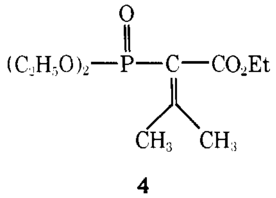
olate anions has wide scope.

Enolates which fail to undergo the normal condensation reaction with ketones can give the aldol condensation product with 2-chloro-2-nitropropane. Thus, the enolate anion from triethyl phosphonoacetate yields **4** in 30% yield.



4

The reaction of cyclohexanone enolate anion with 2-chloro-2-nitropropane clearly follows the $S_{RN}1$ mechanism. In the presence of 5 mol % of di-*tert*-butyl nitroxide products **1–3** are not formed, and the exotherm from 10 to 45 °C is not observed upon the addition of the α-chloro nitroalkane to the enolate solution. Although the initial rate of reaction 1 is quite fast, the reaction slows down and fails to go to completion even with irradiation and long reaction times. Thus the reactions summarized in Table I were accompanied by 20–35% of unreacted starting materials. A side product must be inhibiting the reaction in the later stages. The formation of traces of nitroso compounds which are excellent radical traps ($R\cdot + RNO \rightarrow R_2NO\cdot$, $R_2NO\cdot + R\cdot \rightarrow R_2NOR$) seems to be occurring. In fact, addition of water to the reaction products produces greenish blue solutions.[13]

Cyclopentanone, cyclohexanone, acetophenone, and propiophenone participate in reaction 1 to give products analogous to **1–3** in comparable yields.[14] 4-Methylcyclohexanone yields the 4-methyl derivatives analogous to **1–3,** while 3-methylcyclohexanone undergoes reaction mainly at the 6-position to give pulegone (30%) and 3-methyl-2-isopylidenylcyclohexanone[15] in the ratio of 4:1.[16] Reaction of 2-chloro-2-nitropropane at −25 to 40 °C with the $\Delta^{1(2)}$-enolate ion formed by the methyllithium cleavage of 3-methyl-1-trimethylsiloxycyclohexene[17] for 0.5 h gave 3-methyl-2-isopropylidenylcyclohexanone and pulegone in a ratio of 3:2. The low regioselectivity is apparently a result of proton transfer between the enolate anion and the coupling product **1.** Reaction of 2-octanone demonstrated regioselectivity yielding 3.5 parts of 2-methyl-4-keto-2-decene to one part of 2-methyl-3-acetyl-2-octene.[18]

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(7) Aliphatic ketoximes can be converted to the α-bromo nitro compound by treatment with aqueous KOH and bromine,[8,9] or by treatment with NBS followed by nitric acid oxidation (yields 40–70%).[10] Conversion of cycloalkanones *or* 3-pentanone to the oximes followed by chlorination in CH_2Cl_2 and oxidation with nitric acid in cyclohexane forms the chloro nitro compounds in overall yields of ~70%.

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(14) Products were identified by ^1H NMR, high-resolution mass spectrometry, and elemental analysis. Purity was established by GC–mass spectrometry. The β-nitro ketones do not give a parent peak, but give an intense peak at $m/e = M^+ - 46$. The enolate dimers **3** gave parent peaks and an intense peak at $m/e = M^+/2$.

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Formation of Bis[bis(3,5-di-*tert*-butylcatecholato)oxomolybdenum(VI)] and Related Stable Molybdenum–Catechol Complexes

Sir:

The dianion of catechol is an effective bidentate ligand that forms a variety of complexes with transition metal ions.[1-4] This characteristic as well as the ability of catechol and its derivatives to participate in a wide variety of redox reactions[5] may account for their presence in a multitude of biological systems.[6,7] Such considerations have prompted studies to elucidate the coordination and oxidation–reduction chemistry of catechol complexes and to determine their viability as models for biological processes.[1,2,8] We report here the formation and the properties of the binuclear bis(catechol) complex of oxomolybdenum(VI) and two related catechol complexes of molybdenum(VI) that result from the reaction of molybdenum(VI) with 3,5-di-*tert*-butylcatechol.

Although reactions of molybdenum with various catechols have been studied previously,[9-14] most of these studies have been in aqueous media and, with the exception of the molybdenum carbonyls, have not included the isolation and characterization of stable complexes. When bis(acetylacetonato)-dioxomolybdenum(VI) is combined with 3,5-di-*tert*-butylcatechol in CH_2Cl_2, $CHCl_3$, or benzene, an intense violet-colored solution (λ_{max} 540 nm) is formed. Similarly, a red-brown (λ_{max} 431 nm) solution is obtained when the reagents are combined in methanol, ethanol, or propanol. From either of the above media a complex is isolated with an analytical stoichiometry of two catechols per molybdenum and a molecular weight that is consistent with a binuclear species, **1.**[15] Figure 1 illustrates the absorption spectrum for this complex in acetonitrile. A spectrophotometric titration in methanol confirms the stoichiometry of two catechols per molybdenum. When 1 equiv of tetra-*n*-butylammonium hydroxide (TBAOH)/molybdenum is added to **1**, a bright red-orange solution results (Figure 1) from which an orange species can be isolated, **2.** The latter has an analytical stoichiometry of one

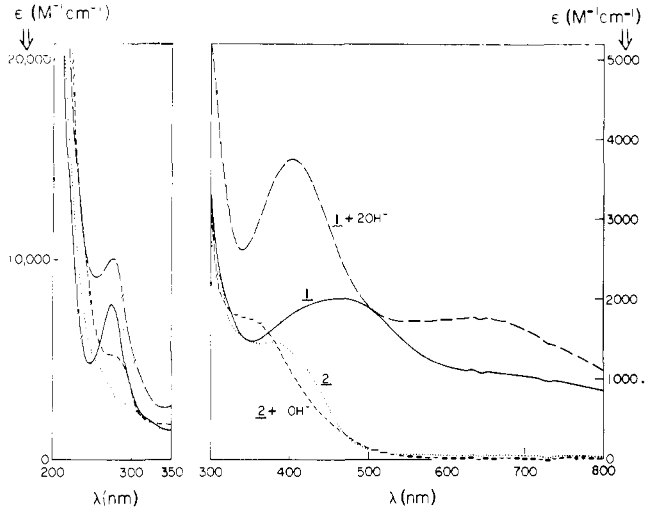


Figure 1. Absorption spectra in acetonitrile for 1 mM bis[bis(3,5-di-*tert*-butylcatecholato)oxomolybdenum(VI)] (**1**), 1 mM **1** plus 1 equiv of tetra-*n*-butylammonium hydroxide (TBAOH)/molybdenum, 0.5 mM bis(tetra-*n*-butylammonium)-μ-oxo-bis[(3,5-di-*tert*-butylcatecholato)-dioxomolybdenum(VI)] (**2**), and 0.5 mM **2** plus 1 equiv of TBAOH/molybdenum. Molar absorptivities, ε, are based on a mononuclear formulation (per molybdenum center).

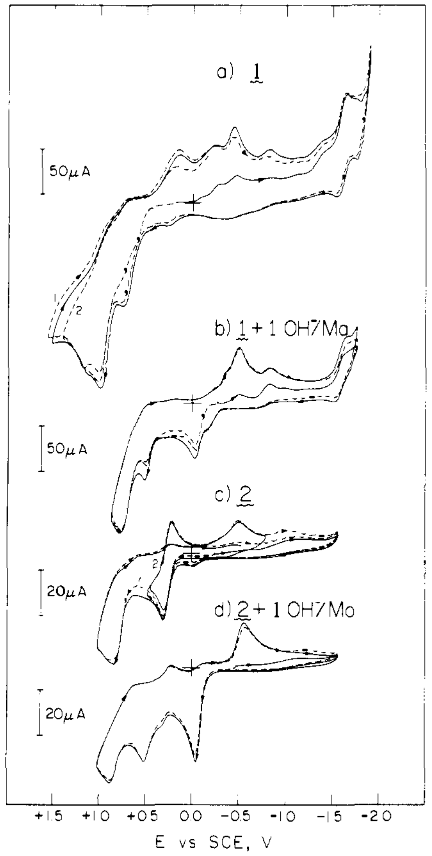


Figure 2. Cyclic voltammograms for acetonitrile (0.1 M tetraethylammonium perchlorate) solutions of (a) 1 mM **1**, (b) 1 mM **1** plus 1 equiv of tetraethylammonium hydroxide (TEAOH)/molybdenum, (c) 0.5 mM **2**, and (d) 0.5 mM **2** plus 1 equiv of TEAOH/molybdenum. Measurements were made at a platinum electrode (area, 0.23 cm^2) at a scan rate of 0.1 V s^{-1}; temperature, 25 °C.

catechol per molybdenum in a binuclear anionic complex.[16]

The absorption spectrum for **2** is illustrated in Figure 1, and the effect of the addition of 1 equiv of TBAOH/Mo also is shown. Analysis of the absorption maxima for **1** and **2** in terms of the corresponding molar absorptivities for the ligand and its semiquinone form[17] indicates that **1** contains two catechol dianions per molybdenum and that **2** contains one catechol dianion per molybdenum. These conclusions are confirmed by the ^{1}H NMR spectra for **1** and **2** in deuterated dimethyl sulfoxide. The monomer of **1** exhibits a single set of resonances for the 3,5-di-*tert*-butyl groups of the ligand (mean resonances at 1.34 and 1.23 ppm vs. Me_4Si).[18] In contrast, **2** exhibits at least four bands of resonances for the ligand *tert*-butyl groups at mean values of 1.17, 1.08, 1.00, and 0.92 ppm vs. Me_4Si. This multiplicity indicates that the binding by the two catechol oxo groups is not as symmetric as in **1**. With respect to the two ring protons of the ligand, these have mean values of 6.70 ppm for **1** and 6.36 and 6.20 ppm for **2**.[18] Again, the presence of two sets of resonances for **2** infers that the two ligands are bound to the molybdenum centers in an unsymmetrical manner.

Two forms of **1** occur in solution media. In noncoordinating solvents (CH_2Cl_2, $CHCl_3$, benzene, toluene) **1** is a dimer and has an intense purple color, while in moderately coordinating solvents (Me_2SO, DMF, DMA) **1** dissociates to a green monomer. The two forms can be interconverted by the addition of the appropriate solvent. Dilution experiments in CH_3CN and CH_2Cl_2 confirm the existence of a monomer-dimer equilibrium. At concentrations of 1 mM or greater, **1** exists principally as the purple dimer in CH_3CN.

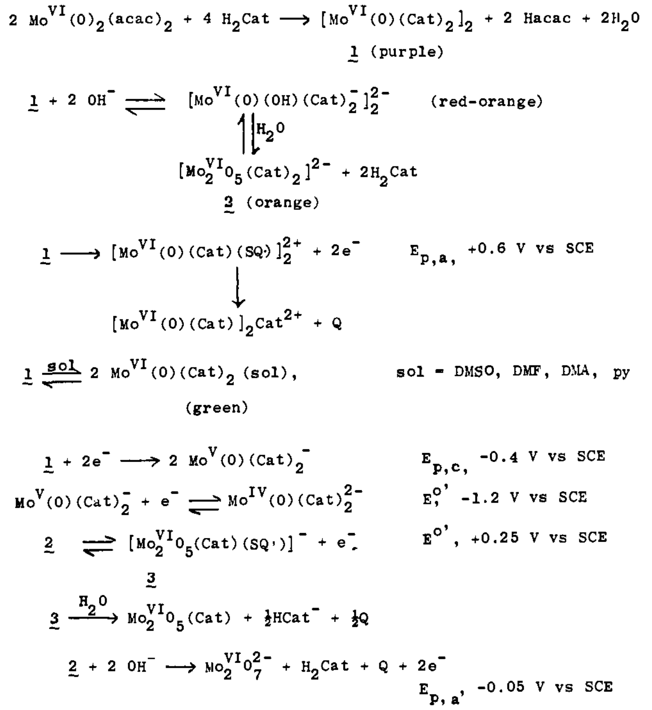
The spectrum for the purple complex, **1**, is not appreciably affected by addition of strong-field ligands such as cyanide ion. Apparently, two five-coordinate molybdenum complexes dimerize with one monomer coordinating to the other through the vacant site to form a pseudo dioxo-bridged dimer. This conclusion also is supported by the osmometric experiments in which the observed molecular weight decreases as the concentration is decreased.[15]

Unlike species **1**, the spectrum for the orange complex **2** exhibits a distinct change when strong-field ligands are added to its solutions. Addition of CN^-, imidazole, or *N*-methylimidazole to solutions of **2** causes the absorption peak at 350 nm to shift to 485–540 nm, depending on the ligand. Hence, the addition (or substitution) of an axial ligand causes a shift in the charge-transfer absorption band for the molybdenum–catechol complex to lower energy. When a large excess of a strong-field ligand is added to a solution of **2**, the mixture becomes colorless on standing and the resulting absorption spectrum is identical with that for 3,5-di-*tert*-butylcatechol. Apparently, such ligands displace the catechol ligands to yield free Mo(VI).

Magnetic susceptibility measurements indicate that both **1** and **2** are diamagnetic, and neither complex exhibits an ESR spectrum. Infrared spectra of the solid complexes in KBr disks exhibit strong absorption bands at 975 and 966 cm^{-1} for **1** and at 976, 917, and 885 cm^{-1} for **2**. The 975-cm^{-1} band is assigned to the C–O bonds of the ligands, and the remaining peaks to the Mo–axial oxygen bond. The 917-cm^{-1} and 885-cm^{-1} bands appear to be due to symmetric and antisymmetric metal–oxygen stretching modes for *cis*-dioxomolybdenum(VI), in accordance with previous assignments.[19,20]

Figure 2 illustrates the cyclic voltammograms for **1** and **2** in acetonitrile and the effect of added base. For **1**, an initial positive scan yields an anodic peak at +0.6 V vs. SCE. Controlled potential coulometry at +0.6 V indicates that this is a one-electron/molybdenum oxidation and that the product species decomposes to quinone and an inactive molybdenum–catechol species (on the basis of UV–visible spectra and

Chart I. Formation and Redox Reactions of Molybdenum–3,5-di-*tert*-butylcatechol Complexes in Acetonitrile



$$2\ \mathrm{Mo^{VI}(O)_2(acac)_2} + 4\ \mathrm{H_2Cat} \longrightarrow \underset{\underset{\sim}{1}\ \text{(purple)}}{[\mathrm{Mo^{VI}(O)(Cat)_2}]_2} + 2\ \mathrm{Hacac} + 2\mathrm{H_2O}$$

$$\underset{\sim}{1} + 2\ \mathrm{OH^-} \rightleftharpoons [\mathrm{Mo^{VI}(O)(OH)(Cat)_2^-}]_2^{2-} \quad \text{(red-orange)}$$

$$\Big\updownarrow \mathrm{H_2O}$$

$$\underset{\underset{\sim}{2}\ \text{(orange)}}{[\mathrm{Mo_2^{VI}O_5(Cat)_2}]^{2-}} + 2\mathrm{H_2Cat}$$

$$\underset{\sim}{1} \longrightarrow [\mathrm{Mo^{VI}(O)(Cat)(SQ\cdot)}]_2^{2+} + 2e^- \qquad E_{p,a},\ +0.6\ \mathrm{V\ vs\ SCE}$$

$$\Big\downarrow$$

$$[\mathrm{Mo^{VI}(O)(Cat)}]_2\mathrm{Cat}^{2+} + \mathrm{Q}$$

$$\underset{\sim}{1} \underset{}{\overset{\text{sol}}{\rightleftharpoons}} 2\ \underset{\text{(green)}}{\mathrm{Mo^{VI}(O)(Cat)_2\ (sol)}}, \qquad \text{sol} = \text{DMSO, DMF, DMA, py}$$

$$\underset{\sim}{1} + 2e^- \longrightarrow 2\ \mathrm{Mo^{V}(O)(Cat)_2^-} \qquad E_{p,c},\ -0.4\ \mathrm{V\ vs\ SCE}$$

$$\mathrm{Mo^{V}(O)(Cat)_2^-} + e^- \rightleftharpoons \mathrm{Mo^{IV}(O)(Cat)_2^{2-}} \qquad E^{o\prime},\ -1.2\ \mathrm{V\ vs\ SCE}$$

$$\underset{\sim}{2} \rightleftharpoons \underset{\underset{\sim}{3}}{[\mathrm{Mo_2^{VI}O_5(Cat)(SQ\cdot)}]^-} + e^- \qquad E^{o\prime},\ +0.25\ \mathrm{V\ vs\ SCE}$$

$$\underset{\sim}{3} \xrightarrow{\mathrm{H_2O}} \mathrm{Mo_2^{VI}O_5(Cat)} + \tfrac{1}{2}\mathrm{HCat^-} + \tfrac{1}{2}\mathrm{Q}$$

$$\underset{\sim}{2} + 2\ \mathrm{OH^-} \longrightarrow \mathrm{Mo_2^{VI}O_7^{2-}} + \mathrm{H_2Cat} + \mathrm{Q} + 2e^- \qquad E_{p,a},\ -0.05\ \mathrm{V\ vs\ SCE}$$

cyclic voltammetry). The product solution is ESR silent. The peak at +1.0 V is characteristic of the oxidation of catechol to quinone. An initial negative scan of **1** yields a series of peaks at −0.4, −0.8, and −1.1 V vs. SCE. The peaks at −0.8 and −1.1 V represent one-electron/molybdenum reductions of the monomer of **1** and of the reduction product of **1**, respectively. The reversible couple at −1.6 V vs. SCE appears to represent a reduction of the ligands. A peak at −0.3 V also is observed which probably is due to a quinone impurity. Controlled potential coulometry of **1** at −0.5 V yields a solution whose spectrum is characteristic of a bis(catechol) complex of molybdenum(V). The presence of an EPR peak at a *g* value of 1.95 indicates that this species is at least partially in a mononuclear form. The product solution from controlled potential coulometry of **1** at −1.2 V is characteristic of a bis(catechol) complex of Mo(IV). Again, it exhibits neither an ESR spectrum nor a magnetic moment.

Cyclic voltammetry of **2** indicates that an initial positive scan yields a reversible couple at +0.25 V, whose height is consistent with a one-electron oxidation. (Addition of 1 equiv of base/molybdenum in **1** results in a species with similar electrochemistry to that of **2**.) However, controlled-potential coulometry of **2** at +0.3 V indicates an overall oxidation of one electron/binuclear complex. Reduction of this product solution at −0.6 V also is a one-electron process which yields a solution of **2**. Addition of 1 equiv of base to **2** yields a species with the electrochemistry of Figure 2d and causes the controlled-potential coulometry at 0.0 V to increase to an overall one-electron/Mo oxidation. The product solution exhibits an ESR resonance at a *g* value of 2.00 which is 10 G wide and characteristic of the semiquinone radical. Both oxidations appear to yield quinone as a major electroactive product.

Consideration of the analytical, spectroscopic, and electrochemical results permits the formation and oxidation-reduction reactions for **1** and **2** to be formulated in Chart I. Additional studies are in progress on the interaction of various dioxygen species (O_2, $O_2^-\cdot$, H_2O_2, and HO_2^-) with **1** and **2**.

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(15) Species **1** was isolated from benzene solution and recrystallized from hot toluene solution as a dark purple microcrystalline product. An amorphous dark purple-brown material was obtained from methanol. Microanalysis of these materials yielded results that are consistent with the formula bis(3,5-di-*tert*-butylcatecholato)oxomolybdenum(VI). Carbon and hydrogen analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. The molybdenum content was determined thermogravemetrically. Anal. Calcd for $MoC_{28}H_{40}O_5$: C, 60.86; H, 7.30; Mo, 17.36. Found: C, 61.09; H, 7.50; Mo, 17.17. The molecular weight of **1** in toluene solution was determined by vapor-pressure osmometry (Mechrolab, Inc., Model 301A) to be 1130 g mol^{-1}, which is consistent with a binuclear complex, $[Mo(O)(Cat)_2]_2$, for **1** (calcd mol wt, 1128).

(16) Species **2** was prepared and isolated by either adding 1 equiv of TBAOH/molybdenum to a CH_2Cl_2 solution of species **1** or by combining in CH_2Cl_2 bis(acetylacetonato)dioxomolybdenum(VI) with 2 equiv of 3,5-di-*tert*-butylcatechol and 1 equiv of TBAOH (in methanol) under an argon atmosphere. The latter combination resulted in a red solution, and upon addition of benzene yielded a yellow microcrystalline material which was filtered, washed with cold benzene, and air dried. The product was recrystallized from hot benzene–chloroform (95:5). Microanalysis gave results that are consistent with the formula bis(3,5-di-*tert*-butylcatecholato)oxomolybdenum(VI). However, preliminary X-ray data for the crystal structure of **2** by C. G. Pierpont and R. M. Buchanan (Department of Chemistry, University of Colorado, Boulder) establish that the correct formula is bis(tetra-*n*-butylammonium)-μ-oxo-bis[(3,5-di-*tert*-butylcatecholato)dioxomolybdenum(VI)]. Anal. Calcd for $Mo_2N_2C_{60}H_{112}O_9$: C, 59.60; H, 9.34; Mo, 15.87. Found: C, 60.61; H, 9.94; Mo, 17.35.

(17) By use of the molar absorptivities for 3,5-di-*tert*-butylcatechol (λ 279 nm (ϵ 2130)), its semiquinone anion (λ 338 nm (ϵ 1240), 377 (1010)), and, where applicable, its quinone (λ 400 nm (ϵ 1550)) in CH_3CN, the concentrations of each of these groups in a solution of the complex have been estimated.

(18) The mean values of the ^1H NMR resonances (vs. Me_4Si) for the 3,5-di-*tert*-butyl groups of the free catechol, its anion, and the related *o*-quinone are 1.33 and 1.21, 1.29 and 1.17, and 1.18 and 1.16 ppm, respectively. The mean resonance values (two doublets) for the two ring protons of free catechol, its anion, and its related quinone are 6.69 (6.72 and 6.66), 6.19 (6.31 and 6.08), and 6.28 ppm (6.49 and 6.07), respectively.

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Bimetallic Copper(I) and -(II) Macrocyclic Complexes as Mimics for Type 3 Copper Pairs in Copper Enzymes

Sir:

The complexing of two metal ions by the same *macrocyclic ligand* is subject to much current interest.[1,6] In principle, such systems allow the study of (i) metal–metal interactions and (ii) insertion of substrates and their possible transformations. Moreover, such structures are often found in biological sys-

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