresponding to O—H and N—H, are found to disappear in complexes **1–4** as a result of complexation. The methylene protons of the ligand and complexes **1–4**, appearing at δ 4.36, 4.43, 4.39, 4.38 and 4.38 ppm respectively, indicate that the S-benzyl sulfur is not involved in coordination. The 10 aromatic protons appear as multiplets within the range δ 7.20–7.33 ppm for the ligand. In complex **1**, 10, in **2**, 14, in **3**, 12 and in **4**, 13 aromatic protons appear as multiplets within the ranges δ 7.27–7.37 (5H) and 7.42–7.50 (5H), 7.17–7.33 and 7.38–7.46 (14H), 7.20–7.35 and 7.37–7.46 (12H), and 7.20–7.32 and 7.37–7.46 (13H) ppm respectively. In complexes **2**, **3** and **4**, the –CH₃ group in γ -picoline/the substituted imidazole moiety showed the usual chemical shift value in the ¹H NMR spectra. Similarly, the –CH₂–CH=CH₂ group in complex **4** also exhibited the usual proton signals.

3.3. Electrochemical properties

Cyclic voltammograms of the ligand and complexes 1-4 at a Ptelectrode were recorded in dry degassed DMF containing 0.1 (M) TBAP as the supporting electrolyte over the potential range 0.08 to -1.5 V. The numerical data are listed in Table 1 and representative voltammograms are shown in Fig. 1. For Mo^{VI}O₂L, only one irreversible reductive response could be located in the potential range 0.0 to -1.23 V. This response is assigned to a metal center 2e⁻ process [10,11,32,38]. A two-electron involvement is established by a comparison of the current height with authentic twoelectron species under identical experimental conditions. On scan reversal, two irreversible one-electron oxidative responses are located in the 0.57-0.82 V range. Cyclic voltammograms of the ligand and its Zn-complex did not exhibit any reductive response within the potential window scan. Cyclic voltammograms of Mo^{VI-} $O_2L \cdot B$ (where B = γ -picoline, 2-methyl imz, l-allyl imz) exhibit little difference from those of the parent complex 1 and therefore the actual species in the solution are MoO₂L(DMF). This is confirmed by

 Table 1

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

J	(
Complexes	$E_{\rm pc}$ (V)	$E_{\rm pa}\left({\sf V}\right)$
$\begin{array}{l} MoO_{2}L(1) \\ MoO_{2}L(\gamma\text{-pic})(2) \\ MoO_{2}L(2\text{-meth imz})(3) \\ MoO_{2}L^{1}(1\text{-allyl imz})(4) \end{array}$	-1.23 -1.07 -1.24 -1.12	+0.57, +0.82 +0.53, +0.76 +0.52, +0.87 +0.55, +0.81
······································		

^a Solvent: DMF (dry, degassed); supporting electrolyte: 0.1 M TBAP; solution strength: 10^{-3} M; electrode: platinum; reference electrode: SCE; scan rate: 100 mV s⁻¹.



Fig. 1. Cyclic voltammogram of MoO₂L (1) in DMF at 298 K.

recording the electronic spectra of the Mo(VI) complexes and their adducts $Mo^{IV}O_2L$ ·B in DMF, which exhibit identical spectral features. It is to be noted that the reduction of di-oxo Mo(VI) complexes in aprotic solvents are generally irreversible [11,39].

3.4. Description of the crystal structures of the complexes $MoO_2L(1)$, $MoO_2L(\gamma-pic)(2)$ and $MoO_2L(1-allyl imz)(4)$

The molecular structures and atom numbering schemes of **1**, **2** and **4** are shown in Figs. 2–4. Crystallographic data are given in Table 2 and selected bond lengths and bond angles are presented in Tables 3 and 4. In **1**, the three donor atoms O(11), N(15) and S(18) of the ligand and one terminal oxo-atom, O(42), occupy the meridonial plane [36,40] and N(15) is situated trans to the oxo-oxygen O(42), the angle O(42)-Mo(1)-N(15) being 155.5(3)°. Along with the two oxo-oxygens, O(42) and O(41), the three ONS donor points of the ligand complete the five coordinate environment around the Mo(VI) acceptor center in complex **1**. The sixth coordination site, trans to the oxo-oxygen O(41), is occupied by an oxo-oxygen O(41) of the next neighboring complex molecule, and this pattern is repeated leading to a chain of MoO_2L molecules (stacking diagram: Fig. 2a).

The dianionic tridentate ligand forms one five-membered and one six-membered metallocycle involving the $[MoO_2]^{2+}$ core, the N(15)-Mo(1)-S(18) and N(15)-Mo(1)-O(11) bite angles being 76.77(19) and 82.8(3)° respectively.

The overall coordination geometry around the Mo(VI) center can be described as distorted octahedral, as is evident from the unequal bond lengths (Table 3). The Schiff base ligand is bonded to the $[MoO_2]^{2+}$ core through the enolate oxygen O(11), thioenolate sulfur S(18) and the azomethine nitrogen N(15). The oxo-oxygen O(41) occupies one apical position, while the other apex is occupied by an oxo-oxygen O(41) of the nearest neighbor complex molecule, the O(41)-Mo(1)-O(41) angle being 173.34(11)°. This may be visualized as the effect of stacking of the complex molecules along the z-axis. The length of the Mo(1)–O(41) bond (2.415 Å) is considerably longer than the other Mo–O bond [Mo(1)– O(11) = 1.950(6)Ål and is indicative of weaker coordination by the oxo-oxygen O(41), and hence is expected to be the point of maximum reactivity in the complex. This can be utilized as a substrate binding site leading to a more stable hexacoordinate species. This expectation is realized in the facile formation of the complex MoO₂L·B (where B is a neutral monodentate Lewis base like γ -picoline, 2-methylimidazole or 1-allylimidazole).

The O(41)–Mo(1)–O(42) bond angle of $104.4(3)^{\circ}$ and the Mo=O bond lengths Mo(1)–O(42) = 1.704(6) Å and Mo(1)–O(41) = 1.666(6) Å are unexceptional [41–44]. The azomethine nitrogen N(15) is trans to the oxo-oxygen O(42) and the Mo(1)–N(15) bond length of 2.238(7) Å is rather long due to the trans influence of the oxo-oxygen. The C(17)–N(16) bond length, 1.279(11) Å, is close to the usual C=N bond length [32,37].

The Mo(1)–S(18) distance of 2.410(2) Å is very near to the values observed in several molybdenum complexes [36,45,46]. Careful analysis of the bond lengths and bond angles data leads to the overall conclusion that complex **1** has a highly distorted octahedral coordination around the Mo(VI) center, and the Mo(VI) center is slightly displaced by 0.369 Å from the median square plane described by N(15), O(11), S(18) and O(42) toward the apical oxo-oxygen O(41).

In complexes **2** and **4**, the Mo (VI) center is also present in a distorted octahedral donor environment consisting of two cis-oxo atoms, O(41) and O(42), phenolate oxygen O(11), thio-enolate sulfur S(18), azomethine nitrogen N(15) and the tertiary nitrogen atom N(51). In fact, the structures of **2** and **4** can be derived from the structure of **1**, MoO₂L, by the addition of γ -picoline and 1-allyl imidazole to the vacant axial position trans to the oxo atom O(41),



Fig. 2. Molecular structure of the complex MoO₂L (1).



Fig. 2a. (a) Stacking diagram of complex MoO₂L (1).



Fig. 3. Molecular structure of complex MoO_2L^1 (γ -pic) (2).

generating an O(41)-Mo(1)-N(51) angle of 170.8(8) and 169.4(3)°, respectively. This points to a considerable distortion of the coordination octahedron around Mo(VI) centers in complexes **2** and **4**, with the Mo center slightly displaced by 0.331 and 0.311 Å from the median plane described by N(15), O(11), S(18) and O(42) toward the apical oxo-oxygen O(41) respectively. A remarkable fea-



Fig. 4. Molecular structure of MoO₂L(1-allyl imz) (4).

Table 2Crystal data and refinement details for complexes 1, 2 and 4.

	Complex 1	Complex 2	Complex 4
Chemical formula	$C_{18}H_{16}MoN_2O_3S_2$	$C_{24}H_{23}MoN_3O_3S_2$	$C_{24}H_{24}MoN_4O_3S_2$
Formula weight (M)	468.39	561.51	576.53
Crystal system	monoclinic	monoclinic	monoclinic
Space group	P21/a	$P2_1/c$	$P2_1/c$
a (Å)	7.9463(3)	11.1998(6)	15.3789(15)
b (Å)	13.3296(5)	13.6358(12)	10.1043(10)
c (Å)	17.4073(8)	15.8342(12)	17.9013(17)
β (°)	91.949(4)	97.029(7)	115.270(3)
V (Å ³)	1842.73(13)	2400.0(3)	2515.5(4)
Ζ	4	4	4
Temperature (K)	150(2)	150(2)	296(2)
D_{calc} (g cm ⁻³)	1.688	1.554	1.522
μ (Mo K $lpha$) (mm ⁻¹)	0.959	0.752	0.720
F(000)	944	1144	1176
Goodness-of- fit on F ²	0.987	0.890	1.073
R_1, wR_2	$R_1 = 0.0782$,	$R_1 = 0.0402$,	$R_1 = 0.0901$,
$[I > 2\sigma(1)]$	$wR_2 = 0.2108$	$wR_2 = 0.1009$	$wR_2 = 0.2313$

ture of the structures of both **2** and **4** is that the metric values of the bond lengths and the bond angles involving the Mo(VI) center of the precursor complex **1** remain mostly unchanged in **2** and **4**.

Complex 1		Complex 2		Complex 4	
Mo(1)-O(42)	1.704(6)	Mo(1)-O(42)	1.708(18)	Mo(1)-O(42)	1.701(6)
Mo(1)-O(41)	1.666(6)	Mo(1)-O(41)	1.704(18)	Mo(1)-O(41)	1.698(6)
Mo(1)-O(11)	1.950(6)	Mo(1)-O(11)	1.954(17)	Mo(1)-O(11)	1.950(5)
Mo(1)-O(41)	2.415(6)	Mo(1)-N(51)	2.430(19)	Mo(1)-N(51)	2.366(6)
Mo(1)-N(15)	2.238(7)	Mo(1)-N(15)	2.279(2)	Mo(1)-N(15)	2.284(6)
Mo(1)-S(18)	2.410(2)	Mo(1)-S(18)	2.420(7)	Mo(1)-S(18)	2.427(2)
C(17) - S(18)	1.739(9)	C(17)-S(18)	1.751(3)	C(17)-S(18)	1.747(8)
C(17)–N(16)	1.279(11)	C(17)-N(16)	1.279(3)	C(17)-N(16)	1.274(10)
N(15)-N(16)	1.406(10)	N(15)-N(16)	1.400(3)	N(15)-N(16)	1.408(8)
C(14)-N(15)	1.322(10)	C(14)–N(15)	1.322(3)	C(14)–N(15)	1.316(9)
C(13)-C(14)	1.445(11)	C(13)-C(14)	1.424(3)	C(13)-C(14)	1.421(10)
C(12)-C(13)	1.351(12)	C(12)-C(13)	1.351(3)	C(12)-C(13)	1.359(10)
C(12)-O(11)	1.338(10)	C(12)-O(11)	1.338(3)	C(12)-O(11)	1.330(8)

 Table 3

 Selected bond lengths (Å) for complexes 1 2 and 4

Table 4

Selected bond angles (°) for complexes 1, 2 and 4.

Complex 1		Complex 2		Complex 4	
O(41)-Mo(1)-O(42)	104.4(3)	O(41)-Mo(1)-O(42)	106.16(9)	O(41)-Mo(1)-O(42)	105.9(3)
O(42)-Mo(1)-O(41)	82.2 (2)	O(42)-Mo(1)-N(51)	83.03(8)	O(42)-Mo(1)-N(51)	84.7(3)
O(42)-Mo(1)-O(11)	104.0(3)	O(42)-Mo(1)-O(11)	106.28(8)	O(42)-Mo(1)-O(11)	102.9(2)
O(41)-Mo(1)-O(41)	173.34(11)	O(41)-Mo(1)-N(51)	170.8(8)	O(41)-Mo(1)-N(51)	169.4(3)
O(41)-Mo(1)-O(11)	99.5(3)	O(41)-Mo(1)-O(11)	98.53(9)	O(41)-Mo(1)-O(11)	97.8(3)
O(11)-Mo(1)-O(41)	77.8(2)	O(11)-Mo(1)-N(51)	77.99(7)	O(11)-Mo(1)-N(51)	78.5(2)
S(18)-Mo(1)-O(41)	99.9(2)	S(18)-Mo(1)-O(41)	100.14(8)	S(18)-Mo(1)-O(41)	96.0(2)
S(18)-Mo(1)-O(41)	80.89(15)	S(18)-Mo(1)-N(51)	80.20(5)	S(18)-Mo(1)-N(51)	84.37(16)
S(18)-Mo(1)-N(15)	76.77(19)	S(18)-Mo(1)-N(15)	76.46(5)	S(18)-Mo(1)-N(15)	76.83(15)
N(15)-Mo(1)-O(41)	97.6(3)	N(15)-Mo(1)-O(41)	89.87(8)	N(15)-Mo(1)-O(41)	93.7(3)
N(15)-Mo(1)-O(41)	76.1(2)	N(15)-Mo(1)-N(51)	81.25(7)	N(15)-Mo(1)-N(51)	76.1(2)
N(15)-Mo(1)-O(11)	82.8(3)	N(15)-Mo(1)-O(11)	82.31(7)	N(15)-Mo(1)-O(11)	82.4(2)
O(42)-Mo(1)-N(15)	155.5(3)	O(42)-Mo(1)-N(15)	160.09(8)	O(42)-Mo(1)-N(15)	158.6(3)
S(18)-Mo(1)-O(11)	153.4(2)	S(18)-Mo(1)-O(11)	151.53(5)	S(18)-Mo(1)-O(11)	155.69(15)
O(42)-Mo(1)-S(18)	88.6(2)	O(42)-Mo(1)-S(18)	88.89(7)	O(42)-Mo(1)-S(18)	92.4(2)

Even the length of metal-oxygen double bond (Mo=O) axial to the coordinated γ -picoline/1-allyl imidazole (which is known to be highly influenced by axial coordination in many oxo metal complexes and is thought to be a measure of the σ -donor capacity of the coordinated ligand) stand practically unchanged [32,41,47]. The lengths of the Mo(1)–N(51) bonds in **2** and **4** are longer [2.430(19) and 2.366(6)Å] than the other Mo–N(azomethine) bonds, Mo(1)–N(15) [2.279(2) and 2.284(6)Å], revealing rather weak attachment of γ -picoline and 1-allylimidazole to the [MoO₂]²⁺ moiety. This is substantiated from a TGA and DTA study of **2** and **4** which exhibited easy loss of γ -picoline/1-allylimidazole on controlled heating.

3.5. DFT and TD-DFT calculations of the ligand and the complexes MoO_{2L} (1), $MoO_{2L}(\gamma$ -pic) (2) and $MoO_{2L}(1$ -allyl imz) (4)

DFT and TD-DFT calculations of the ligand and the structurally characterized complexes **1**, **2** and **4** were performed. In order to gain an insight into the tautomeric forms of the ligand H_2L in solution in the absence of a metal ion, geometry optimizations of all the four possible structures have been performed in CH_2Cl_2 . However, the major objective was to examine whether the calculated data and experimental parameters for complexes **1**, **2** and **4** are in agreement with each other. The total energy of the optimized geometries shows that the diketo form I is more stable and comparable in energy with IV, with an energy gap of 1.91 kcal/mol. So, structures I and IV may be in equilibrium in solution. However, the crystal structures of complexes **1**, **2** and **4** clearly show the involvement of the ligand in the di-enol form (II), which appears to be generated in situ in the presence of the $[MOO_2]^{2+}$ acceptor center, leading to the formation of the isolated complexes.



Table 5

Theoretical bond length parameters (Å) for complexes 1, 2 and 4 calculated by the DFT/B3LYP method.

Complex 1		Complex 2		Complex 4	
Mo(1)-O(42)	1.716	Mo(1)-O(42)	1.721	Mo(1)-O(42)	1.720
Mo(1)-O(41)	1.705	Mo(1)-O(41)	1.708	Mo(1)-O(41)	1.709
Mo(1)-O(11)	1.982	Mo(1)-O(11)	2.001	Mo(1)-O(11)	2.006
Mo(1)-N(15)	2.291	Mo(1)-N(15)	2.312	Mo(1)-N(15)	2.315
Mo(1)-S(18)	2.418	Mo(1)-S(18)	2.456	Mo(1)-S(18)	2.467
C(17)-S(18)	1.765	C(17)-S(18)	1.760	C(17)-S(18)	1.757
C(17)-N(16)	1.293	C(17)-N(16)	1.292	C(17)-N(16)	1.291
N(15)-N(16)	1.381	N(15)-N(16)	1.383	N(15)-N(16)	1.388
C(14)-N(15)	1.331	C(14)-N(15)	1.326	C(14)-N(15)	1.325
C(13)-C(14)	1.423	C(13)-C(14)	1.428	C(13)-C(14)	1.427
C(12)-C(13)	1.379	C(12)-C(13)	1.379	C(12)-C(13)	1.379
C(12)-O(11)	1.321	C(12)-O(11)	1.319	C(12)-O(11)	1.315
		Mo(1)-N(51)	2.507	Mo(1)-N(51)	2.491

The full geometry optimization of complex **1**, which may be visualized as a penta coordinate monomeric unit leading to the observed polymeric structure, was carried out by the DFT/B3LYP method. Complexes **2** and **4** were also subjected to similar treatment. The calculated bond length and bond angle parameters are given in Tables 5 and 6.

The computed structural parameters are in good agreement with the experimental data for complexes **2** and **4**, with maximum deviations of ~0.08 Å for the bond lengths and ~3.0° for the bond angles. In the case of complex **1**, the maximum deviation in the Mo(1)–N(15) bond distance is ~0.12 Å. On optimization, the penta coordinate monomeric structural unit has been considered. A large deviation in bond angles has been observed compared to the polymeric octahedral X-ray structure. The maximum deviations in bond angles have been found for O(42)–Mo(1)–O(11), 5.1° (calculated, 109.1°; X-ray, 104.0°); S(18)–Mo(1)–O(41), 8.9° (calculated, 108.8°; X-ray, 99.9°) and S(18)–Mo(1)–O(11), 16.2° (calculated, 137.2°; X-ray, 153.4°).

The compositions along with the energies of some selected molecular orbitals of the complexes are listed in Tables 7–9. Contour plots of some selected frontier molecular orbitals of the complexes are shown in Figs. 5–7. The highest energy occupied molecular orbital (HOMO) of the complexes has π -bonding nature and is concentrated on the chelated ligand (L). HOMO-2 for **1** and HOMO-1 for complexes **2** and **4** are composed of non-bonding orbitals of S atoms. Other low-lying occupied orbitals have π -bonding character of L with minor contributions from S atoms. The low energy unoccupied orbitals LUMO to LUMO+3 have Mo(d π) character along with minor contributions of L(π^*) and O($p\pi$) orbitals.

To get better insight into the electronic spectra of the complexes, TD-DFT calculations on the optimized geometries of the

Table 7			
Energy and composition	of some selected	MOs of o	complex 1.

МО	Energy (eV)	% of con	% of composition		
		Мо	Охо	Ligand	
LUMO+5	-0.87	05	02	93	
LUMO+4	-0.93	03	01	96	
LUMO+3	-1.77	54	24	22	
LUMO+2	-1.94	46	15	39	
LUMO+1	-2.54	60	24	16	
LUMO	-2.94	37	15	48	
HOMO	-6.24	01	02	97 (S, 23)	
HOMO-1	-6.90	01	02	97	
HOMO-2	-7.04	02	04	94 (S, 72)	
HOMO-3	-7.27	0	01	99	
HOMO-4	-7.38	0	01	99 (S, 21)	
HOMO-5	-7.56	0	0	100	
HOMO-6	-7.64	03	11	86	
HOMO-7	-8.03	01	12	87	
HOMO-8	-8.31	09	23	68 (S, 42)	
HOMO-9	-8.46	05	83	12	
HOMO-10	-9.00	07	30	63	

Table 8		
Energy and composition	n of some selected	MOs of complex 2.

MO	Energy (eV)	% of composition			
		Мо	Oxo	Ligand	γ-pic
LUMO+5	-0.66	01	0	04	95
LUMO+4	-1.11	08	02	01	89
LUMO+3	-1.40	57	22	16	05
LUMO+2	-1.78	36	12	48	04
LUMO+1	-2.15	60	22	18	0
LUMO	-2.43	28	16	54	02
HOMO	-5.63	01	01	97 (S, 24)	01
HOMO-1	-6.37	01	03	94 (S, 67)	02
HOMO-2	-6.71	0	02	97 (S, 25)	01
HOMO-3	-6.88	0	0	100	0
HOMO-4	-7.02	0	0	100 (S, 21)	0
HOMO-5	-7.08	01	08	90	01
HOMO-6	-7.11	01	05	92	02
HOMO-7	-7.40	02	05	83	10
HOMO-8	-7.53	0	01	04	95
HOMO-9	-7.70	03	65	14	18
HOMO-10	-7.86	08	17	54	21

complexes were been performed in CH₂Cl₂. The calculated excitation wavelengths and their assignments are given in Tables 10–12 for the complexes. The low energy bands >400 nm are characterized as mixed $L(\pi) \rightarrow Mo(d\pi)$ and $L(\pi) \rightarrow L(\pi^*)$ transitions. Strong transitions around 375 nm have been observed for the complexes due to $S(p\pi) \rightarrow Mo(d\pi)$ charge transfer transitions. The high

Table 6

Theoretical bond angle parameters (°) for complexes **1**, **2** and **4** calculated by the DFT/B3LYP method.

6 1	() 1	, , , , , , , , , , , , , , , , , , , ,	,		
Complex 1		Complex 2		Complex 4	
O(41)-Mo(1)-O(42)	108.7	O(41)-Mo(1)-O(42)	106.4	O(41)-Mo(1)-O(42)	106.3
O(42)-Mo(1)-O(11)	109.1	O(42)-Mo(1)-O(11)	105.4	O(42)-Mo(1)-O(11)	104.1
O(41)-Mo(1)-O(11)	97.72	O(41)-Mo(1)-O(11)	98.38	O(41)-Mo(1)-O(11)	97.41
S(18)-Mo(1)-O(41)	108.8	S(18)-Mo(1)-O(41)	102.5	S(18)-Mo(1)-O(41)	100.8
S(18)-Mo(1)-N(15)	75.71	S(18)-Mo(1)-N(15)	75.94	S(18)-Mo(1)-N(15)	76.03
N(15)-Mo(1)-O(41)	98.42	N(15)-Mo(1)-O(41)	92.52	N(15)-Mo(1)-O(41)	92.76
N(15)-Mo(1)-O(11)	79.63	N(15)-Mo(1)-O(11)	81.00	N(15)-Mo(1)-O(11)	81.44
O(42)-Mo(1)-N(15)	151.8	O(42)-Mo(1)-N(15)	158.6	O(42)-Mo(1)-N(15)	159.0
S(18)-Mo(1)-O(11)	137.2	S(18)-Mo(1)-O(11)	149.4	S(18)-Mo(1)-O(11)	151.5
O(42)-Mo(1)-S(18)	88.44	O(42)-Mo(1)-S(18)	89.97	O(42)-Mo(1)-S(18)	91.57
O(42)-Mo(1)-N(51)	80.85	O(42)-Mo(1)-N(51)	82.09		
		O(41)-Mo(1)-N(51)	171.7	O(41)-Mo(1)-N(51)	171.2
		O(11)-Mo(1)-N(51)	75.49	O(11)-Mo(1)-N(51)	77.81
		S(18)-Mo(1)-N(51)	81.19	S(18)-Mo(1)-N(51)	81.10
		N(15)-Mo(1)-N(51)	81.11	N(15)-Mo(1)-N(51)	79.31

МО	Energy (eV)	% of compo	% of composition				
		Мо	Охо	Ligand	1-Allyl-im		
LUMO+5	-0.40	0	0	100	0		
LUMO+4	-0.62	03	01	95	01		
LUMO+3	-1.21	60	23	16	01		
LUMO+2	-1.58	38	12	49	01		
LUMO+1	-2.06	59	23	18	0		
LUMO	-2.34	30	16	53	01		
НОМО	-5.50	01	01	97 (S, 23)	01		
HOMO-1	-6.33	0	04	89 (S, 78)	07		
HOMO-2	-6.67	0	0	06	94		
HOMO-3	-6.81	01	04	94 (S, 18)	01		
HOMO-4	-6.92	01	06	92	01		
HOMO-5	-7.01	0	0	100	0		
HOMO-6	-7.06	02	04	93	01		
HOMO-7	-7.18	0	02	97	01		
HOMO-8	-7.31	01	03	92	04		
HOMO-9	-7.61	03	67	08	22		
HOMO-10	-7.65	04	20	21	55		

Table 9Energy and composition of some selected MOs of complex 4.



Fig. 5. Contour plots of some selected molecular orbitals of complex 1.



Fig. 6. Contour plots of some selected molecular orbitals of complex 2.

energy bands around 260 nm are characterized as $O(p\pi) \to Mo(d\pi)$ transitions.

3.6. Study of the reactivity of the dioxo Mo(VI) complexes

3.6.1. Substrate binding

The dioxo molybdenum (VI) complex **1** has been prepared and isolated from methanol, and it is found to be oligomeric in the solid state due to weak coordination between adjacent complex mole-

cules. When **1** is treated with neutral monodentate Lewis bases like γ -picoline, imidazole and a substituted imidazole (B), complexes of the type MoO₂L·B could be isolated.

3.6.2. Oxo-transfer to substrate

Complex **1**, as well as **2**, **3** and **4**, exhibit oxotransfer to PPh₃ when reacted with PPh₃ in CH₃CN/CH₃OH medium. The band around 342 nm due to an $S(p\pi)$ –Mo(d π) LMCT transition in the parent complex is shifted to lower energy, around 420 nm, and a



Fig. 7. Contour plots of some selected molecular orbitals of complex 4.

Table 10	
Vertical electronic excitations of complex 1 calculated by the TD-DFT/CPCM method in CH ₂ Cl ₂	

$E_{\text{excitation}}$ (eV)	$\lambda_{\text{excitation}} (\text{nm})$	Osc. strength (f)	Key transition	Character
2.5908	478.6	0.0104	(90%) HOMO \rightarrow LUMO+1	$L(\pi) \rightarrow Mo(d\pi)$
2.9839	415.2	0.0757	(30%) HOMO \rightarrow LUMO (22%)HOMO-1 \rightarrow LUMO	$L(\pi) \rightarrow MO(d\pi)/L(\pi)$
3.2917	376.7	0.3126	(85%)HOMO-2 \rightarrow LUMO+1	$L(S(p\pi)) \rightarrow Mo(d\pi)$
3.5217	352.1	0.0734	(61%)HOMO-3 → LUMO (20%)HOMO-1 → LUMO+1	$L(\pi) \rightarrow Mo(d\pi)$
4.5125	274.8	0.1247	(56%) HOMO-3 \rightarrow LUMO+3 (29%) HOMO-9 \rightarrow LUMO+1	$L(\pi) \rightarrow Mo(d\pi)$ $O(p\pi) \rightarrow Mo(d\pi)$
4.8257	256.9	0.2592	(47%)HOMO-7 → LUMO+2 (32%)HOMO-8 → LUMO+1	$O(p\pi) \rightarrow Mo(d\pi)$

Table 11

Vertical electronic excitations of complex 2 calculated by the TD-DFT/CPCM method in CH₂Cl₂.

$E_{\text{excitation}}$ (eV)	$\lambda_{\text{excitation}} (\text{nm})$	Osc. strength (f)	Key transition	Character
2.2774	544.4	0.0580	(91%)HOMO → LUMO	$L(\pi) \rightarrow Mo(d\pi)/L(\pi^*)$
3.0528	406.1	0.0528	(61%)HOMO \rightarrow LUMO+2	$L(\pi) \rightarrow Mo(d\pi)/L(\pi^*)$
			(28%) HOMO \rightarrow LUMO+3	$L(\pi) \rightarrow Mo(d\pi)$
3.3058	375.1	0.3788	(45%) HOMO-1 \rightarrow LUMO+3	$L(S(p\pi)) \rightarrow Mo(d\pi)$
			(26%) HOMO-1 \rightarrow LUMO+2	$L(S(p\pi)) \rightarrow Mo(d\pi)/L(\pi^*)$
3.4813	356.1	0.0890	(46%) HOMO-3 \rightarrow LUMO	$L(\pi) \rightarrow Mo(d\pi)/L(\pi^*)$
			(22%) HOMO-6 \rightarrow LUMO	
4.7382	261.7	0.1637	(81%)HOMO-9 \rightarrow LUMO+1	$O(p\pi) \rightarrow Mo(d\pi)$

Table 12

Vertical electronic excitations of complex 4 calculated by the TD-DFT/CPCM method in CH₂Cl₂.

E _{excitation} (eV)	$\lambda_{\text{excitation}} (nm)$	Osc. strength (f)	Key transition	Character
2.1758	569.8	0.0291	(90%)HOMO → LUMO	$L(\pi) \rightarrow Mo(d\pi)/L(\pi^*)$
3.0593	405.3	0.0213	(44%) HOMO \rightarrow LUMO+2	$L(\pi) \rightarrow Mo(d\pi)/L(\pi^*)$
			(29%) HOMO \rightarrow LUMO+3	$L(\pi) \rightarrow Mo(d\pi)$
3.3010	375.6	0.2598	(48%)HOMO+1 \rightarrow LUMO+3	$L(S(p\pi)) \rightarrow Mo(d\pi)$
			(35%) HOMO+1 \rightarrow LUMO+2	$L(S(p\pi)) \rightarrow Mo(d\pi)/L(\pi^*)$
3.9415	314.6	0.1012	(62%)HOMO-9 \rightarrow LUMO	$O(p\pi) \rightarrow Mo(d\pi)$
4.8204	257.2	0.1247	(79%)HOMO-9 \rightarrow LUMO+1	$O(p\pi) \rightarrow Mo(d\pi)$

new band appears around \sim 626 nm. The isolated complex, Mo^{IV}OL, exhibits the same spectral features. The reaction, indicating oxo-transfer to the substrate, may be represented as:

which may be considered as a direct oxygen atom transfer (OAT) process. The reverse process exhibiting oxo-transfer from DMSO/ pyridine N-oxide can be represented as:

$$Mo^{VI}O_2L + PPh_3 \stackrel{CH_3CN}{\rightarrow} Mo^{VI}OL + OPPh_3$$

 $Mo^{VI}OL + DMSO/C_5H_5NO \overset{CH_3CN}{\rightarrow} Mo^{VI}O_2L + Me_2S/C_5H_5N$

4. Conclusion

The desired dioxomolybdenum (VI) complexes of the type MoO₂L and MoO₂L·B have been successfully synthesized and characterized by various physico-chemical techniques, and complexes 1, 2 and 4 were structurally characterized by X-ray crystallographic analysis. The substrate binding characteristic of model complexes is demonstrated by the formation of MoO₂L·B adducts involving a neutral monodentate Lewis base such as γ -picoline and substituted imidazole.

The resemblance of these complexes with the active center of some known oxo-transfer molybdoenzymes containing a ONS donor environment has been demonstrated through oxo-abstraction of the dioxo Mo(VI) complexes by PPh₃ to the corresponding mono-oxo Mo(IV) species, and re-oxidation of the resultant mono-oxo Mo(IV) complexes to the parent Mo(VI) species by the use of DMSO/pyridine N-oxide has been achieved. The one step two electron reduction of MoO₂L is supported by electrochemical studies. Relevant DFT calculations on the ligand and complexes 1, **2** and **4** were also carried out and the data was used to identify the composition of the relevant HOMOs and LUMOs and also to assign the experimentally observed transitions.

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Appendix A. Supplementary data

CCDC 874432-874434 contain the supplementary crystallographic data for 1, 2 and 4, respectively. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033: or e-mail: deposit@ccdc.cam.ac.uk.

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