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Formation and Characterization of Bis(tetramethylammonium) Bis(3,5-di-*tert*-butylcatecholato)oxoperoxomolybdate(VI)

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Addition of 2 equiv of superoxide ion to the bis[bis(3,5-di-*tert*-butylcatecholato)oxomolybdenum(VI)] complex results in the formation of a dianionic peroxide adduct, Mo^{VI}(O)(O$_2$)(DTBC)$_2^{2-}$, and the release of 1 equiv of dioxygen. The same peroxide adduct results from the addition of 2 equiv of 3,5-*tert*-butylcatechol ((DTBC)H$_2$) and 3 equiv of base to Mo^{VI}(O)(O$_2$)$_2$ in acetonitrile. The isolated peroxo complex has been characterized by UV–visible and IR spectroscopy and cyclic voltammetry.

Molybdenum is an essential cofactor in a number of enzymes that catalyze biological redox reactions[1–4] and appears to undergo oxidation-state changes during the catalytic processes.[1,2,5–8] Several model systems have been studied to gain insight into the nature and reactivities of molybdenum in its various oxidation states.[9,10] These include the molybdenum complexes that are formed by catechols and dithiocarbamates, which stabilize several oxidation states.[11–14] A number of well-defined molybdenum–catechol complexes have been isolated and their structures characterized in the solid state by *x*-ray crystallography.[13,15] The present paper discusses the reactivity between one of these and superoxide ion in aprotic media and the properties of the resultant peroxo adduct.

Experimental Section

Cyclic voltammetric measurements were performed with a three-electrode potentiostat–amperostat constructed with solid-state operational amplifiers.[16] The voltammograms were recorded on a Houston Instrument Omnigraphic Model 2000 X-Y recorder. A Princeton Applied Research Corp. Model 173 potentiostat–galvanostat, in conjunction with a Model 179 digital coulometer, was used for controlled-potential coulometry.

The electrochemical cell consisted of a Brinkman Model EA 875-20 cell with corresponding plastic cell top. The cell top supported the electrodes and the auxilliary compartment (a Pyrex tube with a medium-porosity frit at one end). The top also had access holes for addition and withdrawal of samples and for a gas bubbler for argon or oxygen.

The working electrode for cyclic voltammetry was a Beckman platinum-inlay electrode, Model 39273. For controlled-potential electrolysis a cylindrical platinum wire-mesh electrode was used. The auxiliary electrode was a 1-cm^2 foil of platinum. The reference electrode consisted of a silver wire coated with AgCl in a Pyrex tube closed by a soft-glass cracked-bead tip. The electrode was filled with a solution of aqueous tetramethylammonium chloride with the concentration adjusted such that the potential of the electrode was 0.000 V vs. SCE. The reference electrode was placed inside a luggin capillary in the cell assembly.

Infrared spectra of the complexes were recorded as Nujol mulls on AgCl plates with a Perkin-Elmer Model 283 infrared spectrophotometer. The UV–vis spectra for solutions of the complexes were recorded with a Cary Model 17D spectrophotometer, proton NMR with a Varian Model E17-390 spectrometer, and ESR spectra with a Bruker Model ER200 spectrometer.

Reagents. Acetonitrile, dimethyl sulfoxide (Me$_2$SO), and *N*,*N*-dimethylformamide (DMF) (all Burdick and Jackson Laboratories, "distilled in glass") were used without further purification. Ammonium molybdate (Mallinckrodt), 3,5-di-*tert*-butylcatechol (Aldrich), tetramethylammonium hydroxide pentahydrate (Southwestern Analytical Chemicals, Inc.), and tetraethylammonium perchlorate (G. Frederick Smith) were used as received. Bis[bis(3,5-di-*tert*-butylcatecholato)oxomolybdenum(VI)] (**1**), Mo^{VI}(O)(O$_2$)$_2$·2DMF, and tetramethylammonium superoxide were prepared by previously reported methods.[17–19]

Bis(tetramethylammonium) Salt of Bis(3,5-di-*tert*-butylcatecholato)oxoperoxomolybdate(VI), [(CH$_3$)$_4$N]$_2$[Mo^{VI}(DTBC)$_2$(O)(O$_2$)]$_2$ (2). This complex was prepared by two procedures.

Procedure A. After 1.128 g (1 mmol) of bis[bis(3,5-di-*tert*-butylcatecholato)oxomolybdenum(VI)] (**1**) was suspended in 100 mL of dry acetonitrile, 0.42 g (4 mmol) of solid tetramethylammonium superoxide was added. The mixture was stirred on a magnetic stirrer until the evolution of oxygen gas ceased. The red solution was filtered and the filtrate evaporated to dryness on a rotary evaporator. The crude product was dissolved in hot dimethyl sulfoxide and filtered with suction. The filtrate, on standing overnight at room temperature, yielded red needlelike crystals. These were collected by suction filtration in a drybox under a dry-nitrogen atmosphere, washed with a small amount of Me$_2$SO, and dried under high vacuum.

Procedure B. After 3.22 g (10 mmol) of Mo^{VI}(O)(O$_2$)$_2$·2DMF was suspended in 100 mL of dry acetonitrile, a solution of 4.44 g (20 mmol) of 3,5-di-*tert*-butylcatechol in 40 mL of acetonitrile was added. While the mixture was stirred with a magnetic stirrer, 5.43 g (30 mmol) of solid tetramethylammonium hydroxide pentahydrate was added; the resulting solution was stirred overnight. The red product solution was filtered and the filtrate processed as in procedure A.

Analysis of the isolated products by IR, UV–vis, NMR, and cyclic voltammetry confirmed that they are identical. The solid complex (**2**) is hygroscopic and soluble in most organic solvents (except pentane and hexane), but it decomposes in chlorinated solvents such as carbon tetrachloride, chloroform, and dichloromethane. Characterization of the isolated complex by elemental analysis confirmed that it has the formula [(CH$_3$)$_4$N]$_2$[Mo^{VI}(DTBC)$_2$(O)(O$_2$)]·3Me$_2$SO. Anal. Calcd for C$_{42}$H$_{82}$N$_2$O$_{10}$S$_3$Mo$_1$: C, 52.17; H, 8.49; N, 2.90; Mo, 9.94. Found: C, 52.78; H, 8.40; N, 3.20; Mo, 10.96 (Galbraith Laboratories, Inc.).

Results

The addition of 4 equiv of tetramethylammonium superoxide/equiv of molybdenum(VI) 3,5-di-*tert*-butylcatecholate

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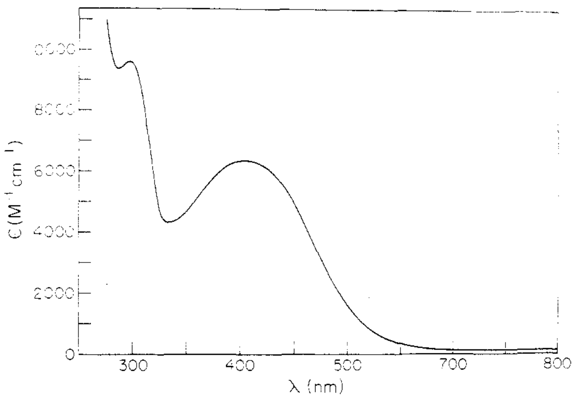
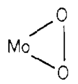


Figure 1. Absorption spectrum of $[(CH_3)_4N^+]_2[Mo(DTBC)_2(O)(O_2)]\cdot 3Me_2SO$ (**2**) in acetonitrile.

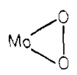
dimer, $[Mo^{VI}(O)(DTBC)_2]_2$ (**1**), in acetonitrile results in a solution with electrochemical and spectroscopic properties that are identical with those for a solution of the synthesized peroxo complex, $[(CH_3)_4N]_2[Mo^{VI}(O)(O_2)(DTBC)_2]$ (**2**).

Spectroscopy. The UV–vis spectrum of the complex (**2**) in acetonitrile (Figure 1) includes two distinct ligand-to-metal charge-transfer bands at λ_{max} 405 nm (ϵ_{max} 6.35 × 10^3 M^{-1} cm^{-1}) and λ_{max} 297 nm (ϵ_{max} 9.78 × 10^3 M^{-1} cm^{-1}); the same spectrum is obtained with DMF or Me_2SO as solvent. A comparison of the spectroscopic parameters for the complex with those for 3,5-di-*tert*-butylcatechol, its semiquinone, and its quinone confirms that the ligands that are bound to the molybdenum in the complex are catechol dianions.[18]

The infrared spectra of **2** as well as of **1** and $Mo^{VI}(O)(O_2)_2\cdot 2DMF$ in Nujol mulls are shown in Figure 2. All three compounds exhibit a peak at 940–960 cm^{-1}, which is characteristic of the Mo═O group.[20] The relative intensity of this peak for **2** is considerably smaller than for the other two compounds. The peak at 855 cm^{-1} has been assigned to the

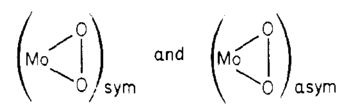


group in $Mo(O)(O_2)_2\cdot 2DMF$;[18] the value ranges from 845 cm^{-1} to 900 cm^{-1} for a series of similar complexes.[18,21] A sharp peak at 870 cm^{-1} is a major feature of the IR spectrum for **2** and is consistent with the presence of a



group. Although **1** also exhibits small peaks in this region, their relative intensities are much weaker.

The absorption bands for the



vibrations appear as two sharp peaks at 540 and 590 cm^{-1}, respectively, for $Mo(O)(O_2)_2\cdot 2DMF$. For **2**, a strong peak occurs at 560 cm^{-1} together with a weaker peak at 590 cm^{-1}. Only minor peaks are observed in this region for **1**.

The proton NMR spectrum of **2** in Me_2SO-d_6 includes doublets at 1.20 ppm (vs. Me_4Si) and 1.32 ppm, which are due to the *tert*-butyl groups of the catechol ligands, and a pair of doublets with mean resonances of 6.10 and 6.17 ppm, which are due to the ring protons of the ligands. A peak at 3.10 ppm is due to the methyl protons of the tetramethylammonium group and another at 2.57 ppm is due to the protons of the Me_2SO associated with the complex. Integration of the peak areas confirms that the mole ratio of *tert*-butyl groups:tetramethylammonium groups:Me_2SO solvates is 4:2:3.

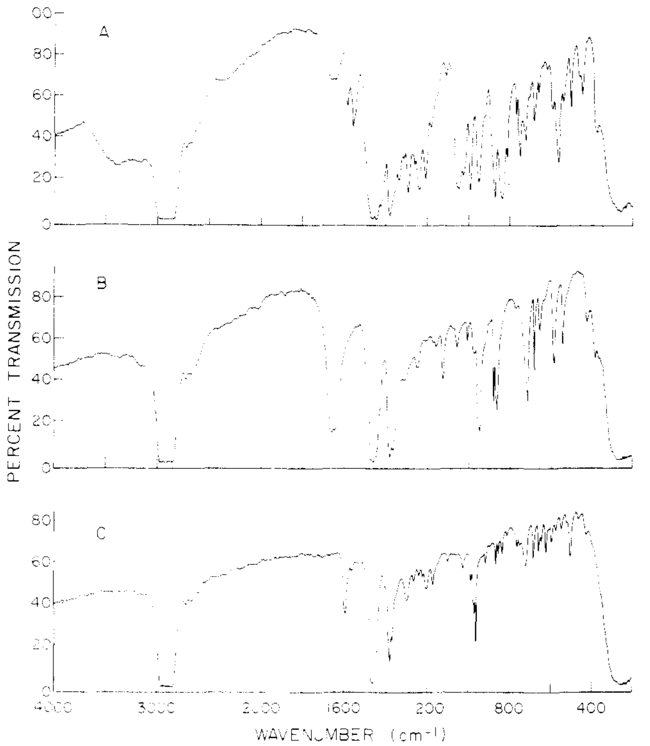


Figure 2. Infrared spectra of molybdenum complexes as Nujol mulls on AgCl plates: (A) $[(CH_3)_4N^+]_2[Mo^{VI}(DTBC)_2(O)(O_2)]\cdot 3Me_2SO$ (**2**); (B) $Mo^{VI}(O)(O_2)_2\cdot 3Me_2SO$; (C) $[Mo^{VI}(DTBC)_2(O)]_2$ (**1**).

The ESR spectrum of a powdered sample of **2** at room temperature exhibits a single resonance signal at $g = 2.00$ with a peak-to-peak separation of 7.95 G. The signal practically disappears when the sample is dissolved in Me_2SO at room temperature as well as at liquid-nitrogen temperature.

Electrochemistry. The cyclic voltammograms of **2** in acetonitrile, DMF, and Me_2SO are similar and also are analogous to those obtained from solutions that contain a 1:2 mole ratio of **1** and O_2^- ions (generated by electrochemical reduction of O_2 gas at −1.15 V vs. SCE in these solvents with 0.1 M tetraethylammonium perchlorate (TEAP) supporting electrolyte). The cyclic voltammograms are shown in Figure 3.

Upon addition of **1** to the O_2^- solution, an oxygen reduction peak appears at 0.95 V vs. SCE (DMF) and the O_2^- oxidation peak at −0.75 V decreases. The superoxide oxidation peak completely disappears when the ratio of **1** to O_2^- is 1:4 (one Mo(VI) per two O_2^-). At this point the solution is orange-red. The reduction peak for molecular oxygen disapperas after the solution has been bubbled with argon for 20 min. A negative scan over the entire accessible range in these solvents does not yield any reduction peaks for the complex. A positive scan to 0.0 V yields a reversible couple at −0.125 V. When scanned to more positive potentials, three other peaks appear at +0.40, +0.625, and +0.825 V. The last two are coupled to reduction peaks at −0.20 and −0.40 V. Addition of 1 equiv of tetraethylammonium hydroxide in methanol to the solution does not alter the solution color nor the electrochemistry.

Controlled-potential coulometric oxidation of **2** at 0.0 V vs. SCE results in the removal of one electron per molecule of the complex to yield a bound semiquinone and causes the solution color to fade. The peak potential for this oxidation (−0.125 V) is significantly more negative than that for bis(tetra-*n*-butylammonium) μ-oxo-[bis(3,5-di-*tert*-butylcatecholato)di-

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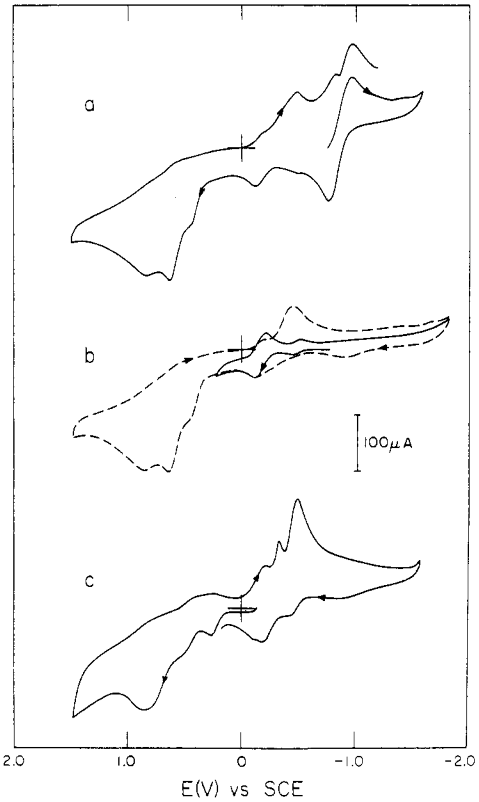
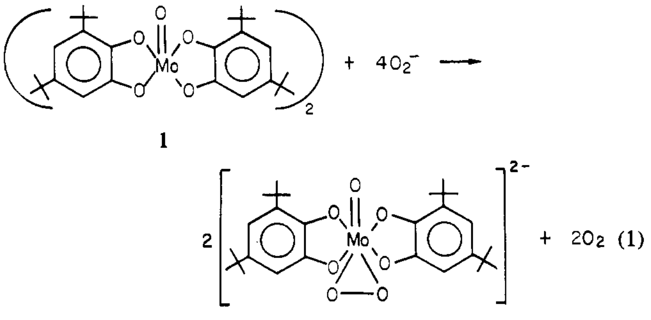


Figure 3. Cylic voltammograms in dimethylformamide (DMF) (0.1 M TEAP) for the combination of $[Mo^{VI}(DTBC)_2(O)]_2$ (**1**) and O_2^- in a mole ratio of 1:4 (1 mM Mo^{VI}): (a) solution before deaeration with argon gas; (b) solution after deaeration; (c) solution b after exhaustive oxidative electrolysis at 0.0 V vs. SCE. Scan rate = 0.1 V s^{-1} (Pt electrode, area 0.23 cm^2)).

oxomolydbate(VI)] (+0.25 V).[13]

Discussion and Conclusions

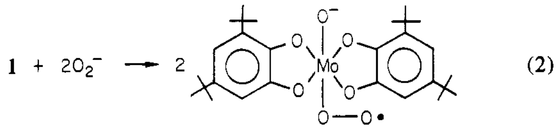
The overall reaction between superoxide ion and bis[bis(3,5-di-*tert*-butylcatecholato)oxomolybdenum(VI)] (**1**) in aprotic solvents may be presented by (1).



1

2

Because superoxide ion is prone to act as a nucleophile and a ligand, the formation process probably consists of two steps. After an initial ligation by O_2^- of each Mo(VI) center in **1** and dissociation into monomeric units, the latter are reduced by a second O_2^-. Reaction 2 is, in this case, catalyzed by the molybdenum center, which acts as a Lewis acid. The peroxide ion, which is formed by reduction of **3**, adds to the coordinatively unsaturated molybdenum center. It has been shown that complex **1** readily coordinates with ligands such as imidazole or coordinating solvents such as DMF and Me_2SO.[17]



3

$$3 + O_2^- \longrightarrow 2 + O_2 \qquad (3)$$

The proton peaks for the tetramethylammonium group in the NMR spectrum for **2** confirm that the complex is an anion. The IR data provide evidence for the presence of a coordinated peroxo group in the complex. That the complex can be synthesized from a species that contains two peroxide groups (procedure B) adds futher support for the formula of **2**.

The facile oxidation of one of the catechol ligands to semiquinone may account for the observed EPR signal of the complex in the solid state. The *g* values of the signal is consistent with the presence of semiquinone in the complex (at least in the solid state).

Among the transition elements, molybdenum is the most prone to form stable peroxide complexes.[18] Peroxide complexes such as $Mo(O)(O_2)_2 \cdot 2DMF$ are effective oxidants of organic substrates such as olefins, aliphatic amines, ketones, and sulfides.[22,23] The facile reaction of superoxide ion with **1** results in the introduction of a peroxide ion into a coordinatively unsaturated, but otherwise stable, molybdenum(VI) compound. The resulting complex contains a potential source of activated oxygen for the selective oxidation of organic substrates.

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Registry No. **1**, 69847-07-0; **2**, 81643-56-3; $Mo^{VI}(O)(O_2)_2$, 53474-95-6.

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