Synthesis and Structural Characterization of a 4-Coordinate Molybdenum(VI) Dioxo Diaryloxide, MoO$_2$(O-2,6-t-Bu$_2$C$_6$H$_3$)$_2$·HO-2,6-t-Bu$_2$C$_6$H$_3$

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High oxidation state metal alkoxides, aryloxides, and oxoalkoxides are interesting because they can be used to produce high-purity metal oxide materials in chemical vapor deposition and sol−gel processes. Metal alkoxides have also been cited as models for heterogeneous catalysts, precursors for supported materials, and modifiable homogeneous catalysts.[3,4] Few molybdenum(VI) oxoalkoxides have been reported, however, that are suitable for such uses.

In Mo(VI) structural chemistry, the MoO$_2$$^{2+}$ unit has by far received the most attention. Mo(VI) dioxo compounds are viewed as models for the active sites of oxo-transfer molybdoenzymes[5,6] and for heterogeneous catalysts,[4] as well as materials precursors.[3] The predominant structural types found for these compounds are octahedral and pseudo-octahedral. Some examples of 6-coordinate nonoctahedral complexes have been reported, as well as a few 5-coordinate complexes.[7,8] Four-coordinate MO$_2$(OAr)$_2$ complexes have not been structurally characterized for M = Mo, Cr, or W. A search of the Cambridge Structural Database[9] reveals only one molybdenum dioxo compound of the formula MoO$_2$(OR)$_2$: MoO$_2$-(OSiPh$_3$)$_2$.[10] The tetrahedral structure is known for the MoO$_4$$^{2-}$ ion, and MoO$_2$X$_2$ (X = halide) is tetrahedral in the gas phase.[7,8]

We have synthesized and structurally characterized a second example of a 4-coordinate Mo(VI) dioxo species, and a first example of a structurally characterized MO$_2$(OAr)$_2$ species.

Workers attempting to produce MoO$_2$(OR)$_2$ where R = bulky alkyl or aryl have encountered difficulties stabilizing the resulting compounds in the absence of a donating nitrogen base,[11] leading to the use of cumbersome metal vapor synthetic methods.[12] In contrast to these esoteric techniques, we describe the facile solution synthesis and spectroscopic and structural characterization of 4-coordinate MoO$_2$(OAr)$_2$·ArOH (**1**) where Ar = 2,6-di-*tert*-butylphenyl.

MoO$_2$Cl$_2$ reacts quickly with 2 equiv of LiO-2,6-t-Bu$_2$C$_6$H$_3$ (**2**) in acetonitrile to form a deep red solution (eq 1). Proton NMR of the crude reaction mixture reveals three major components: MoO$_2$(O-2,6-t-Bu$_2$C$_6$H$_3$)$_2$·ArOH (**1**),[13] HO-2,6-t-Bu$_2$C$_6$H$_3$ (**3**), and 3,3′,5,5′-tetra-*tert*-butyl-4,4′-diphenoquinone (**4**). Repeated crystallization from pentane yields pure orange/yellow crystals of **1** suitable for X-ray diffraction, in 31% yield. In order to determine

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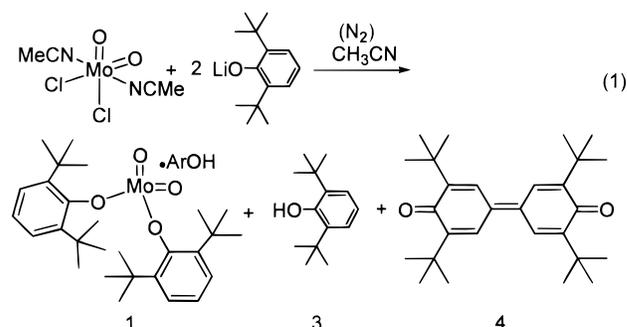
whether the diphenoquinone **4** was a decomposition product of **1** or originating from a side reaction, compound **1** was heated in C$_6$D$_6$ to 140 °C. Although black solid was slowly formed, no diphenoquinone formation was observed by ^{1}H NMR.

The source of the 2,6-di-*tert*-butylphenol in the crystals of **1** appears to be the lithium salt **2** acting as a hydrogen acceptor in the formation of diphenoquinone. If 1 equiv of 2,6-di-*tert*-butylphenol is added to the reaction mixture, the formation of diphenoquinone **4** is inhibited, though the yield of the desired product is not substantially improved. The same effect is observed if the reaction is done in the presence of trace water. Interestingly, in the synthesis of MoO$_2$(OSiPh$_3$)$_2$ the authors noted that a small amount of acetonitrile was necessary to avoid the formation of byproduct (hexamethylsiloxane), possibly due to saturation of the inner sphere of the Mo dioxo complex.[10] In our case a similar explanation is unlikely to hold, as 2,6-di-*tert*-butylphenol is clearly too large to fit into the coordination sphere, and acetonitrile itself does not have the same inhibition effect.

X-ray quality crystals of **1** were obtained by recrystallization from pentane. An ORTEP drawing is shown in Figure 1, and selected bond distances and angles are outlined in Tables 1 and 2.[14] The molecular structure of **1** shows a distorted tetrahedral coordination geometry.

The Mo−O bond angles of **1** are similar to those of MoO$_2$-(OSiPh$_3$)$_2$. All the angles are close to tetrahedral values. The

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(13) MoO$_2$Cl$_2$ (117.5 mg, 0.5909 mmol) and 260.7 mg of LiO(2,6-t-Bu$_2$C$_6$H$_3$) (1.228 mmol) were each dissolved in 5 mL of CH$_3$CN. The MoO$_2$Cl$_2$ solution was added to the LiOAr solution with stirring to cause an immediate color change to deep red. The mixture was stirred for 1 h, and then the solvent was removed in vacuo. The product was brought up in approximately 50 mL of pentane, leaving black undissolved material, filtered to remove residual solid, and placed in a −35 °C freezer for 2 days. The resulting solid was recrystallized from pentane to produce 94.4 mg of air-sensitive orange blocky crystals of MoO$_2$(O-2,6-t-Bu$_2$C$_6$H$_3$)$_2$·HO-2,6-t-Bu$_2$C$_6$H$_3$ (126.9 mmol, 31.0% yield): mp 124−125 °C. IR (C$_6$H$_6$): 3636 m, 2961 s, 2874 w, 1466 w, 1426 m, 1402 s, 1395 m, 1366 w, 1264 w, 1231 w, 1206 m, 1186 s, 1119 s, 1109 m, 963 s, 941 s (Mo=O), 911 s (Mo=O), 882 w, 795 w, 748 m, 698 w, 685 s. ^{1}H NMR (thf-d_8) δ 7.32 (d, 2H, *J* = 7.88 Hz), 6.98 (t, 1H, *J* = 7.87 Hz), 1.50 (s, 18H). ^{13}C NMR (C$_6$D$_6$) δ 31.8 (^{t}Bu CH$_3$), 35.4 (^{t}Bu quat), 124.4 (*p* to O), 126.1 (*m* to O), 140.0 (aryl quat), 164.0 (*C*−O) (ArOH NMR peaks not listed). UV−vis (C$_6$H$_6$): λ$_{max}$ = 278 (ϵ 7.9 × 10^3), 346 (ϵ 6.1 × 10^3). Anal. Calcd for C$_{42}$H$_{64}$MoO$_5$: C, 67.72; H, 8.66. Found: C, 67.61; H, 8.82.
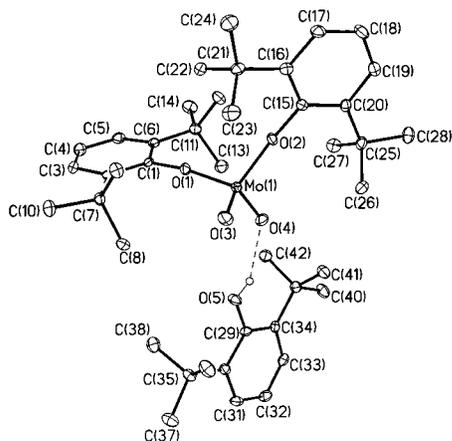
Figure 1. ORTEP diagram of $MoO_2(O\text{-}2,6\text{-}t\text{-}Bu_2C_6H_3)_2 \cdot HO\text{-}2,6\text{-}t\text{-}Bu_2C_6H_3$ (**1**). Thermal ellipsoids are shown at 30% probability; hydrogen atoms, with the exception of H(1), are omitted for clarity.

Table 1. Selected Bond Lengths (Å)

Mo(1)−O(3)	1.703(2)	Mo(1)−O(4)	1.706(2)
Mo(1)−O(1)	1.857(2)	Mo(1)−O(2)	1.861(2)
O(1)−C(1)	1.405(4)	O(2)−C(15)	1.392(4)
O(5)−C(29)	1.379(4)		

Table 2. Selected Bond Angles (deg)

O(3)−Mo(1)−O(4)	106.55(13)	O(3)−Mo(1)−O(1)	110.47(11)
O(4)−Mo(1)−O(1)	109.14(12)	O(3)−Mo(1)−O(2)	108.81(12)
O(4)−Mo(1)−O(2)	109.14(12)	O(1)−Mo(1)−O(2)	111.26(10)
C(1)−O(1)−Mo(1)	170.3(2)	C(15)−O(2)−Mo(1)	174.2(2)
O(1)−C(1)−C(2)	118.4(3)	O(1)−C(1)−C(6)	118.1(3)

angles O(4)−Mo(1)−O(1) and O(3)−Mo(1)−O(2) are 109.14-(12)° and 108.81(12)°, while O(4)−Mo(1)−O(2) and O(3)−Mo-(1)−O(1) are 110.50(11)° and 111.26(10)°. This is similar to that observed in $MoO_2(OSiPh_3)_2$, which has analogous angles of 109.9-(3)° and 110.3(3)°.[10] The angles between the two bulky ligands (O(1)−Mo(1)−O(2) = 111.26°) are comparable as well.

Likewise, the Mo−O bond distances are similar to those reported for the siloxy complex $MoO_2(OSiPh_3)_2$. The Mo(1)−O(3) and Mo(1)−O(4) distances (1.703(2) and 1.706(2) Å, respectively) and the O(3)−Mo(1)−O(4) angle (106.55(13)°) are typical of those in 6-coordinate Mo dioxo compounds. These values are also very similar to the corresponding values in $MoO_2(OSiPh_3)_2$ (1.692(7) Å and 106.4(5)°, respectively).[10] The Mo=O IR (KBr) stretches for **1** (898 and 884 cm^{-1}) are almost identical to the stretches observed for $MoO_2(OSiPh_3)_2$ (898 and 873 cm^{-1}).[10]

The solution species, however, does not appear to be identical to that found in the solid state. The solution Mo=O stretches for **1** (941 and 911 cm^{-1}, C_6H_6) are much higher than those in KBr (898 and 884 cm^{-1}). These values are relatively high for 6-coordinate MoO_2 complexes, and significantly higher than those observed for $MoO_2(OSiPh_3)_2$. They approach those observed in molybdenum dioxo halide complexes, probably due to the electron-poor metal center in **1** and increased Mo=O back-bonding.

The most interesting aspect of this structure is that electron donation from the aryloxy oxygen appears to stabilize the 4-coordinate geometry. The Mo(1)−O(2)−C(15) and Mo(1)−O(1)−C(1) angles are almost linear (174.2(2)° and 170.3(2)°), suggesting some interaction between the oxygen lone pair and

the neighoring molybdenum atom, possibly incipient bond formation. Consistent with such an interpretation, the Mo(1)−O(2) and Mo(1)−O(1) bond lengths (1.861(2) and 1.857(2) Å, respectively) are significantly shorter than the analogous bond lengths in a 6-coordinate Mo dioxo diaryloxide species (**5**) (1.938(17) Å).[15] In the coordinatively unsaturated $MoO_2(OSiPh_3)_2$ the Mo−O internal bond lengths are also relatively short, at 1.815(5) Å.[10]
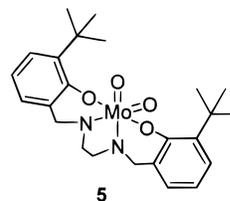
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The relatively short Mo−alkoxy bonds in our system could indicate incipient conversion of the alkoxo to an oxo group: one step in such a process must involve the shortening of the molybdenum−alkoxy bond. The coordinative unsaturation of this metal center favors such bond shortening and may decrease the barrier to interconversion. Indeed, Mo and W oxo alkoxide clusters such as $Mo_6O_{10}(O\text{-}i\text{-}Pr)_{12}$ are fluxional on the NMR time scale, indicating facile interconvertibility of the oxo and alkoxide groups in coordinatively unsaturated systems.[11]

The crowding of the coordination sphere in **1** is evidenced by the solid-state distance between a terminal oxo group and the nearest carbon of the adjacent *tert*-butyl group, ~3.1 Å (O(4)−C(27)), as compared to the estimated van der Waals contact for an O−CH$_3$ group interaction of 3.6 Å.[16]

The nature of the interaction between the phenol and the MoO_2-(OAr)$_2$ unit is ambiguous. The distance between the phenolic hydrogen and the closest Mo oxo group (O(4), shown by a dotted line in Figure 1) is 2.327 (8) Å, and the angle is 115.5°. Although the bond distance indicates that some hydrogen-bonding interaction may be present, the similarity between the Mo=O bond lengths (1.703(2) and 1.706(2) Å) in the solid state argues against such interaction. H-bonding interaction between the free phenol and the Mo=O units is almost certainly absent in the solution state, as evidenced by the relatively high solution IR stretches for the Mo=O bonds.

In conclusion, we have reported the first X-ray structure of a 4-coordinate group VIB metal(VI) dioxo diaryloxide complex. The synthesis of $MoO_2(O\text{-}2,6\text{-}t\text{-}Bu_2C_6H_3)_2 \cdot HO\text{-}2,6\text{-}t\text{-}Bu_2C_6H_3$ (**1**) is facile, though yields are reduced by concurrent oxidation of the phenolic anion to form 3,3′,5,5′-tetra-*tert*-butyl-4,4′-dipheno-quinone (**4**). Relatively strong Mo=O double bonds and p-electron donation from the aryloxide oxygens appear to compensate for the unsaturation of the metal center.

Supporting Information Available: Synthetic procedures and spectroscopic and analytical data for complex **1**, crystal data and structure refinement, atomic coordinates, bond lengths and angles, anisotropic displacement coefficients, and H-atom coordinates. An X-ray crystallographic file for **1** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(14) Crystal data for $C_{42}H_{64}MoO_5$ (**1**): monoclinic, $P2_1/c$, $a = 11.4344(2)$ Å, $b = 19.4277(3)$ Å, $c = 18.5445(3)$ Å, $\beta = 99.1385(6)°$, $V = 4067.27$-(12) Å^3, $Z = 4$, $Z' = 1$, fw = 744.87 g mol^{-1}, $T = 173(2)$ K, $D_{calc} = 1.216$ g/cm^3, yellow block, GOF = 1.250, μ(Mo Kα) = 0.71073 Å, $R(F) = 4.86\%$ for 8275 observed independent reflections ($4° \leq 2\theta \leq 56°$), wR2 = 0.1505. R indices (all data): R = 0.0650, wR2 = 0.1675.

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