Synthesis and physicochemical studies of a new molybdenum (IV)-pterin complex undergoing reaction with trimethylamine N-oxide

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A new compound, [Mo\textsuperscript{IV}L\textsubscript{2}].3CH\textsubscript{3}OH (2), has been synthesized using a redox reaction between Na\textsubscript{2}MoO\textsubscript{4}.2H\textsubscript{2}O and 2-pivaloylamino-6-phenacyl-isoxanthopterin, and characterized by elemental analysis, electrospray ionization mass spectrometry, various spectroscopic methods and cyclic voltammetry. Its optimized geometry (with lowest steric energy) has been obtained by molecular mechanics method; the optimized bond lengths and bond angles data tally with the literature X-ray structural data. Both the kinetic and stoichiometric aspects of its reaction with Me\textsubscript{3}N→O have been studied. The negative $\Delta S^\circ$ (J K\textsuperscript{-1} mol\textsuperscript{-1}) value (-282.8) is consistent with an associative mechanism for this process. The product of this reaction has been isolated and characterized to be a $\mu$-oxo binuclear Mo(V) complex, indicating oxygen atom transfer nature of this reaction.$^1$H-NMR, fluorescence spectra and CV data indicate the redox “non-innocent” behavior of the pterin ligand in the present case.

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Pterins (2-amino-4-oxopteridines) represent a system of heterocycles with unique structure and are found in a wide range of biological functions including the essential components of a large number of metal containing enzymes (e.g., Fe, Mo, W)\textsuperscript{1, 2}. The well-known ability of pterins to act as redox partners in biological redox system is intimately connected with the ability of the pyrazine moiety (of the pterin ring) to exist in different oxidation states, thereby exhibiting multiple redox activity like the redox capabilities of the transition metal counterparts in the above-mentioned metalloenzymes\textsuperscript{3}. These facts have inspired symbiotic developments in the coordination chemistry of pterin ligands and the assignment of oxidation states of both the metal and ligand centers in the new complexes along with their electronic structure is an involved task\textsuperscript{4-6}.

Molybdenum is an element widespread in the environment because of water solubility of its high valent compounds. Also, different life forms need molybdenum for survival and growth. The oxomolybdoenzymes catalyze net oxygen atom transfer reaction (Eq. 1) to and from a variety of biologically important substrates (where X or XO may be, SO\textsubscript{3}\textsuperscript{2-}, Me\textsubscript{2}SO, NO\textsubscript{3}′, Me\textsubscript{3}NO etc), with the metal centre undergoing simultaneous redox change from Mo(VI) to Mo(IV) or vice versa\textsuperscript{2}.

\[
X + H_2O + Mo^{VI} \rightleftharpoons XO + 2H^+ + Mo^{IV} \quad \ldots \quad (1)
\]

We report herein a new molybdenum(IV) complex with a 6-substituted pterin ligand 1 (H\textsubscript{2}L, Scheme 1) and its characterization through physicochemical, spectroscopic data. Its reactivity towards a typical enzyme substrate like Me\textsubscript{3}NO has also been studied\textsuperscript{2}. The results are expected to serve as benchmark data for understanding the possible electron exchange cooperativity between formally metal-based and pterin-based redox systems\textsuperscript{3}.

Materials and Methods
Reagent grade chemicals were used as received. Pivalic anhydride, trimethylamine N-oxide and Na\textsubscript{2}MoO\textsubscript{4}.2H\textsubscript{2}O were obtained from Fluka, Switzerland, Aldrich, U.S.A. and J. Baker, U.S.A. respectively. Various solvents were purified following literature procedures. Silica gel (230–400 mesh) for flash chromatography (dried at 180°C for 6h before use), silica gel (GF\textsubscript{254}) for TLC and spectroscopic
grade DMF for CV measurements were purchased from SRL, Mumbai. All synthetic steps were carried out under dinitrogen atmosphere using Schlenk procedure, red lamps/subdued light and paraffin oil bath heating system; flash chromatography was also performed under flow of dinitrogen.

FTIR spectra (KBr) were recorded on a Shimadzu FTIR-8300 spectrophotometer. Fluorescence spectra were recorded on a Elico(SL-174) spectrofluorometer. 

Preparation of 2-pivaloylamino-6-phenacyl-isoxanthopterin monohydrate (1) (H₂L, H₂O)

The starting material, 6-phenacyl-isoxanthopterin, was obtained in 78% yield by modifying its original synthetic method in the light of subsequent developments (e.g., darkness, dinitrogen atmosphere). The desired ligand (1) was prepared by boiling under reflux a mixture of 6-phenacyl-isoxanthopterin (0.50g, 1.68mmol) and pivalic anhydride (9.3g, 50mmol) in controlled conditions (6h, dinitrogen atmosphere, paraffin oil bath at 200°C). The reaction mixture was evaporated on a rotary evaporator (90°C, 15mm Hg) and the deep brown crude product was purified by flash chromatography using CH₂Cl₂:CH₃OH (9:1 v/v) as eluant. The final product was recovered through evaporation of solvent, dried in vacuo over P₂O₅. The compound (1) was obtained in 78% yield by modifying its original synthesis in the light of subsequent developments (e.g., darkness, dinitrogen atmosphere).

Preparation of [MoIVL₃]3CH₃OH (2)

A solution of the pterin ligand (1) (0.2g, 0.52 mmol) in CH₂OH (50ml) was treated with a solution of Na₂MoO₄,2H₂O (0.065g, 0.26mmol) in H₂O (5ml). The pH of the mixture was adjusted to 5.5 by addition of 3 N HCl and then the solution was boiled (paraffin oil bath) under reflux in the dark and dinitrogen atmosphere for 6h. The orange-yellow solution was evaporated in a rotary evaporator and the residue was purified through flash chromatography using CH₂Cl₂:CH₃OH (95:5 v/v) as eluant. The pertinent compound (2) was obtained after evaporation of the solvent and drying in vacuo over P₂O₅ (yield 29%). Its purity was checked through TLC (UV lamp). Found: C, 51.7; H, 5.2; N, 14.3%. Calc. for MoC₄₁H₄₈N₁₀O₁₁ (950.81): C, 51.8; H, 4.9; N, 14.7%. UV/vis (CH₃OH): λ_max, nm: (log ε): 218(4.14), 261 (3.91), 311sh(3.61), 325sh(3.52), 386(3.74), 439sh(3.27). Λ_M (6.5 ohm⁻¹ cm² mol⁻¹, CH₃OH) at 20°C is consistent with the formulation as nonelectrolyte.

Preparation of [L₂MoIII-O-MoIII]₃CH₃OH (3)

A solution of (2) (0.057g, 0.06mmol) in CH₃OH (60ml) was stirred (in the dark) with trimethylamine N-oxide (0.0045g, 0.06mmol) for 6h (first 24h at 29°C and rest of the period at 40°C). The gaseous product of the reaction, i.e., Me₇N (b.pt. 3°C) was driven off under gentle dry dinitrogen gas flow over the entire period into another flask containing a measured excess of perchloric acid in glacial acetic acid and the carrier gas allowed to escape to the atmosphere through a silicone oil bubbler. Finally, the residual excess of perchloric acid was back-titrated using a standard sodium acetate solution. For every two moles of (2) added, ca. 0.85 mol of Me₇N was recovered, indicating a reaction represented by Eq. 2.

2 Complex (2) + Me₇N→O ⇄ [2 Complex (2) Me₇N→O] →Me₇N + µ-oxoMo(V) complex (3) … (2)

The solution in the reaction flash was evaporated in a rotary evaporator and the residue was purified through flash chromatography using CH₂Cl₂:CH₃OH (93:7 v/v) as eluant. The relevant fraction (purity checked through TLC) was evaporated once again and the residue was purified through flash chromatography using CH₂Cl₂:CH₃OH (95:5 v/v) as eluant. The pertinent compound (3) was obtained after evaporation of the solvent and drying in vacuo over P₂O₅ (yield 29%). Its purity was checked through TLC (UV lamp). Found: C, 57.5; H, 5.0; N, 17.6%. Calc. for C₉₉H₁₇₂N₇O₁₇ (399.4): C, 57.1; H, 5.3; N, 17.5%. UV/vis (CH₃OH): λ_max nm: (log ε): 242sh (4.20), 285sh(4.06), 325sh(3.52), 386(3.74), 439sh(3.27). Λ_M (6.5 ohm⁻¹ cm² mol⁻¹, CH₃OH) at 20°C is consistent with the formulation as nonelectrolyte.

Results and Discussion

Low solubility associated with hydrogen bonding (involving hydrophilic groups like amino, hydroxy etc.) is a characteristic feature of pterin chemistry. This problem is overcome in the present study to a large extent through replacement of one of the hydrogen atoms of the NH₂ (2) group by a pivaloyl group [(CH₃)₂CCO] through reaction with pivalic anhydride. This paraffin oil bath reaction has to be carried out in the dark under dinitrogen atmosphere in order to protect (1) from light and moisture. The same precautions have to be taken during the synthesis of (2) and (3). Presence of the pivaloyl...
substituent in these compounds, enhances their solubility substantially in common organic solvents, thereby facilitating their ease of handling as well as purification through flash chromatography. The agreement between the experimental analytical data and the expected values for (1), (2) and (3) is good. Reactivity of (2) towards trimethylamine N-oxide (vide infra) indicates that molybdenum exists here in the lower oxidation state, e.g., Mo(IV).\(^2\) The conversion of tetrahedral \(\text{MoO}_4^{2-}\) ion into octahedral oxomolybdenum(VI) species with the lowering of \(pH\), is a well-characterized process\(^10\). Again, as per Scheme 1, either both the heterocyclic rings or one of them (e.g., the pyrazine ring) is in a reduced state in (1). A redox reaction accompanies the complex formation process (between \(\text{Na}_2\text{MoO}_4\cdot2\text{H}_2\text{O}\) and (1)), leading to the molybdenum (IV) species (2). Conversely, its ligand residue (L\(^1\)) and its associated water molecule in (1), are indicated \(^{11a,11b}\). Presence of such hydrogen bonding has been verified through matching with the calculated distribution pattern using a computer program developed by Prof. Junhua Yan. Architectural stability of (1) containing two major substituents at the 2- and 6-positions of the pterin ring as well as existence of a strong hydrogen bonding between the pterin ligand (H\(_2\)L) and its associated water molecule in (1), are indicated \(^{11a,11b}\). Presence of such hydrogen bonding has been verified through single crystal X-ray structure determination of a closely related pterin compound, e.g., 2-pivaloylamino-7-acetylbenzoxanthopterin monohydrate, where the H\(_2\)O molecule is hydrogen bonded to the NH(2) group [the N(2)-H...O hydrogen bonding distance is 2.945 Å (ref. 12)].

In the ESMS spectrum of (2) the characteristic Mo isotope distribution profile for the essentially intact desolvated species \([\text{M-CH}_3\text{OH}]^+\) is observed at \(m/z = 851\), corresponding to its theoretical value\(^11c,13\). Another significant fragment, e.g., \([\text{M(3CH}_3\text{OH+H}_2\text{O+3H)}]^+\) may be assigned at \(m/z = 833\)(ref. 12).

ESMS data of (3) helps to assign some of important binuclear fragments through comparison of experimental and simulated isotope distribution patterns, e.g., the desolvated species \([\text{M-CH}_3\text{OH}]^+\) at \(m/z = 1725\) and the fragment \([\text{M-(CH}_3\text{OH+12CH}_3\text{H}_2\text{O+2H)}]^+\) at \(m/z = 1524\) where the 12CH\(_3\) groups correspond to the pivaloyl methyl groups of the four pterin ligand residues of (3)\(^2\). The peak at \(m/z = 865\) is assigned to the fragment \([\text{M-4(CH}_3\text{COO-NH+4CH}_2\text{COCH}_3)}]^+\), involving loss of all the 2- and 6-substituents of the four pterin ligands along with the bridging oxygen atom(O\(_b\))\(^{11b}\). The difference in intensity between the isotope peaks and calculated values in some of these cases is due to ion-molecule interaction, e.g., involving transfer of a hydrogen atom\(^{11a}\).

On comparing the IR spectra of (1) and (2)\(^{12}\), it is evident that the free ligand IR bands at 1346 cm\(^{-1}\) and 1261 cm\(^{-1}\) due to \(\delta(\text{O-H})\) and \(\nu(\text{C=O}) + \delta(\text{O-H})\) vibrations respectively, of OH(4), undergo considerable modifications in (2) and a new strong band appears at 1261 cm\(^{-1}\) due to \(\nu(\text{C-O})(4)\) mode of the corresponding phenoxy group\(^{11a}\). Beside these, most of the IR bands in the region 1676-1500cm\(^{-1}\) of (1) (where the \(\nu(\text{C=O})(11)^{1a}\), \(\nu(\text{C=O})(2), \nu(\text{C}=\text{O})(7)\) modes as well as the \(\nu(\text{C}=\text{N})\) and \(\nu(\text{C}=\text{C})\) vibrations of the pterin and aromatic rings are present) undergo change (with respect to number, relative intensity and shape) in (2) due to tautomerism/deprotonation/electronic redistribution during the complex formation process involving the N(3)-C(4)-N(5)-C(6)-C(1\(^{1}\)) system (Scheme 1). The \(\nu(\text{C}=\text{O})(11)^\prime\) mode (1681-1676 cm\(^{-1}\)) remains essentially unchanged during this process. For (2) no strong IR band assignable to the \(\nu(\text{Mo}=\text{O})\) mode could be located in the region 980-880 cm\(^{-1}\). In case of (3), a new intense IR band appears at 804 cm\(^{-1}\) corresponding to the \(\nu(\text{Mo-O}_b\text{-Mo})\) mode\(^{10}\).

The possible schematic structures of the pertinent compounds were optimized by molecular mechanics calculations (MM2), giving the lowest steric energy (kcal/mol) CHEM3D models. Figure 1 shows the CHEM3D model of (1) with lowest steric energy of 0.21 kcal/mol, while Fig. 2 shows that of (2) with lowest steric energy of 29.6 kcal/mol, indicating their stability as well as geometry\(^{14}\). The molecular modelling force fields in use for molecular system, can be interpreted in terms of the four key contributions, e.g., bond stretching, angle bending, torsional terms and non-bonded interactions\(^{14}\). Apart from the lowest steric energies of the molecules, two basic parameters for (2) were evaluated, i.e., bond distances (Å) and bond angles (deg.), (Table 1), and compared with the literature data obtained through
X-ray structural studies on molybdenum complexes with different pterin ligands and other relevant systems. Here, the Mo-N(5) distance shows a fair agreement between the computed and experimental literature data. In the chelating aspect of the pterin ligand towards molybdenum, the Mo-N(5) bond plays a pivotal role. It has a significant multiple bond character as verified through X-ray structural data.

Joule and coworkers concluded from both chemical and X-ray structural studies that sufficiently greater basicity/nucleophilicity resides at N(5) than at N(8), thereby supporting such coordination property. Table 1 shows essentially four types of computed bond angles involving the Mo(IV) atom, in agreement with the four types of such bond angles (72°-74°, 80°-88°, 92°-98° and 158°-170°) found from X-ray structural studies in different molybdenum-pterin systems with distorted octahedral geometry around the Mo atom (in both mono and binuclear complexes). Good agreement is observed (Table 2) between the selected optimized bond lengths (Å) of the CHEM3D model of (1) and the corresponding literature X-ray structural data of a pterin compound. Table 2 also compares several optimized bond length data (Å) of (1) and (2), some of which undergo change during the complex formation process. It is evident that the pterin ring is attached to the Mo atom (in 2) through the O(4) and N(5) atoms resulting from the dianion formation (Scheme 1) involving the amide function in position 3, 4 and the vinylogous amide in position 5 including the adjacent side-chain i.e., the proton from C(1') is located at N(5). Each pterin ligand residue (L²) in (2) acts as a tridentate one (Fig. 2). A CHEM3D representation (MM2 calculations; steric energy: 82.9 kcal/mol) of

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**Table 1**—Comparison of selected computed bond lengths (Å) and bond angles (deg.) in (2) from the optimized geometry [Fig. 2, MM2 calculations] with the available literature data (in parentheses) from X-ray structural studies

<table>
<thead>
<tr>
<th>Bond distances (Å)</th>
<th>Bond angles (deg.)</th>
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<tbody>
<tr>
<td>Mo(53)-O(104)</td>
<td>O(18)-Mo(53)-O(1) 87.9 (80.16-88.0)</td>
</tr>
<tr>
<td>Mo(53)-O(18)</td>
<td>O(63)-Mo(53)-O(1) 161.1 (158.0-169.2)</td>
</tr>
<tr>
<td>Mo(53)-N(76)</td>
<td>N(76)-Mo(53)-O(1) 97.5 (92.1-98.8)</td>
</tr>
<tr>
<td>Mo(53)-N(9)</td>
<td>N(76)-Mo(53)-O(104) 77.5 (72-74)</td>
</tr>
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*a* X-ray structural data have been collected from Ref. 4.

*b* Here O(104), O(18) and N(76), N(9) correspond to O(4) and N(5) donor atoms respectively, of the pterin ring as per Scheme 1, while O(63), O(1) correspond to O(2') of the 6-substituent.

*c* Bond length data for the two ligand residues in (2).

*d* One set of selected bond angle data involving Mo(53) for (2), is presented here.
The optimized geometries (MM2 method) of the present compounds correspond to their lowest steric energies (just as X-ray structural data of a compound correspond to its thermodynamically most stable form). On the other hand, in solution, intrinsic relative stabilities of different forms (tautomers, conformers, etc.) of a compound are determined by different factors, e.g., hydrogen bonding and other intermolecular interactions, which can easily outweigh the small intrinsic energy barriers, leading to their labile equilibrium in solution. For the pterin compounds, the roles of hydrogen bonding and tautomerism are well-documented. 1H-NMR data (both 1D and 2D) of (1) and (2) in d$_6$-DMSO (δ in ppm versus TMS) reflect this aspect. For (1) the OH(4), NH(5) and NH(8) signals appear at δ13.25(bs), δ12.44(bs) and δ10.90(bs) respectively (Scheme 1) and disappear when the 1H-NMR spectrum is recorded afresh in CD$_3$OD indicating their exchangeable nature. The phenyl ring (2’) protons appear at δ7.94 (2H,m) and δ7.56 (3H,m) and the cross peaks (1H-1H COSY) connect both to the CH(1’) signal at δ 6.68(1H) (Fig. 3). For the 2-pivaloylamino substituent, two distinct signals characterize the NH(2) proton (δ4.20 q; δ3.96 q). They are connected by off-diagonal peaks (1H-1H COSY data) to the two CH$_2$(2”) signals at δ1.202 (6H, double doublet) and δ1.046 (3H, singlet) respectively. Again, the residual methyl signal (δ 2.47, s) of d$_6$-DMSO is related by off-diagonal peaks to the CH$_3$(2”) signal at δ1.202 as well as the NH(2) signal at δ4.20, indicating the existence of strong hydrogen bonding interaction between the NMR solvent and the NH(2) group, with its influence (spin-spin-interaction) extending all the way upto CH$_2$(2”) (Fig. 4). This hydrogen bond restricts free rotation around the N(2)-
C(1")-C(2") σ skeleton, leading to the appearance of two separate signals for both the NH(2) and CH₃(2") type protons. ¹H-NMR data (1D and 2D) of ribavirin in d₆-DMSO show that restricted rotation around a C-N bond can make even the two primary amide NH protons non-equivalent on the NMR time-scale.¹⁸

Compound (2) also exhibits more than one type of NMR signal for most its ligand protons. The phenyl (2') ring protons appear at δ 7.88 (2H,m) and δ 7.46 (3H,m). As per ¹H-¹H COSY data, the former signal is connected by cross peaks to the three separate CH(1') signal appearing at δ6.67(s), δ6.10(s) and δ5.70(s) respectively (Fig. 5). The NH(8) proton is also characterized by three separate signals (bs), i.e., δ11.50, δ11.17 and δ11.05 respectively. Possible tautomerism in solution involving the amide function in position 7, 8 cannot be ruled out. The proton signals of the 2-pivaloylamino substituent of (1) remain essentially unchanged (with respect to position, relative intensity and multiplicity) in (2), indicating nonparticipation of this functional group in the metal coordination process.

The difference in positions of the CH(1') and NH(8) proton signals (Δδ) in (1) and (2) indicates that while the former signal is shielded (up to 0.98 ppm), the latter is deshielded (to a limit of 0.60 ppm) during the coordination (to the Mo atom) process. There is increase in electron density around the Mo atom in (2) with electron depletion from the NH(8) region of its pterin ligand residues (L²). This attribute is utilized by the metal centre of (2) in the reduction of Me₃N→O to Me₃N. In the ¹H- NMR spectrum of (3) (d₆-DMSO), the phenyl (2') ring protons may be assigned at δ8.13 (2H,m) and δ7.55(3H,m); the three separate CH(1') signals appear at δ7.37(s), δ6.98(s) and δ6.81(s) respectively. The three signals (bs) for
the NH(8) proton are characterized at δ12.28, δ11.78 and δ11.55, i.e., all these proton signals are deshielded from their corresponding positions in (1). Reaction between (2) and Me$_3$N→O involves transfer of electron density from the former to the latter with the pterin ligand residues (L$^2$) acting as the source of electrons here.

The complex formation process, (1)→(2), is accompanied by a significant increase in fluorescence property. The moderate fluorescence spectral intensity for (1) is due to the presence of the phenyl(2$'$) group. In the case of (2), several factors contribute towards its more rigid framework, e.g., the pyrimidine ring of the pterin ligand residue (L$^2$) achieves aromaticity and the chelation process makes the entire complex molecule rigid (Fig. 2). As a result, dissipation of the excitation energy in manners other than by the emission of fluorescent light is prevented$^{19a}$. In fact, strong fluorescence property of pterins (essentially the oxidized forms with aromatic rings, e.g., pterin-6-carboxy-7-sulphonic acid) has served as a probe for their detection in the molybdenum cofactor (of oxomolybdoenzymes) after oxidative degradation$^{19b}$. Even pH dependence of fluorescence property of biopterin is interesting, since no fluorescence of the protonated form and strong fluorescence for the anion is observed$^9$. Figure 6 represents spectrophotometric monitoring of the reaction of (2) with Me$_3$N→O in CH$_2$OH at 28°C. Similar absorption spectral changes are observed for the molybdenum fragment of several oxomolybdoenzymes$^{20}$. The UV-vis spectra of pterins depend on the oxidation state of the constituent pyrimidine and 1,4-diazine rings. For (2) the 261 nm band is due to an intraligand (π→π*) transition, the bands at 386 nm and 439 nm (broad shoulder) with large molar extinction coefficient values are assigned to charge transfer (L→Mo) transition and intensity stealing respectively. The last two bands account for the orange-yellow colour of (2)$^{12a}$. Continuous increase in optical density with time is observed at 261 nm, 386 nm and 439 nm respectively (Fig. 6). Kinetics of this reaction was followed at 386 nm under pseudo first order conditions (maintaining ca. 3–50 times excess of Me$_3$N→O) in CH$_2$OH. Observed rate constants were determined by least square method from the plots of log($A_\infty$→$A_t$) versus time, which were linear for more than two half lives. The $k_{obs}$ values are within the range of literature data for oxygen atom transfer reactions of different Mo(IV) complexes$^{13}$. Activation parameters ($\Delta H^\# = 33.3$ k J mol$^{-1}$; $\Delta S^\# = -282.8$ J K$^{-1}$ mol$^{-1}$) were obtained from the Eyring Plot (ln($k/T$) versus 1/T) using pseudo first order rate constants data determined (keeping a three fold excess of Me$_3$N→O) at four different temperatures. The negative $\Delta S^\#$ value supports the formation of an intermediate here (Eq. 2) and accordingly Fig. 6 lacks any tight isosbestic point$^{22}$. Isolation and characterization of (3) help in establishing the stoichiometry of this reaction (Eq. 2). The $k_{obs}$ values represent neither a substrate saturation kinetics nor a second order reaction; the $k_{obs}$ value falls off (from $12.4 \times 10^3$ s$^{-1}$) with increasing substrate concentration only to achieve a steady value of $6.0 \times 10^3$ s$^{-1}$ at high concentration. Most likely, an optimum balance is achieved at this stage among the oxygen atom transfer step from Me$_3$N→O, the binuclear complex formation process and the release of Me$_3$N from the reaction site. Cyclic voltametric data of (1) is characterized by a single irreversible reduction peak at -0.86V, while that for (2), three such peaks appear at -0.59V, -1.10V and -1.44V respectively. For the latter, the Mo(IV)→Mo(III) reduction occurs at -0.59V, whereby the reduced species is decomposed through solvent attack. The appearance of ligand reduction peaks at -1.10V and -1.44V is interesting. The complex formation process, (1)→(2), is associated with considerable electronic
redistribution involving the pterin ligand residue in (2), as evident from \(^1\)H-NMR and fluorescence spectral data, making it less susceptible to reduction as compared to the free ligand (1).

**Conclusions**

Using carefully controlled conditions, a new molybdenum complex (2) of the pterin ligand (1) has been synthesized and its composition established through standard analytical methods including ESMS data. Molecular mechanics calculations have provided the optimized geometry. The calculated structural parameters (bond lengths and bond angles) show reasonable agreement with the literature X-ray structural data of related systems, indicating realistic nature of the molecular structure reflected in the CHEM3D model. Different spectroscopic and cyclic voltammetric data provided insight into the electronic structures of (1) and (2), especially their changes during the process (1)→(2). Kinetic and stoichiometric aspect of the reaction of (2) with \(\text{Me}_2\text{N}\rightarrow\text{O}\), indicates the presence of a molybdenum atom in the lower oxidation state in (2), i.e., Mo(IV) state. Isolation and characterization of the reaction product (3), has established the metal centered oxygen atom transfer aspect of this reaction. Comparable nature of the spectrophotometric overlay scans of this reaction with those of molybdenum cofactors of different oxomolybdoenzymes is instructive regarding metal centred oxygen atom transfer activity. The reactivity of (2) is useful in understanding the redox noninnocent nature of the pterin ligand here.

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**Supplementary Material**

Supplementary material includes some of the ESMS data, FTIR spectra, cyclic voltammetric data and X-ray structural information regarding hydrogen bonding in 2-pivaloylamino-7-acetonyl-xanthopterin monohydrate. These may be obtained from the authors on request.

**References**

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