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An Analogue System Displaying All the Important Processes of the Catalytic Cycles Involving Monooxomolybdenum(VI) and Desoxomolybdenum(IV) Centers

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A majority of the pyranopterin-containing molybdoenzymes catalyze the formal transfer of an oxygen atom between substrate and solvent water,[1,2] and these enzymes take part in the global nitrogen, sulfur, and arsenic cycles. A long-standing hypothesis states that the Mo active sites shuttle between dioxomolybdenum(VI) ($[Mo^{VI}O_2]^{2+}$) and monooxomolybdenum(IV) ($[Mo^{IV}O]^{2+}$) centers during the course of catalysis. Studies in several laboratories[3,4,5] have demonstrated that a variety of discrete oxomolybdenum complexes can carry out this chemistry when reacted with oxygen atom abstractors such as tertiary phosphines. Although, tertiary phosphines are not physiological substrates, they are the most commonly used substrates in for studying oxygen atom transfer (OAT) reactions in model inorganic systems. Interestingly, using ^{18}O-labeling it has been convincingly demonstrated that the DMSO reductase (DMSOR) from *Rhodobacter sphaeroides* can catalyze the transfer of an oxygen atom from DMSO to a water-soluble tertiary phosphine.[6] The subsequent crystal structures,[7,8] EXAFS[9] and resonance Raman studies[10] on the *R. sphaeroides* enzyme were interpreted in terms of monooxomolybdenum(VI) ($[Mo^{VI}O]^{4+}$) and desoxomolybdenum(IV) ($[Mo^{IV}]^{4+}$) centers, respectively. The oxidized $[Mo^{VI}O]^{4+}$ center regains the catalytic competency by coupled electron proton-transfer processes. Similar structure-based reaction mechanisms have also been proposed for dissimilatory nitrate reductase[11] and arsenite oxidase.[12] Importantly, small molecule OAT reactivity in $[Mo^{VI}O]^{4+}$ centers are less common,[13,14] and CEPT reactions involving this center or $[Mo^{IV}]^{4+}$ are unknown. Furthermore, in all previous cases of OAT reactivity involving discrete $[Mo^{VI}O]^{4+}$ centers, the metal center is coordinated by sulfur donor ligands. This implies that Mo−S coordination may be essential for such reactivity. Here we report an example of OAT reactivity in a six-coordinate monooxo Mo(VI) compound which does not possess sulfur donor ligands. In addition, we report the isolation of the intermediate in the OAT reaction and the regeneration of the oxo Mo(V) center using water as a source of the terminal oxygen. To our knowledge, this is the first demonstration of OAT and CEPT reactions involving discrete monooxo Mo(VI) and desoxo Mo(IV) centers.

A six-coordinate monooxo Mo(VI) compound was synthesized from the corresponding Mo(V) complex, $LMo^{V}O(p\text{-}O\text{-}C_6H_4{-}OC_2H_5)_2$ (**1**), where $L^- =$ hydrotris (3,5-dimethyl-1-pyrazolylborate). Compound **1** exhibits reversible one-electron oxidative and reductive couples.[15] Bulk electrolysis confirmed the one-electron nature of the oxidative process and demonstrates that the cationic $[LMo^{VI}O(p\text{-}O\text{-}C_6H_4{-}OC_2H_5)_2]^+$ ([**2**]) species is stable enough to be isolated. This dark colored cationic species has been synthesized by chemical oxidation with $(NH_4)_2Ce(NO_3)_6$ and isolated as the nitrate salt [**2**]NO_3 in very good yields (74%). Solutions of the blue compound degrade to intractable products upon prolonged standing. Although, the instability of solutions of [**2**]NO_3 has frustrated attempts at obtaining single crystals, the complex has been thoroughly characterized by a variety of spectroscopic techniques. The ^1H NMR spectrum of [**2**]NO_3 is consistent with a six-coordinate species, and the IR spectrum exhibits a strong Mo═O stretch at 939 cm^{-1}. Acetonitrile solutions of the dark blue solid display strong absorptions at 850 and 575 nm assignable as phenolate to Mo charge-transfer transitions.

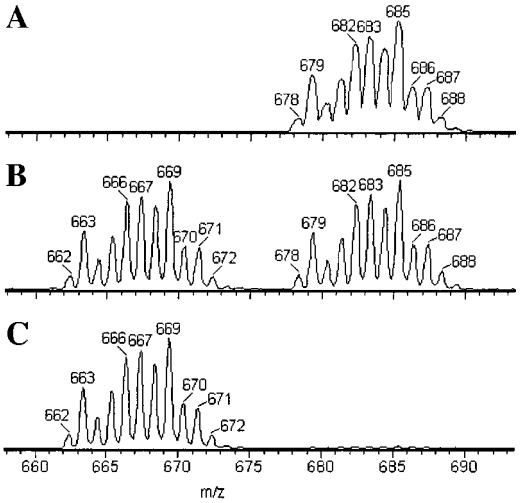

Figure 1. Positive ESIMS spectra of [**2**]NO_3 in MeCN (A) before, (B) after addition of PPh_3, and (C) isolated [**3**]NO_3.

Positive electrospray ionization mass spectra (ESI-MS) of MeCN solutions of [**2**]NO_3 show the isotope pattern characteristic for the molecular ion around *m*/*z* 685 ($C_{31}H_{40}BO_5N_6Mo$) (Figure 1a), affirming the composition of the complex. The positive FAB mass spectrum of [**2**] shows a characteristic isotope pattern of the molecular ion peaks in the region *m*/*z* 685 and a fragmentation peak around *m*/*z* 546 associated with loss of a phenolic ligand. The deep blue color of **2** in acetonitrile is bleached by addition of tertiary phosphines such as PMe_3, PEt_3, PPh_3, and $PEtPh_2$, and the product of the PPh_3 reaction has been investigated by mass spectrometry. This product displays new peaks centered at *m*/*z* 669. Additionally, a peak for $OPPh_3$ is also present in the FAB ($[M + H]^+$), ESI ($[M + H]^+$) and EI ($M^{\bullet+}$) mass spectra. The isotope distribution agrees well with that expected for the $[LMo^{IV}(p\text{-}O\text{-}C_6H_4{-}OC_2H_5)_2]^+$ ([**3**]) ion, consistent with the loss of an O atom from [**2**]. High-resolution

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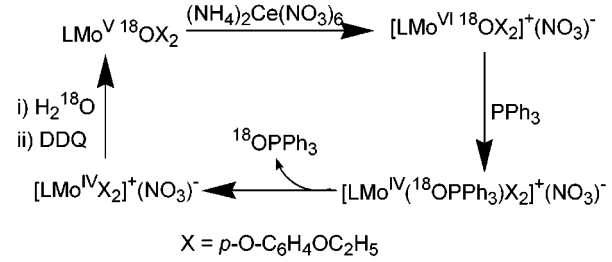
Scheme 1



accurate mass measurements have been used to confirm the elemental composition of both [**3**] ($C_{31}H_{40}BO_4N_6Mo$) and [**2**] ($C_{31}H_{40}BO_5N_6Mo$). It is important to note that the peaks associated with [**3**] (base peak *m*/*z* 669) appear in the positive ESI mass spectrum (Figure 1) in the absence of added acid, affirming the cationic nature of the new desoxo Mo species. A control experiment involving neutral **1** and PPh_3 did not show peaks around *m*/*z* 669. Also, the mass spectra of the reaction mixtures (with PMe_3, PEt_3, PPh_3, and $PEtPh_2$) exhibit peak clusters corresponding to the phosphine oxide adduct. The mass spectra suggest that the OAT reaction from monooxo Mo(VI) centers proceeds through phosphineoxide-bound intermediate similar to the intermediate described for dioxo Mo(VI) centers.[16] For reaction with PPh_3 this adduct, $[LMo(OPPh_3)(p\text{-}O\text{-}C_6H_4{-}OC_2H_5)_2]^+NO_3^-$, has been isolated and spectroscopically characterized.

The brown residue obtained from reacting [**2**]NO_3 with PPh_3 has been purified by column chromatography on silica gel using acetonitrile as an eluent. Evaporation of the first brown band yielded a brown compound whose positive ion ESI mass spectrum exhibits a strong peak centered at 669 and the isotope distribution pattern agrees well with the solution study undertaken for [**3**]NO_3 (Figure 1C).[17] The isolated product displays no characteristic Mo═O stretch, confirming the desoxo nature of [**3**]NO_3. The putative intermediate, $[LMo(OPPh_3)(p\text{-}O\text{-}C_6H_4OC_2H_5)_2]^+NO_3^-$, elutes as the second brown band from the same column. This compound exhibits characteristic mass spectrum, and no Mo═O vibration. The complex is further characterized by ^1H and ^{31}P NMR spectroscopies. The OAT reaction was further probed by resonance Raman (rR) spectroscopy.[18] The rR spectra of [**2**]NO_3 and the brown residue obtained by reacting [**2**]NO_3 with PPh_3 exhibit no Mo═O vibration (Supporting Information) indicating the Mo═O stretch observed for [**2**]NO_3 is lost upon addition of PPh_3.

The Mo═O vibration in the isotopically labeled $LMo^{V}{}^{18}O(p\text{-}O\text{-}C_6H_4{-}OC_2H_5)_2$ shifts 40 cm^{-1} to lower frequency; a similar shift is also observed for Mo(VI) complex. When $[LMo^{VI}\,{}^{18}O(p\text{-}O\text{-}C_6H_4{-}OC_2H_5)_2]^+NO_3^-$ is reacted with PPh_3, peaks due to $^{18}OPPh_3$ and $[LMo(^{18}OPPh_3)(p\text{-}O\text{-}C_6H_4{-}OC_2H_5)_2]^+$ could be detected by ESI-MS.[19] These findings clearly demonstrates that the terminal oxo group in [**2**]NO_3 has been transferred to PPh_3. When [**3**]NO_3 was reacted with $H_2[^{18}O]$ in the presence of 2,3-dicyano-5,6-dichloro-1,4-benzoquinone (DDQ), the resulting solution exhibit a peak cluster due to $LMo^{V}\,{}^{18}O(p\text{-}O\text{-}C_6H_4{-}OC_2H_5)_2$. Evaporation of the solution resulted a brown mass, whose IR spectrum is almost identical to that of authentic $LMo^{V}\,{}^{18}O(p\text{-}O\text{-}C_6H_4{-}OC_2H_5)_2$.[20] These experiments demonstrate that not only has the terminal oxo group of [**2**]NO_3 been transferred to PPh_3 but it can be regenerated from water. Thus, the analogue system displays all of the fundamental aspects of the catalytic cycle represented in Scheme 1.

In summary, we have demonstrated that a six-coordinate monooxo Mo(VI) center can carry out OAT chemistry *in the absence of thiolate (or ene-dithiolate) donor ligands and the monooxo Mo(VI) center can be regenerated from a physiologically relevant water molecule*. In addition, *we have isolated a putative OAT intermediate from a monooxo Mo(VI) center*. Thus, the chemistry described here parallels the previously proposed enzymatic reactions. These are important findings with respect to fully understanding the primary role of the pyranopterin ene-1,2-dithiolate in the oxidative and reductive half reactions of enzymes that cycle between monooxo Mo(VI) and desoxo Mo(IV) centers.

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Supporting Information Available: All synthetic procedures and characterization data for complexes, a table containing the results of accurate mass measurements for [**2**], [**3**], and $OPPh_3$, and Figures of rR spectra and IR spectra of isotopically labeled compounds (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(17) The mass spectrum of the isolated desoxo compounds also exhibit a peak cluster ~*m*/*z* 710 due to the formation of a six-coordinate MeCN adduct. However, no characteristic stretch for nitrile could be identified in solid-state IR.
(18) Solid-state rR spectra of [**2**]NO_3 and the brown residue obtained by reacting [**2**]NO_3 with PPh_3 were collected as a solids dispersed in an NaCl/$NaNO^{3-}$ matrix. No Mo═O stretch was observed for the brown residue using 647.1, 514.5, 488.0, 457.9, or 413.1 nm excitation. For [**2**], excitation at 676 and 647 nm exhibit vibrations at 1150, 1247, 1493, and 1586 cm^{-1}, indicating coordinated phenol.
(19) An OAT reaction has also been observed from $[LMo^{VI}O(OMe)_2]^+$ Nemykin, V. and Basu, P. Unpublished results.
(20) The estimated ^{18}O-enrichment of [**2**]NO_3 (from direct synthesis) based on ESI MS is 38%, while it is 54% when prepared from [**3**]NO_3 with $H_2{}^{18}O$/DDQ.

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