Synthesis, Structure, and Reactivity of a New Mononuclear Molybdenum(VI) Complex Resembling the Active Center of Molybdenum Oxotransferases

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Keywords: Molybdenum / Bioinorganic chemistry / Substrate binding / Enzyme models

The design, synthesis, and structure determination of a pentacoordinate square-pyramidal molybdenum(VI) complex MoO_2L (where LH_2 is a diacidic tridentate ONO donor ligand) is reported. The substrate binding capacity of MoO_2L has been demonstrated by the formation and isolation of six-coordinate octahedral complexes $[MoO_2L(B)]$ (where B = imidazole, 1-methylimidazole, pyridine, or γ-picoline) and the structures of $[MoO_2L(Imz)]$ and $[MoO_2L(Py)]$ have been solved by X-ray crystallography. Oxo transfer of MoO_2L to the substrate PPh_3 has been demonstrated by the formation of MoOL and [MoOL(bipy)]. Thus, the complex MoO_2L behaves as a model for the active center of oxotransfer molybdoenzymes and is of interest in bioinorganic chemistry.

Introduction

It is now established that suitable models for the active centers of oxotransfer molybdoenzymes should be capable of: (1) oxygen atom transfer to or from the substrate,[1] (2) approaching the coordination environment of the oxomolybdenum center of the relevant enzyme(s), and (3) being unresponsive to the formation of (μ-oxo)Mo^V dimers.[2] To meet criterion (3) sterically hindered ligands, like 2,6-bis(2,2-diphenyl-2-mercaptoethenyl)pyridine $[LN(SH)_2]$, have been synthesized. The Mo^{VI} complex (MoO_2LNS_2) was subsequently isolated and structurally characterized by single-crystal X-ray analysis.[3,4] This complex was shown to be a viable structural model of the active sites of several oxotransfer molybdoenzymes and it was proposed that the presence of at least one coordinated sulfur atom as well as a proper steric environment provided by the ligand to prevent Mo^V-O-Mo^V dimer formation are essential features of a model complex.[3] One of our studies on the Mo^{VI} complexes of thiosemicarbazone-type ONS donor ligands showed for the first time that the steric factor is not absolutely essential[5] to prevent the (μ-oxo)Mo^V dimer formation. In this paper we report our recent findings that indicate that even Mo^{VI} complexes of some selected ONO donor ligands may mimic the active sites of some oxotransfer molybdoenzymes.

We report the synthesis, characterization, substrate binding, and oxo transfer reactions of the complex MoO_2L, where H_2L is the ONO donor ligand 2-hydroxyacetophenone hydrazone of 2-aminobenzoylhydrazine. The five-coordinate complex (MoO_2L) is quite interesting with respect to coordination chemistry because pentacoordinated Mo^{VI} complexes, in general, are rare[2,6,7] and those with an ONO donor environment are rarer still. Most pentacoordinate Mo^{VI} complexes with oxygen−sulfur donor ligands are mono(μ-oxo)-bridged dimers, each Mo^{VI} center featuring an S_2O_3 coordination, and are trigonal-bipyramidal.[6] The structures of the pentacoordinate complex MoO_2L (**1**) and its adducts $MoO_2L(Imz)$ (**2**) and $MoO_2L(Py)$ (**4**) are determined by a single-crystal X-ray diffraction technique.

The (oxo)Mo^{IV} complexes MoOL (**6**) and [MoOL(bipy)] (**7**), obtained by oxo transfer of MoO_2L to the substrate PPh_3, are isolated and characterized. MoO_2L (**1**) is found to mimic the active center of oxotransfer molybdoenzymes and hence is of interest in bioinorganic chemistry.

Results and Discussion

In this work, a tridentate diacidic Schiff base (H_2L) is used as ligand. It is prepared by condensing 2-hydroxyacetophenone with anthranilhydrazide in ethanol.[8] The stoichiometric reaction (Scheme 1) of bis(acetylacetonato)-dioxomolybdenum(VI) with H_2L in refluxing ethanol afforded the orange five-coordinate complex MoO_2L (**1**) in excellent yield. The $[MoO_2L(B)]$ complexes **2**−**5** were prepared by reaction of MoO_2L with different heterocyclic bases (B) in ethanol [B = imidazole (**2**), 1-methylimidazole (**3**), pyridine (**4**), or γ-picoline (**5**)].

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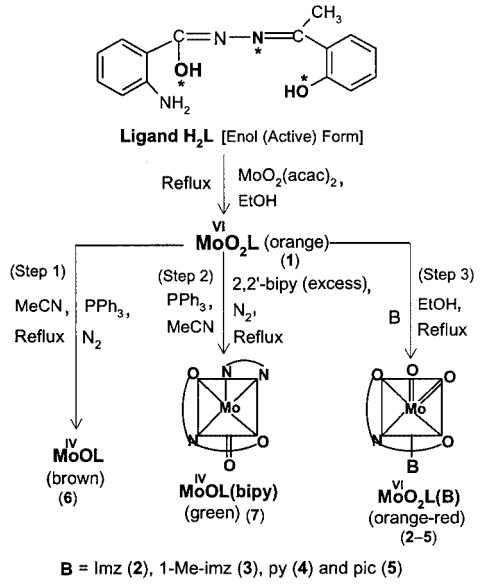

Scheme 1. Reaction diagram for the isolation of dioxomolybdenum(VI) and oxomolybdenum(IV) complexes

All these complexes are diamagnetic, indicating the presence of molybdenum in the +6 oxidation state, and are nonconducting in solution.

Selected spectroscopic data of the complexes are summarized in Table 1. In all of them, the ligand is found to act in its enol form coordinating through the deprotonated phenolate oxygen, enolate oxygen, and the azomethine nitrogen atoms. The IR spectra of the complexes do not exhibit the ligand bands at 3477 cm^{-1} [ν(OH)], 3209 cm^{-1} [ν(NH)], and 1640 cm^{-1} [ν(C=O)].[9,10] Characteristic strong bands at 1600 and 1540 cm^{-1} due to ν(C=N) and ν(C=C/aromatic) stretching modes of the ligand[10,11] are located in the spectra of both the ligand and the complexes. The Mo=O stretching modes occur as a pair of sharp strong peaks in the 930−894 cm^{-1} range.[5,12−14]

Table 1. Characteristics IR bands [cm^{-1}] and electronic spectral data [nm ($dm^3 \cdot mol^{-1} \cdot cm^{-1}$)] for the complexes

	ν(Mo=O)[a]	λ_{max} (ε)[b]
MoO_2L (**1**)	912, 894	420 (10034), 312 (15419)
MoO_2L(Imz) (**2**)	920, 895	428 (8352), 316 (17032)
MoO_2L(1-Me-Imz) (**3**)	923, 889	429 (8492), 318 (16912)
MoO_2L(Py) (**4**)	929, 902	432 (9400), 327 (14272)
MoO_2L(γ-Pic) (**5**)	929, 912	427 (8372), 319 (16703)
MoOL (**6**)	964	691 (265), 426 (1091), 312 (1997)
MoOL(bipy) (**7**)	937	679 (121), 427 (2067), 318 (5345)

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

Electronic spectra of the complexes in DMF display an intense band in the 440−420-nm region associated with a relatively weak band in the 330−310-nm region; these are believed to be of O (phenolate and enolate) → Mo LMCT origin.[5,14−16]

The ^1H NMR ([D_6]DMSO) spectrum of the free ligand exhibits an OH (phenolic) resonance at δ = 13.4 ppm. Signals for CH_3 protons at δ = 2.46 ppm and aromatic protons at 7.64−6.57 ppm are also found.[8] In the complex, the signal for the OH proton disappears, indicating deprotonation of the phenolic OH group in the complex MoO_2L. The NMR spectroscopic data of all the complexes are given in the Exp. Sect.

The relevant electrochemical data for the Mo^{VI} complexes **1**−**5** in DMF vs. SCE are summarized in Table 2. All reductions are irreversible. The cyclic voltammograms of the parent complex **1** show (Figure 1) only one reductive response at −1.22 V. The process may be represented as a metal-centered one-electron transfer involving the Mo^{VI} and the Mo^{V} oxidation states.[17−19] The CV traces of complexes **2**−**5** (Figure 2) exhibit two irreversible reductive responses[5,14−16] within the potential window −0.6 to −1.4 V, which are assigned to Mo^{VI}/Mo^{V} and Mo^{V}/Mo^{IV} processes, respectively. The lack of anodic response, even at a high scan rate, is clearly due to rapid decomposition of the reduced species.[19]

Table 2. Cyclic voltammetric results for dioxomolybdenum(VI) complexes at 298 K

Complex	E_{pc} [V][a]
1	−1.22
2	−0.72, −1.02
3	−0.64, −0.93
4	−0.82, −1.28
5	−0.78, −1.23

[a] Solvent: DMF; working electrode: platinum; reference electrode: SCE; supporting electrolyte: 0.1 M TEAP; scan rate: 100 mVs^{-1}. E_{pc} is the cathodic peak potential.

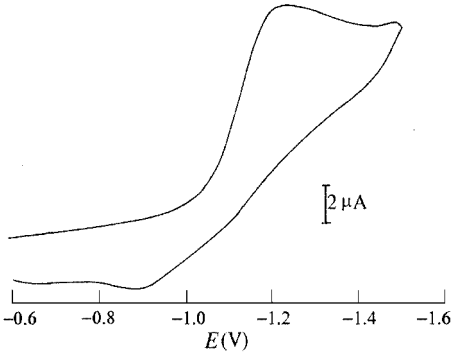

Figure 1. Cyclic voltammograms of MoO_2L (**1**) in DMF (0.1 M TEAP) at a platinum electrode; scan rate 100 mV/s and potentials recorded vs SCE

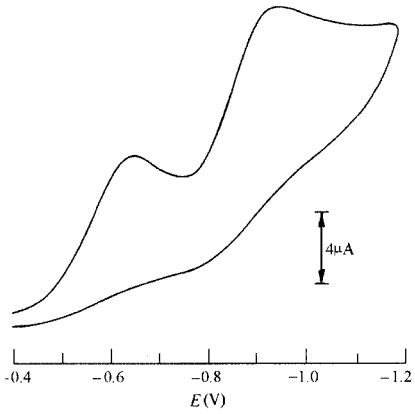

Figure 2. Cyclic voltammograms of [MoO_2L(1-Me-Imz)] (**3**) in DMF (0.1 M TEAP) at a platinum electrode; scan rate 100 mV/s and potentials recorded vs SCE

Description of the Crystal Structures

MoO_2L

Crystals of this orange compound consist of discrete molecules of MoO_2L. The structure is presented in Figure 3 and the geometric data are given in Tables 3 and 4. The coordination environment of the Mo^{VI} acceptor center consists of two oxo oxygen atoms, one enolate oxygen, one phenolate oxygen, and an azomethine nitrogen atom. This is a rare example of a five-coordinate Mo^{VI} complex.[2] No structural evidence for the achievement of hexacoordination through Mo=O···Mo bridging is observed. This MoO_2L complex could be isolated from an alcohol (MeOH, EtOH) or acetonitrile medium, from which it is found to crystallize without any solvent molecule. The molecular geometry of MoO_2L is best represented as a distorted square-pyramid with one axial oxo oxygen atom [O(2)], and three O atoms [O(1,3,4)] and the N(1) atom describing the equatorial plane. Distortion of the square plane is evident from the difference in the Mo−O(1), Mo−O(3), Mo−N(1), and Mo−O(4) bond lengths as well as the difference in the bond angles at the Mo atom [72.51(6) to 155.20(8)°]. The length of the Mo=O(1) bond lying *trans* to N(1) is practically equal to Mo=O(2); the position *trans* to O(2) remains unoccupied. The length of the two Mo−O bonds corresponding to the enolate [O(3)] and phenolate [O(4)] oxygen atoms are found to differ by only 0.077 Å. The bite angles of the ligand at Mo, O(4)−Mo−N(1) and O(3)−Mo−N(1), are 72.51(6) and 81.11(7)°, respectively, generating five-membered and six-membered chelate rings at the Mo^{VI} center. The tendency of the *cis* MoO_2 group to compress bond angles is reflected in the mean value of 76.81° for these bite angles. The lengths of the Mo=O, Mo−O and Mo−N bonds are unexceptional.[12,14,20,21] The Mo acceptor center is displaced from the average equatorial plane described by O(1)−O(3)−N(1)−O(4) towards the axial oxo oxygen atom O(2), the distance of O(2) from this plane being 2.0511 Å. Such a displacement of the Mo atom from the equatorial plane towards the apical oxo oxygen atom is also found in the aldehyde oxidoreductase of *Desulfovibrio gigas*.[22,23] This displacement, naturally, makes the Mo^{VI} acceptor center somewhat inaccessible to the donor approaching from the opposite direction. Hence, it is evident that the discrete MoO_2L molecule has a square-pyramidal structure with the sixth position, *trans* to the oxo oxygen atom O(2), vacant. This vacant sixth position is expected to act like the substrate-binding site of a molybdoenzyme. This expectation was fulfilled when MoO_2L yielded a host of six-coordinate adducts of the type MoO_2L(B), where B is a monodentate Lewis base like imidazole, substituted imidazole, pyridine or picoline. The structures of two such adduct molecules [MoO_2L(Imz)] (**2**) and [MoO_2L(Py)] (**4**) were determined by single-crystal X-ray diffraction techniques and one (**4**) is discussed below. As the structures of **2** and **4** are similar, all crystallographic data, as well as the corresponding ORTEP diagram of **2**, are included in the Supporting Information.

[MoO_2L(Py)]

Crystals of [MoO_2L(Py)] (**4**) consist of discrete molecular species and the structure is presented as Figure 4. The molybdenum(VI) center is present in a distorted octahedral donor environment consisting of *cis*-oxo atoms O(1,2), *trans*-phenolate and enolate oxygen atoms O(3,4), which are

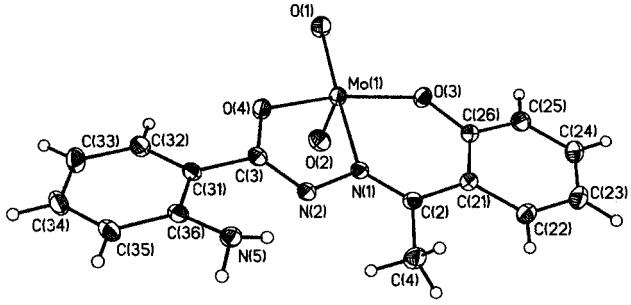

Figure 3. ORTEP plot of MoO_2L (**1**) with atom labeling scheme

Table 3. Crystal and refinement data for complexes **1** and **4**

	1	**4**
Empirical formula	$C_{15}H_{13}MoN_3O_4$	$C_{20}H_{18}MoN_4O_4$
Formula mass	395.22	474.32
Crystal symmetry	monoclinic	monoclinic
Space group	*P*2(1)/*n*	*C*2/*c*
a [Å]	7.0559(14)	20.800(5)
b [Å]	11.131(2)	10.970(2)
c [Å]	18.321(4)	17.532(4)
β [°]	95.68(3)	97.724(16)
V [Å^3]	1431.8(5)	3964.1(16)
Z	4	8
$D_{calcd.}$ [g.cm^{-3}]	1.833	1.590
F(000)	792	1920
μ(Mo-K_α) [mm^{-1}]	0.941	0.696
Collected refl.	6907	7134
Independent refl.	3288	3464
R_1 [$I > 2\sigma(I)$]	0.0271	0.0427
wR_2 (all data)	0.0614	0.1034
S (goodness of fit)	1.085	1.076
Min./max. res. [e·Å^{-3}]	0.59/−0.46	0.440/−0.685

Table 4. Selected bond lengths [Å] and bond angles [°] for complexes **1** and **4**

	Complex **1**	Complex **4**
Mo(1)−O(2)	1.696(19)	1.695(3)
Mo(1)−O(1)	1.704(16)	1.701(3)
Mo(1)−O(3)	1.906(16)	1.919(3)
Mo(1)−O(4)	2.003(16)	1.996(3)
Mo(1)−N(1)	2.249(18)	2.262(3)
Mo(1)−N(3)	−	2.433(4)
O(2)−Mo(1)−O(1)	105.95(9)	106.41(17)
O(2)−Mo(1)−O(3)	100.32(9)	100.28(16)
O(1)−Mo(1)−O(3)	102.08(8)	102.71(14)
O(2)−Mo(1)−O(4)	96.89(8)	98.09(15)
O(1)−Mo(1)−O(4)	96.39(8)	98.58(14)
O(3)−Mo(1)−O(4)	150.11(7)	146.52(13)
O(2)−Mo(1)−N(1)	97.51(8)	92.76(14)
O(1)−Mo(1)−N(1)	155.20(8)	159.70(14)
O(3)−Mo(1)−N(1)	81.11(7)	79.80(12)
O(4)−Mo(1)−N(1)	72.51(6)	71.55(12)
O(2)−Mo(1)−N(3)	−	170.04(14)
O(1)−Mo(1)−N(3)	−	82.87(14)
O(3)−Mo(1)−N(3)	−	80.76(14)
O(4)−Mo(1)−N(3)	−	76.56(12)

cis to O(1,2), an azomethine nitrogen atom N(1) and the tertiary nitrogen atom N(3). The structure of complex **4** can be derived from the structure of the coordinately unsaturated pentacoordinate square-pyramidal complex MoO_2L (**1**) by the addition of pyridine to the vacant axial position *trans* to the oxo atom O(2). The angle between the equatorial plane defined by O(1)−O(3)−N(1)−O(4) and that of the coordinated pyridine ring is 95.7°. The angle O(2)−Mo−N(3) is 170.04°, pointing to considerable distortion of the coordination octahedron around the Mo^{VI} center in compound **4**. A remarkable feature is that the values of the bond lengths and bond angles around the Mo^{VI} center in **1** are essentially the same in **4** (Table 4). Even the length of the metal−oxygen double bond (Mo=O) axial to the coordinated pyridine ligand, 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, remains practically unchanged.[12,14,20,21] The length of the relevant bond [N(3)−Mo] is found to be longer than the other type of molybdenum−nitrogen (azomethine) bond N(1)−Mo, and indicates rather weak attachment of the pyridine ligand to the MoO_2^{2+} moiety. This is substantiated by TG and DTA studies of **4**, which reveal rather easy loss of the pyridine ligand on controlled heating.

Reactivity of the Complex 1 (MoO_2L)

Substrate Binding

The reaction (Scheme 1, step 3) can be considered as a substrate-binding reaction of the MoO_2L core when a heterocyclic base (substrate) binds to the distorted square-pyramidal MoO_2L moiety forming a distorted octahedral species. This reaction reminds us of the substrate binding of molybdoenzymes.

Oxo Transfer to Substrate

The tendency of the Mo^{VI} complex MoO_2L to transfer an oxygen atom to substrates has been examined in CH_3CN using PPh_3 as the substrate. The parent complex **1** has a band at 420 nm due to an L(O)→ M(Mo) LMCT transition. When the complex is treated with PPh_3, this band is found to be shifted towards a lower energy region and a new band appears at 691 nm. The oxo-transfer reaction may be represented as $Mo^{VI}O_2L + PPh_3 \rightarrow Mo^{IV}OL + OPPh_3$.

PPh_3O has been isolated and identified by IR and ^{31}P NMR spectroscopic data. This oxo-transfer reaction may be visualized[24] as a simple bimolecular reaction.[5]

Oxomolybdenum(IV) Complexes

The oxomolybdenum(IV) complexes were synthesized by two different methods (Scheme 1, steps 1 and 2) described later. Complexes **6** and **7** have poor solubility in many common organic solvents but are highly soluble in DMF and DMSO, and when the solutions are exposed to air they slowly oxidize to the parent MoO_2L in solution. As four-coordinate (oxo)Mo^{IV} complexes are unlikely, they are probably polymeric species in the solid state.[5] All the complexes are nonelectrolytes in DMF, and measurement of magnetic susceptibility indicated that they are diamagnetic at room temperature.[5,25,26]

Some spectral characteristics of compounds **6** and **7** are listed in Table 1. As already found in the case of its MoO_2^{2+} complexes, the ligand H_2L binds in a dianionic tridentate manner in its Mo^{IV} complexes. The IR spectra of these MoO^{IV} complexes clearly reveal that coordination takes place from the deprotonated phenolic and enolic oxygen atoms and the azomethine nitrogen atom. These complexes exhibit a single strong sharp band in the 964−937-cm^{-1} region,[5] representing the $\nu(Mo{=}O)_t$ mode.

The electronic spectra of the (oxo)Mo^{IV} compounds were recorded in dry DMF solution, and the compounds are found to display (Table 1) several absorption maxima in the 691−320-nm range, including a new band of moderate intensity in the low-energy 691−679-nm region. Absorption in this region is a characteristic feature of the $[MoO]^{2+}$ core.[5,27,28]

The proposed structure of **7**, which can be derived from the structure of its precursor complex **1**, is shown in Scheme 1.

The electron-transfer behavior of the complexes **6** and **7** (Table 5) was examined in CH_3CN using the conditions described in the Exp. Sect. The representative cyclic voltammograms of the complexes are shown in Figure 5. Controlled-potential coulometry indicates that these are one-electron processes. The (oxo)Mo^{IV} complexes undergo one-electron reduction to the corresponding Mo^{III} complexes and are oxidized by a one-electron process to Mo^{V} complexes. Similar observations were noted by Boyd and Spence,[27] as well as our own group.[5]

Table 5. Cyclic Voltammetric Results for Oxomolybdenum (IV) Complexes at 298 K

Complex[a]	Mo^{V}/Mo^{IV}	Mo^{IV}/Mo^{III}			
	E_{pa} [V]	E_{pc} [V]	E_{pa} [V]	ΔE_p [mV]	$E_{1/2}$ [V]
6	+1.02	−1.03	–	–	–
7	+1.10	−0.24	−0.15	90	−0.195

[a] Solvent: CH_3CN; working electrode: platinum; reference electrode: SCE; $E_{1/2} = 0.5\ (E_{pa} + E_{pc})$; $\Delta E_p = E_{pc} - E_{pa}$; E_{pc} and E_{pa} are the cathodic and anodic peak potentials, respectively; scan rate: 100 mVs^{-1}.

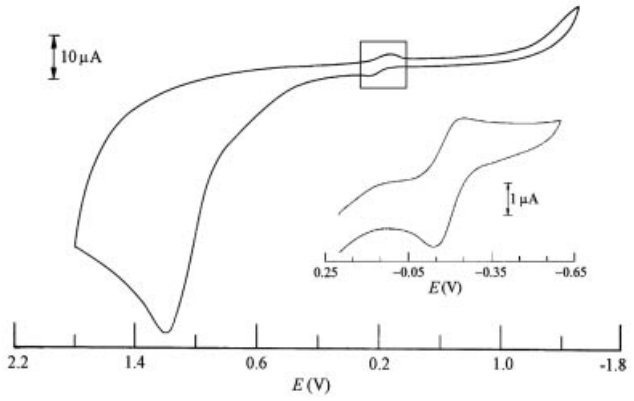

Figure 5. Cyclic voltammograms (scan rate 100 mV/s, solvent CH_3CN, 0.1 M TEAP) of MoOL(bipy) (**7**), cathodic scan (inset)

MoOL (6)

The redox behavior of this complex is found to be irreversible. At a scan rate of 100 mV s^{-1}, there is a reduction peak near −1.03 V corresponding to Mo^{IV} to Mo^{III} reduction and an anodic peak at +1.02 V for the Mo^{IV} to Mo^{V} oxidation.

MoOL(bipy) (7)

The cyclic voltammogram of this complex exhibits an irreversible anodic response (Figure 5) and a quasi-reversible cathodic response (inset, Figure 5). An initial anodic scan at a rate of 100 mV s^{-1} reveals an irreversible oxidation wave near +1.10 V, which is assigned to the one-electron oxidation of the Mo^{IV} complex to the corresponding Mo^{V} species. On the cathodic side, there is a minor reversible peak at $E_{1/2} = -0.195$ V whose current height is less than 1/10 that of the anodic peak. This small peak probably arises due to the generation of a very small amount of an Mo^{V} or Mo^{VI} species from the parent Mo^{IV} complex **7** during the preparation of the solution and performing the CV experiment. As Mo^{V} or Mo^{VI} species are expected to be more easily reduced than the corresponding Mo^{IV} species, this couple is observed at a much less negative potential than the Mo^{IV}/Mo^{III} couple observed in complex **6**. Due to the introduction of a strong donor bipy ligand the Mo^{IV}/Mo^{III} couple for **7** is expected to shift to a more negative potential and was therefore not observed within the potential window scanned in our experiment.

Conclusion

Preparation and characterization of dioxomolybdenum(VI) and oxomolybdenum(IV) complexes involving a diacidic tridentate ONO donor in the form of the 2-hydroxyacetophenone hydrazone of *o*-aminobenzoylhydrazine (LH_2) is reported. The main complex MoO_2L is a structurally characterized pentacoordinate distorted square-pyramidal species with one vacant position (*trans* to one of the M=O oxygen atoms). This vacant position is found to act as a substrate-binding site, and six-coordinate adducts, like $[MoO_2L(Py)]$ and $[MoO_2L(Imz)]$, are easily formed by the attachment of pyridine or imidazole to this position. The molybdenum center of MoO_2L is found to mimic the active site of some oxotransfer molybdoenzymes, as evidenced by the transfer of an oxo oxygen atom to the substrate PPh_3. Careful analysis of the structural data of MoO_2L indicates that the metric values of the structural features of the complex resemble those of the aldehyde oxidoreductase from *Desulfovibrio gigas* in which the Mo^{VI} center is also pentacoordinate and distorted square-pyramidal.[22,23] The magnitude of the deviation of the Mo^{VI} center towards the apical oxygen atom O(2) is also similar to that found in the molybdoenzymes referred to above.[22,23] It is known that the active sites of some oxotransfer molybdoenzymes contain at least one S donor atom around MoO_2^{2+} or MoO^{2+} cores along with N and O donor points. However, in the present case, the donor environment around the MoO_2^{2+}/MoO^{2+} core consists only of N and O donor points. This work suggests that the presence of at least one sulfur donor in the coordination sphere of the oxomolybdenum core may not be absolutely essential for all oxotransfer molybdoenzymes.

Experimental Section

General Remarks: $[MoO_2(acac)_2]$ was prepared as described in the literature.[29] 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.[30] Elemental analyses were performed with a Perkin−Elmer 240 C, H, N analyzer. IR spectra were recorded with a Perkin−Elmer 783 spectrometer. ^1H NMR spectra were recorded with a Bruker AVANCE DPX 300 MHz spectrometer using $SiMe_4$ as an internal standard. Electronic spectra were recorded with a Shimadzu 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 using an EG&G PARC electrochemical analysis system (model 250/5/0) and a PC-controlled EG&G/PARC−VERSASTAT2 potentiostat at 298 K under dry nitrogen. Cyclic voltammetry experiments were carried out with a platinum working electrode, a platinum auxiliary electrode, SCE as the reference electrode, and TEAP as the supporting electrolyte. The value

for the ferrocenium/ferrocene couple under the experimental conditions was 0.40 V.

Synthesis of Ligand H_2L: The Schiff base ligand 2-aminobenzoylhydrazone of 2-hydroxyacetophenone was prepared by the same procedure reported in our previous work.[8]

Synthesis of $[MoO_2L]$ (1): A sample of H_2L (0.28 g, 1.04 mmol) was dissolved in 30 mL of ethanol by warming in a water bath, solid $MoO_2(acac)_2$ (0.33 g, 1.01 mmol) was added to the ligand solution and the mixture was refluxed for 3 h and then filtered. Slow concentration of the orange filtrate over 3 d produced dark orange crystals. Yield 0.32 g (81%). $C_{15}H_{13}MoN_3O_4$ (395.04): calcd. C 45.54, H 3.32, N 10.63; found C 45.94, H 3.30, N 10.01. ^{1}H NMR ([D$_6$]DMSO): δ = 7.93−6.57 (m, 8 H, C_6H_4), 2.78 (s, 3 H, CH_3) ppm.

Synthesis of $[MoO_2L(Imz)]$ (2; Imz = Imidazole): Imidazole (0.05 g, 0.75 mmol) was added to a clear orange solution (obtained by refluxing) of **1** (0.22 g, 0.55 mmol) in ethanol (50 mL) and the mixture was allowed to reflux for 3 h. The volume of this dark orange solution was reduced to 20 mL in a rotary evaporator. On standing at room temperature, the solution deposited shiny brown crystals. Yield 0.21 g (80%). $C_{18}H_{17}MoN_5O_4$ (463.08): calcd. C 46.62, H 3.69, N 15.10; found C 46.31, H 3.49, N 15.07. ^{1}H NMR ([D$_6$]DMSO): δ = 7.94−6.57 (m, 8 H, 3 H, C_6H_4, $C_3N_2H_4$), 2.77 (s, 3 H, CH_3), 12.01 (s, NH, $C_3N_2H_4$) ppm.

Synthesis of $[MoO_2L(1\text{-}Me\text{-}Imz)]$ (3; 1-Me-Imz = 1-Methylimidazol): This compound was prepared using the same procedure as for compound **2**. Yield 0.21 g (78%). $C_{19}H_{19}MoN_5O_4$ (477.09): calcd. C 47.76, H 4.01, N 14.66; found C 47.61, H 3.95, N 14.49. ^{1}H NMR ([D$_6$]DMSO): δ = 7.93−6.57 (m, 8 H, 3 H C_6H_4, $C_4N_2H_6$), 2.78 (s, 3 H, CH_3), 3.71 (s, 3 H, $C_4N_2H_6$) ppm.

Synthesis of $[MoO_2L(py)]$ (4; py = Pyridine): Complex **1** (0.22 g, 0.55 mmol) was treated with 2 mL of pyridine and the mixture was heated until a clear deep yellow solution was produced. Dry ethanol (20 mL) was added to this solution, which was then refluxed for 3 h. Slow concentration of the reaction mixture over 5 d produced yellow crystals. Yield 0.19 g (74%). $C_{20}H_{18}MoN_4O_4$ (474.08): calcd. C 50.59, H 3.82, N 11.80; found C 49.94, H 3.85, N 12.09. ^{1}H NMR ([D$_6$]DMSO): δ = 8.58−6.57 (m, 8 H, 5 H, C_6H_4, C_5H_5N), 2.77 (s, 3 H, CH_3) ppm.

Synthesis of $[MoO_2L(\gamma\text{-}pic)]$ (5; γ-pic = Picoline): This compound was prepared using the same procedure as above (compound **4**). Yield 0.19 g (70%). $C_{21}H_{20}MoN_4O_4$ (488.10): calcd. C 51.60, H 4.12, N 11.46; found C 51.84, H 3.90, N 11.51. ^{1}H NMR ([D$_6$]DMSO): δ = 8.42−6.57 (m, 8 H, 4 H, C_6H_4, C_6H_7N), 2.77 (s, 3 H, CH_3), 2.31 (s, 3 H, CH_3, C_6H_7N) ppm.

Synthesis of [MoOL] (6): A solution of PPh_3 (0.393 g, 1.5 mmol) in 5 mL of acetonitrile was added to a refluxing solution of MoO_2L (0.22 g, 0.55 mmol) in 25 mL of degassed acetonitrile. 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 0.15 g (70%). $C_{15}H_{13}MoN_3O_3$ (379.04): calcd. C 47.46, H 3.45, N 11.07; found C 47.34, H 3.12, N 11.23. ^{1}H NMR ([D$_6$]DMSO): δ = 7.94−6.57 (m, 8 H, C_6H_4), 2.78 (s, 3 H, CH_3) ppm.

Synthesis of [MoOL(bipy)] (7; bipy = 2,2′-Bipyridine): A solution of 2,2′-bipyridine (bipy; 0.78 g, 5.0 mmol) and PPh_3 (0.393 g, 1.5 mmol) in 5 mL of degassed acetonitrile was added to a refluxing solution of 0.22 g (0.55 mmol) of MoO_2L in 25 mL of degassed acetonitrile. The orange-red solution turned green after 1 h of refluxing and refluxing was continued for another 4 h. The green product was precipitated by adding excess dichloromethane (50 mL) followed by excess *n*-hexane (50 mL). The precipitate was rapidly filtered and washed well with *n*-hexane and dried in vacuo; yield 0.18 g (60%). $C_{25}H_{21}MoN_5O_3$ (535.10): calcd. C 55.02, H 3.88, N 12.83; found C 54.91, H 3.90, N 12.41. ^{1}H NMR ([D$_6$]DMSO): δ = 8.70−6.59 (m, 8 H, 8 H, C_6H_4, $C_{10}H_8N_2$), 2.77 (s, 3 H, CH_3) ppm.

Crystallography: Crystal data for compounds **1** and **4**, along with other experimental details, are summarized in Tables 3 and 4. Single-crystal data collection was performed at 293(2) K with a Siemens P4 four-circle diffractometer using graphite-monochromatized Mo-K_α radiation (λ = 0.71073 Å). The complex MoO_2L (**1**) crystallizes in the monoclinic space group $P2_1/n$ whereas the complex $MoO_2L(Py)$ (**4**) crystallizes in the monoclinic space group $C2/c$. The intensities were corrected for Lorentz and polarization effects and semi-empirical absorption corrections were performed on the basis of Ψ scans for nine chosen reflections with high χ values. Following structural solution, positional parameters and temperature factors were refined by full-matrix least squares against F_o^2 with SHELX 97.[31] All non-hydrogen atoms were refined anisotropically and a riding model with isotropic temperature factors was employed for hydrogen atoms. The X-ray crystallographic structure and the corresponding data for the complex **2** [MoO_2L-(Imz)] are reported as Supporting Information. CCDC-186348 (**1**), -186349 (**2**) and -186350 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

We thank Dr. S. K. Chattopadhyay, Bengal Engineering College (Deemed University) for fruitful discussions.

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Received May 23, 2002
[I02270]