The foregoing results illustrate several effects of the catechol ligand on electrochemical behavior of MoO^{4+} complexes. First, the electron-donating character of catechol shifts the Mo(VI) reduction potential to more negative values and increases the separation between the potentials of Mo(VI)/Mo(V) and Mo(V)/Mo(IV) reduction. These effects increase with increasing donor strength of the catechol substituents. The net result is that the separation between Mo(VI)/Mo(V) and Mo(V)/Mo(IV) potentials increases from effectively 0 V in compounds **1a** and **1b** to ca. 0.4 V in compounds **3c** and **3d** while the Mo(VI) reduction potential itself shifts negatively by about 0.4 V. The electronic character of the catechol substituents also influences the mechanism of $MoO(cat)(S_2CNEt_2)_2$ reduction. When electron-withdrawing substituents are present, a concentration-dependent reaction occurs that consumes species undergoing reduction at the potential of the second wave and produces a material that is reducible at a more negative potential. When electron-donating or nonwithdrawing substituents are present, a different reaction ensues that causes more than one electron to be transferred at the potential of the first reduction wave. We do not know the mechanisms or products of these chemical reactions. Voltammetric analyses of solutions prepared by coulometric reduction of **3a–d** reveal large waves for oxidation of $Et_2NCS_2^-$, but no indication of the Mo(IV) complexes described in eq 3 and 12 nor of free catecholate ligands. Presumably, the ultimate reduction products are molybdenum catecholate species.

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Registry No. **1a**, 57146-54-0; **1b**, 53548-92-8; **2**, 58760-67-1; **2**·BPh_4, 104598-32-5; **3a**, 104574-85-8; **3b**, 104574-86-9; **3c**, 104574-84-7; **3d**, 104574-87-0; **4**, 25395-92-0; **5**, 67673-25-0; $[MoO(Cl_4cat)(S_2CNEt_2)_2]^-$, 104574-88-1; $[MoO(Cl_4cat)(S_2CNEt_2)]^-$, 104574-89-2; $[MoO(NO_2cat)(S_2CNEt_2)_2]^-$, 104575-90-8; $[MoO(NO_2cat)(S_2CNEt_2)]^-$, 104574-90-5; $[MoO(cat)(S_2CNEt_2)]^-$, 104574-91-6; $MoO(Cl_4cat)(S_2NEt_2)$, 104574-92-7; $MoO(NO_2cat)(S_2CNEt_2)$, 104574-93-8; $MoO(cat)(S_2CNEt_2)$, 104574-94-9; $Na[S_2CNEt_2]$, 148-18-5; $[Et_4N]Cl$, 56-34-8; $[(heptyl)_4N]Br$, 4368-51-8; Cl^-, 16887-00-6; CH_3CN, 75-05-8.

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Synthesis and Properties of Seven-Coordinate (Catecholato)bis(dithiocarbamato)oxomolybdenum(VI) Complexes Exhibiting Metal- and Ligand-Centered Electrochemistry

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Seven-coordinate complexes containing two diethyldithiocarbamate and one of nine different catecholate (cat) ligands bound to oxomolybdenum(VI) (MoO^{4+}) are prepared by two synthetic routes: (i) oxidative addition of *o*-quinone to oxomolybdenum(IV) ($MoO(S_2CNEt_2)_2$) and (ii) replacement of an oxo ligand by catechol on dioxomolybdenum(VI) ($MoO_2(S_2CNEt_2)_2$). These $MoO(cat)(S_2CNEt_2)_2$ complexes undergo electron-transfer reactions that encompass the Mo(VI), -(V), and -(IV) oxidation states of the metal and the catecholate, semiquinone (SQ), and quinone (Q) oxidation levels of the ligand. The electronic character of the catechol ligand influences the mechanism of metal-centered reduction. Complexes with electron-withdrawing catechol substituents undergo reduction in two one-electron steps separated by 0.2–0.3 V in CH_2Cl_2. Compounds with nonwithdrawing or electron-donating substituents also undergo separate Mo(VI)/Mo(V) and Mo(V)/Mo(IV) reductions, but a rapid chemical reaction in conjunction with charge transfer causes more than one electron to be transferred at the potential of the first wave. The ligand-centered oxidations of the $MoO(cat)(S_2CNEt_2)_2$ complexes occur at potentials ca. 1.7 V more positive than the $cat^{2-} \rightarrow SQ^{\bullet-}$ and $SQ^{\bullet-} \rightarrow Q$ oxidations of the free ligands. Such large differences reflect a strong electrostatic interaction between the oxomolybdenum(VI) center and the catechol. A strong interaction is required to compensate for unfavorable electron-transfer energetics (calculated on the basis of redox potentials to be as large as 3.6 V) between $MoO(S_2CNEt_2)_2$ and Q and to provide the necessary driving force for the two-electron oxidative-addition reaction (i) by which five of the nine complexes are formed. The solution EPR spectrum of the one-electron-oxidized product of the 3,5-di-*tert*-butylcatecholate complex exhibits coupling constants of 3.6 G to the C-4 ring proton and 2.2 G to Mo consistent with its assignment as the coordinated semiquinone, $[MoO(DTBSQ)(S_2CNEt_2)_2]^+$.

Introduction

Interest in metal–catecholate complexes[2] is stimulated by knowledge that interactions of this type occur in microbial iron transport reagents,[3] dioxygenase enzymes,[4] and electron-transfer pathways in bacterial photosynthesis.[5] Current research objectives include investigation of ligand-centered redox processes[6-14] and metal–semiquinone interactions.[15-22] Redox-active ligands on Mo are of interest with regard to the molybdenum hydroxylases,[23]

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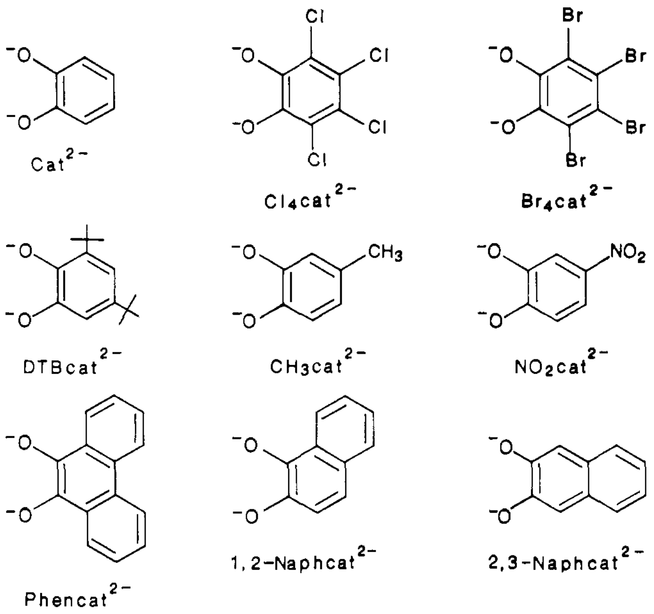
0020-1669/86/1325-4416$01.50/0

Chart I



enzymes that contain an oxomolybdenum center and a pterin cofactor which may interact with Mo.[24]

This paper describes the synthesis and characterization of seven-coordinate oxomolybdenum(VI) complexes of the type $MoO(cat)(S_2CNEt_2)_2$, where cat^{2-} is one of the nine catecholate ligands in Chart I.[25] The compounds are prepared by two synthetic routes: (i) oxidative addition of *o*-quinone to oxomolybdenum(IV) ($MoO(S_2CNEt_2)_2$) and (ii) replacement of an oxo ligand by catechol on dioxomolybdenum(VI) ($MoO_2(S_2CNEt_2)_2$). The $MoO(cat)(S_2CNEt_2)_2$ complexes undergo electron-transfer reactions that encompass the Mo(VI), -(V), and -(IV) oxidation states of the metal and the cat^{2-}, $SQ^{\bullet-}$, and Q oxidation levels of the ligand. We reported the results of a detailed investigation of the metal-centered electrochemistry of four of these species in the preceding paper.[26] This report describes the general features of metal- and ligand-centered electrochemistry for all nine $MoO(cat)(S_2CNEt_2)_2$ complexes. We also examine relationships among metal- and ligand-based redox potentials, the strength of the metal–catecholate interaction, and the energetics of the oxidative-addition reaction (i) by which five of the complexes are formed.

Table I. Spectral Data for $MoO(cat)(S_2CNEt_2)_2$ Complexes

compd	$\nu_{Mo=O}$, cm^{-1}	λ_{max}, nm (ϵ, M^{-1} cm^{-1})[a]
$MoO(Cl_4cat)(S_2CNEt_2)_2$	922	538 (4900)
$MoO(Br_4cat)(S_2CNEt_2)_2$	920	540 (5070)
$MoO(NO_2cat)(S_2CNEt_2)_2$	921	517 (5930), 370 (9620)
$MoO(Phencat)(S_2CNEt_2)_2$	911	666 (4590)
$MoO(2,3\text{-}Naphcat)(S_2CNEt_2)_2$	909	560 sh (5700), 475 (6740)
$MoO(Cat)(S_2CNEt_2)_2$	909	556 (4540)
$MoO(CH_3cat)(S_2CNEt_2)_2$	906	571 (5930)
$MoO(DTBcat)(S_2CNEt_2)_2$	906	578 (5670), 385 sh (3900)

[a] In CH_2Cl_2.

Experimental Section

Materials and Methods. All reactions were carried out under an argon atmosphere with use of Schlenk apparatus. The reagents 3,5-di-*tert*-butyl-*o*-benzoquinone, tetrachloro-*o*-benzoquinone, tetrabromo-*o*-benzoquinone, 9,10-phenanthrenequinone, catechol, 4-methylcatechol, 4-nitrocatechol, 3,5-di-*tert*-butylcatechol, 2,3-dihydroxynaphthalene (Aldrich), 1,2-naphthoquinone (Alfa), and $NOBF_4$ (Matheson Coleman and Bell) were purchased commercially and used as received. $MoO(S_2CNEt_2)_2$[27] and $MoO_2(S_2CNEt_2)_2$[28] were prepared by literature methods.

Preparation of Complexes by Oxidative Addition. $MoO(DTBcat)(S_2CNEt_2)_2$. A solution of 3,5-di-*tert*-butyl-*o*-benzoquinone (0.85 g, 3.86 mmol) in CH_2Cl_2 (10 mL) was added dropwise with stirring to a solution of $MoO(S_2CNEt_2)_2$ (1.58 g, 3.86 mmol) in CH_2Cl_2 (20 mL). After 15 min the deep blue solution was filtered and the filtrate reduced under vacuum to a volume of ca. 4 mL. Methanol (20 mL) was added and the volume reduced again to ca. 10 mL. After storage at −10 °C for 12 h deep blue crystals were collected, washed twice with methanol, and dried under vacuum; yield 2.14 g (88%). Anal. Calcd for $C_{24}H_{40}N_2O_3S_4Mo$: C, 45.8; H, 6.4; N, 4.5; S, 20.4; Mo, 15.3. Found: C, 46.2; H, 6.3; N, 4.5; S, 20.4; Mo, 15.9. ^1H NMR ($CDCl_3$, ppm vs. Me_4Si): 6.67 (d, 2 H, aromatic): 3.78 (q, 8 H, $-CH_2-$); 1.27 (s + t, 30 H, $-CH_3$).

The following compounds were prepared similarly from $MoO(S_2CNEt_2)_2$ and the respective *o*-quinone.

$MoO(Cl_4cat)(S_2CNEt_2)_2$: yield 79%. Anal. Calcd for $C_{16}H_{20}N_2O_3S_4Cl_4Mo$: C, 29.4; H, 3.1; N, 4.3. Found: C, 28.9; H, 3.0; N, 4.2.

$MoO(Br_4cat)(S_2CNEt_2)_2$: yield 77%. Anal. Calcd for $C_{16}H_{20}N_2O_3S_4Br_4Mo$: C, 23.1; H, 2.4; N, 3.4. Found: C, 22.3; H, 2.4; N, 3.2.

$MoO(Phencat)(S_2CNEt_2)_2$: yield 86%. Anal. Calcd for $C_{24}H_{28}N_2O_3S_4Mo$: C, 46.7; H, 4.6; N, 4.6. Found: C, 44.8; H, 4.5; N, 4.7.

$MoO(1,2\text{-}Naphcat)(S_2CNEt_2)_2$. The expected product proved difficult to isolate and store in pure form. A deep blue solid (27% yield), examined several days after preparation, gave an unsatisfactory elemental analysis and exhibited an infrared spectrum in the Mo=O stretching region that was not typical of other $MoO(cat)(S_2CNEt_2)_2$ complexes (see Table I). After longer storage under argon, the solid gave visible evidence of decomposition (color change to red). For electrochemical studies, solutions of $MoO(1,2\text{-}Naphcat)(S_2CNEt_2)_2$ were prepared in situ by mixing equimolar quantities of $MoO(S_2CNEt_2)_2$ and 1,2-naphthoquinone.

Preparation of Complexes by Oxo Replacement. $MoO(DTBcat)(S_2CNEt_2)_2$. A suspension of $MoO_2(S_2CNEt_2)_2$ (2.03 g, 4.8 mmol) and 3,5-di-*tert*-butylcatechol (1.12 g, 5.0 mmol) in methanol (30 mL) was stirred at room temperature for 4 h. A deep blue precipitate was collected, recrystallized from CH_2Cl_2/methanol/hexane, and dried under vacuum; yield 1.86 g (62%). Elemental analyses, spectroscopic

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properties, and electrochemical behavior of this product were indistinguishable from those of the material prepared by oxidative addition.

The following compounds were prepared similarly by reaction of $MoO_2(S_2CNEt_2)_2$ with the appropriate catechol. Reaction rates varied, and the approximate time allowed for each reaction is noted.

MoO(Cat)(S_2CNEt_2)$_2$: 1 h; yield 81%. Anal. Calcd for $C_{16}H_{24}N_2O_3S_4Mo$: C, 37.2; H, 4.7; N, 5.4. Found: C, 36.4; H, 4.8; N, 5.4.

MoO(CH_3cat)(S_2CNEt_2)$_2$: 12 h; yield 37%. Anal. Calcd for $C_{17}H_{26}N_2O_3S_4Mo$: C, 38.5; H, 4.9; N 5.3. Found: C, 37.8; H, 5.0; N, 5.2.

MoO(NO_2cat)(S_2CNEt_2)$_2$: 2 h; yield 83%. Anal. Calcd for $C_{16}H_{23}N_3O_5S_4Mo$: C, 34.2; H, 4.1; N 7.5. Found: C, 31.1; H, 4.2; N, 7.7.

MoO(2,3-Naphcat)(S_2CNEt_2)$_2$: 1.5 h; yield 90%. Anal. Calcd for $C_{20}H_{26}N_2O_3S_4Mo$: C, 42.4; H, 4.6; N, 4.9. Found: C, 41.5; H, 4.6; N, 4.9.

Physical Measurements. Infrared spectra were recorded as KBr pellets on a Beckman 20A spectrophotometer and were calibrated with polyethylene film. Electronic spectra were obtained with a Cary 118C instrument. Room-temperature EPR spectra were acquired with a Varian 4502 spectrophotometer; *g* values were calibrated with DPPH. ^1H NMR spectra were recorded with a Varian A-60 instrument. Elemental analyses were performed either with an automated Perkin-Elmer 240 analyzer or by Galbraith Laboratories, Inc., Knoxville, TN.

Equipment and procedures for cyclic voltammetry (CV), normal pulse voltammetry (NPV), and controlled-potential coulometry (CPC) experiments are described in the preceding paper.[26] Electrode potentials were standardized against the ferrocenium/ferrocene ($Fc^{+/0}$) redox couple according to the procedure in ref 29. Potentials are converted to V vs. SCE by use of a value of 0.40 ± 0.02 V vs. SCE for the $E°'$value of $Fc^{+/0}$ in 0.1 M $[Bu_4N]PF_6/CH_2Cl_2$. This quantity was determined as the mean of anodic and cathodic peak potentials in 15 separate CV experiments.

All electrochemical experiments were carried out at ambient temperature (22 ± 2 °C). Dichloromethane was the distilled-in-glass reagent from Burdick & Jackson and was used as received. The supporting electrolyte was 0.1 M tetra-*n*-butylammonium hexafluorophosphate ($[Bu_4N]PF_6$) from Southwestern Analytical Chemicals. All solutions were deoxygenated and blanketed by a stream of argon that had been saturated with solvent.

Results and Discussion

Preparation and Spectral Properties. Two procedures were used to synthesize the $MoO(cat)(S_2CNEt_2)_2$ complexes: two-electron oxidative addition of *o*-quinone to oxomolybdenum(IV)

$$MoO(S_2CNEt_2)_2 + Q \rightarrow MoO(cat)(S_2CNEt_2)_2 \quad (1)$$

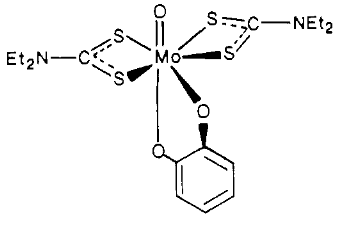
and neutralization and replacement of an oxo ligand on dioxomolybdenum(VI) by catechol

$$MoO_2(S_2CNEt_2)_2 + H_2cat \rightarrow MoO(cat)(S_2CNEt_2)_2 + H_2O \quad (2)$$

The Cl_4cat, Br_4cat, Phencat, and 1,2-Naphcat complexes were prepared by reaction 1 in dichloromethane and the Cat, CH_3cat, NO_2cat, and 2,3-Naphcat complexes by reaction 2 in methanol. $MoO(DTBcat)(S_2CNEt_2)_2$ was prepared by both reactions; the products were identical in all respects. Table I contains infrared and electronic spectral data for the eight complexes isolated.

We anticipated that reaction 1 might result in the formation of $MoO(cat)(S_2CNEt_2)_2$, because other catecholate species have been prepared by oxidative addition of *o*-quinones to coordinatively unsaturated metal centers[7,30] and because $MoO(S_2CNEt_2)_2$ is known to undergo reactions of this type with other two-electron oxidants (e.g., halogens, acetylenes, diazenes, tetracyanoethylene).[31,32] The five examples of reaction 1 proceed rapidly and nearly quantitatively to the expected product. Because not all catechol ligands could be obtained in their quinone form, other synthetic routes were pursued to extend the range of $MoO(cat)(S_2CNEt_2)_2$ complexes prepared. Reaction 2 was selected for this purpose because conversion of six-coordinate MoO_2^{2+} to seven-coordinate MoO^{4+} complexes has been achieved with other acidic substrates.[33-35] While successful in the preparation of five compounds, reaction 2 was slower and less quantitative than reaction 1, particularly for catechols with electron-donating substituents. This fact suggests that acidity of the catechol protons may be an important factor influencing the rate and extent of reaction 2.

A reasonable structural formulation[36] for the $MoO(cat)(S_2CNEt_2)_2$ complexes is a seven-coordinate pentagonal bypyramid with an axial Mo=O group and the large-bite-angle catecholate ligand bound across axial and equatorial sites:



I

This geometry is found in the related seven-coordinate complex $MoO(cat)(C_5H_{10}NO)_2$,[37] where $C_5H_{10}NO^-$ is the 1-piperidinolate ligand.

Infrared spectra of I exhibit no bands at 1660–1700 or 1420–1470 cm^{-1} that would result from Q or $SQ^{\bullet-}$ forms of the ligand; thus, formulation of the species as catecholate complexes appears correct. The ^1H NMR spectrum of $MoO(DTBcat)(S_2CNEt_2)_2$ exhibits integrated intensities for methyl, methylene, and aromatic protons in the ratio 30:18:2 consistent with the 1:2 stoichiometry of catechol and dithiocarbamate ligands. The Mo=O stretching frequencies (Table I) are distinct from those of the $MoO(S_2CNEt_2)_2$ (962 cm^{-1})[38] and $MoO_2(S_2CNEt_2)_2$ (910, 877 cm^{-1})[38] starting materials and fall at and beyond the lower range of values (ca. 915–950 cm^{-1})[31-35] usually observed for seven-coordinate MoO^{4+} complexes. The relatively low values of $\nu_{Mo=O}$ probably reflect the strong electron-donating character of the catechol ligand, a conclusion that is supported by the trend from high to low frequencies with increasing electron-donor strength of the substituent groups. The complexes also exhibit an intense visible absorption band at 517–666 nm that is responsible for their deep blue to burgundy color in solution. Transitions of this nature are observed in other metal–catecholate and –semiquinone species and have been assigned variously[8,14,20] to catechol $\pi \rightarrow \pi^*$ or ligand-to-metal change transfer.

Metal-Centered Electrochemistry. In the preceding paper[26] we reported details of the electrochemical reduction of $MoO(cat)(S_2CNEt_2)_2$ complexes with Cl_4cat, NO_2cat, Cat, and DTBcat ligands in CH_3CN, DMF, and CH_2Cl_2. The behavior of all nine complexes of this type in CH_2Cl_2 is reported in the present work. Figure 1 contains normal pulse voltammograms illustrating the reductive behavior of several of these compounds; NPV and controlled-potential coulometric data are collected in Table II.

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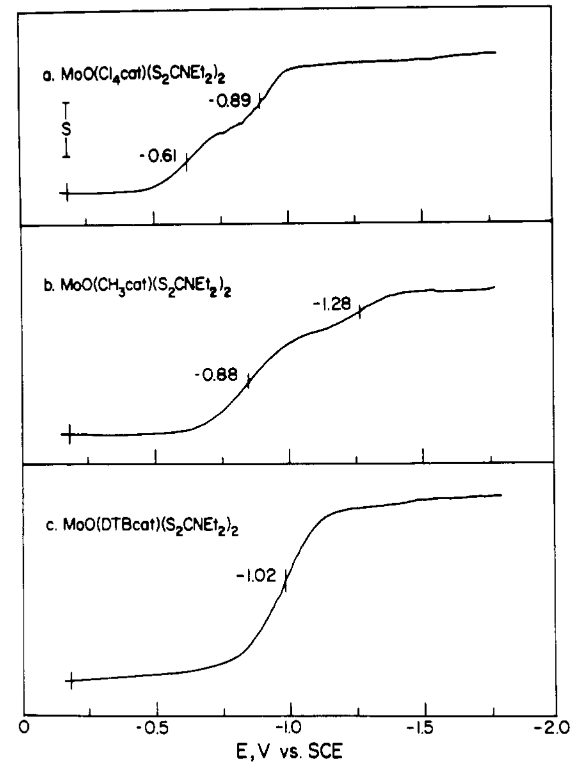

Figure 1. Normal pulse voltammetric reduction of (a) 0.50 mM $MoO(Cl_4cat)(S_2CNEt_2)_2$, (b) 0.53 mM $MoO(CH_3cat)(S_2CNEt_2)_2$, and (c) 0.20 mM $MoO(DTBcat)(S_2CNEt_2)_2$ in 0.1 M $[Bu_4N]PF_6/CH_2Cl_2$. S = 100 μA in (a) and (b) and 33.3 μA in (c).

The half-wave potential for the first reduction step of the $MoO(cat)(S_2CNEt_2)_2$ complexes occurs between −0.6 and −1.0 V vs. SCE in CH_2Cl_2 and varies in the negative direction with increasing electron-donor strength of the catechol substituents. Assignment of metal-centered electrochemistry is made by comparison with the behavior of other seven-coordinate MoO^{4+} complexes (e.g., $MoOCl_2(S_2CNEt_2)_2$, $MoOBr_2(S_2CNEt_2)_2$, $MoO(S_2CNEt_2)_3^+$),[26] which undergo reduction at about the same potential. Overall two-electron reduction of the MoO^{4+} center is confirmed by NPV and CPC. The total NPV current parameter measured on the plateau of the second reduction wave averages 2180 ± 130 μA cm^{-2} mM^{-1} for the nine compounds in Table II. This value is twice the magnitude of i_d/AC for a standard one-electron reduction in CH_2Cl_2 (995 μA cm^{-2} mM^{-1}).[39] CPC reduction at this potential shows n = 2.1 ± 0.1 for the last five entries in Table II.

The NPV in Figure 1a illustrates that reduction of $MoO(Cl_4cat)(S_2CNEt_2)_2$ consists of two waves of equal height separated by 0.2–0.3 V. Thus, reduction proceeds from Mo(VI) → Mo(V) → Mo(IV) in discrete one-electron steps. This behavior is typical of the three complexes that contain a single catechol ring with electron-withdrawing substituents (Cl_4cat, Br_4cat, NO_2cat). NPV experiments do not reveal the electrochemical reversibility nor possible existence of chemical reactions coupled to these electron-transfer steps. However, if a cyclic voltammetric scan is extended through both reduction waves before reversal, the return sweep shows that the second reduction is irreversible and that a dithiocarbamate ligand (observable by its oxidation wave at ca. 0.0 V)[26] is lost in this step. If the CV scan is restricted to the first electron transfer, only a wave for Mo(V) reoxidation is observed on reverse sweep, indicating quasi-reversible behavior for the Mo(VI)/Mo(V) couple. Values of $E^{\circ\prime}$ = +0.55 and 0.56 V and ΔE_p = 122 and 127 mV are obtained by CV at 0.05 V s^{-1} for $MoO(Cl_4cat)(S_2CNEt_2)_2$ and $MoO(Br_4cat)(S_2CNEt_2)_2$, respectively. The foregoing results are consistent with the following electrode reactions for reduction of the Cl_4cat, Br_4cat, and NO_2cat complexes in CH_2Cl_2:

Table II. Electrochemical Data for Reduction of $MoO(cat)(S_2CNEt_2)_2$ Complexes in Methylene Chloride[a]

	NPV		CPC[b]	
catechol	$E_{1/2}$, V	i_d/AC, μA cm^{-1} mM^{-1}	E_{app}, V	n
Cl_4cat	−0.61 −0.89	1100 1090 (2190)		
Br_4cat	−0.62 −0.90	1110 1010 (2120)	−1.2	1.4
NO_2cat	−0.63[c] −0.89[c]	990 1000 (1990)	−1.0	1.5
Phencat	−0.67 −1.18	1450 860 (2310)	−1.3	2.2
1,2-Naphcat[d]	−0.76[c] −1.20[c]	1360 620 (1980)		
2,3-Naphcat	−0.74 −1.08	1380 880 (2260)	−1.2	2.1
Cat	−0.89 −1.21	1680 500 (2180)	−1.35	2.1
CH_3cat	−0.88 −1.28	1580 590 (2170)	−1.4	1.8
DTBcat	−1.02	2060 (2060)	−1.4	2.1

[a] Recorded for 0.2–1.4 mM solutions of complexes in 0.1 M $[Bu_4N]PF_6$. The numbers in parentheses with the i_d/AC values are the total NPV current parameters measured on the limiting current plateau of the second reduction wave. [b] Value of n determined by extrapolating plots of i vs. Q to zero current. A small steady-state current (typically 5–10% of the initial current) that persisted at the end of each electrolysis was neglected in carrying out the i vs. Q extrapolations. [c] Data not referenced to $Fc^{+/0}$. [d] Complex prepared in situ.

$$Mo^{VI}O(cat)(S_2CNEt_2)_2 + e^- \rightleftharpoons [Mo^{V}O(cat)(S_2CNEt_2)_2]^- \quad (3)$$

$$[Mo^{V}(cat)(S_2CNEt_2)_2]^- + e^- \rightarrow [Mo^{IV}O(cat)(S_2CNEt_2)]^- + Et_2NCS_2^- \quad (4)$$

A schematic representation of eq 3 and 4 was presented in ref 26. There we concluded that changes in coordination number from 7 to 6 to 5 accompany Mo(VI) to Mo(V) to Mo(IV) reduction of MoO^{4+} species. For the Cl_4cat, Br_4cat, and NO_2cat complexes a chemical reaction was found to occur subsequent to these charge-transfer steps that consumed material reducible at the potential of the second wave. This reaction is slower in CH_2Cl_2 than in CH_3CN (the major solvent in ref 26) but still occurs to an extent sufficient to give CPC results of $n < 2$ in Table II. When examined on the time scale of NPV, the reaction is slow enough in CH_2Cl_2 that electrochemical reduction of the Cl_4cat, Br_4cat, and NO_2cat complexes is described solely by eq 3 and 4.

For the remaining $MoO(cat)(S_2CNEt_2)_2$ complexes (i.e., those with nonwithdrawing or electron-donating catechol substituents) a different electrochemical behavior is observed. The Phencat, 1,2-Naphcat, 2,3-Naphcat, Cat, and CH_3cat complexes display two reduction waves separated by 0.3–0.5 V. The first wave is larger than the second, but the total NPV current parameter remains consistent with an overall two-electron transfer and CPC yields n = 2 (Table II). The NPV of $MoO(CH_3cat)(S_2CNEt_2)_2$ in Figure 1b illustrates these observations. Electrochemical behavior of this group of complexes is interpreted in terms of the sequence of reactions[26]

$$MoO(cat)(S_2CNEt_2)_2 + e^- \rightleftharpoons [MoO(cat)(S_2CNEt_2)_2]^- \quad (5)$$

$$[MoO(cat)(S_2CNEt_2)_2]^- \xrightarrow{k_2} P2 \quad (6)$$

$$P2 + e^- \rightarrow Mo(IV) \quad (7)$$

$$[MoO(cat)(S_2CNEt_2)_2]^- + e^- \rightarrow [MoO(cat)(S_2CNEt_2)]^- + Et_2NCS_2^- \quad (8)$$

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(39) See Table I in ref 26.

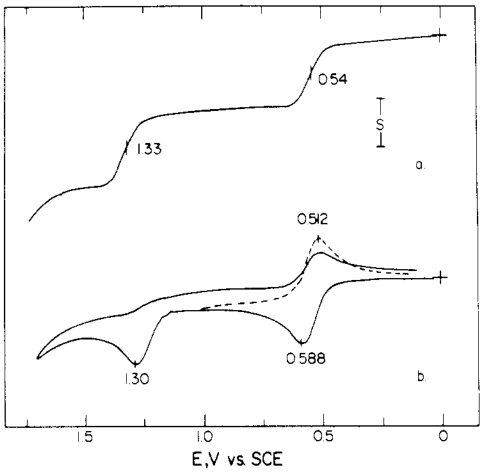

Figure 2. Oxidation of $MoO(DTBcat)(S_2CNEt_2)_2$ in 0.1 M $[Bu_4N]PF_6/CH_2Cl_2$: (a) normal pulse voltammetry, 0.20 mM complex, S = 33.3 μA; (b) cyclic voltammetry, 0.29 mM complex, sweep rate 0.05 V s^{-1}, S = 10 μA (broken line is a scan-reversal experiment illustrating the reversible character of the first oxidation wave).

Equations 5 and 8 are analogous to eq 3 and 4 except that eq 5 has an unstable product which decomposes to a substance (P2) that is reducible by one electron at the potential of the first wave. As sufficient time is allowed for eq 5, 6 and 7 to occur, the first reduction wave grows in size at the expense of the second, while unreacted $[MoO(cat)(S_2CNEt_2)_2]^-$ is reduced at the potential of the second wave to give a net two-electron transfer. Chemical rate constant k_2 must be appreciable because eq 6 proceeds to a noticeable extent during NPV, which with our instrumentation involves current measurement during an interval only 33–50 ms after pulse application. On the longer time scale allowed by slow-sweep-rate CV or CPC, eq 6 proceeds essentially to completion and irreversible two-electron reduction in a single step is observed for these compounds.

Reduction of $MoO(DTBcat)(S_2CNEt_2)_2$ in CH_2Cl_2 represents the limiting behavior for these $MoO(cat)(S_2CNEt_2)_2$ complexes. Rate constant k_2 is apparently so large for this compound that eq 6 proceeds to completion even on the time scale of NPV. Thus, only a single two-electron wave is observed for reduction of $MoO(DTBcat)(S_2CNEt_2)_2$ in CH_2Cl_2 (Figure 1c).

Ligand-Centered Electrochemistry. The $MoO(cat)(S_2CNEt_2)_2$ complexes exhibit two oxidation waves in aprotic solvents. Figure 2 illustrates the voltammetric behavior of $MoO(DTBcat)(S_2CNEt_2)_2$ in CH_2Cl_2. In this solvent the first oxidation wave is reversible by cyclic voltammetry for all complexes except $MoO(2,3\text{-}Naphcat)(S_2CNEt_2)_2$; the second is irreversible for all complexes. Electrochemical data for these oxidations are collected in Table III.

The anodic electrode reactions are assigned to ligand-centered charge transfers resulting in oxidation of the coordinated catechol to the semiquinone and quinone levels:

$$MoO(cat)(S_2CNEt_2)_2 \rightleftharpoons [MoO(SQ)(S_2CNEt_2)_2]^+ + e^- \quad E^{\circ\prime}(9) \qquad (9)$$

$$[MoO(SQ)(S_2CNEt_2)_2]^+ \rightarrow [MoO(Q)(S_2CNEt_2)_2]^{2+} + e^- \quad E_{pa}(10) \qquad (10)$$

The one-electron character of these reactions is established by NPV and by controlled-potential coulometry of $MoO(DTBcat)(S_2CNEt_2)_2$. The average NPV current parameters in Table III are 1040 ± 100 $\mu A\ cm^{-2}\ mM^{-1}$ for the first oxidation wave and 1050 ± 110 $\mu A\ cm^{-2}\ mM^{-1}$ for the second. These values are consistent with a one-electron transfer in CH_2Cl_2.[39] CPC oxidation of $MoO(DTBcat)(S_2CNEt_2)_2$ at +0.90 V vs. SCE in 0.1 M $[Bu_4N]PF_6/CH_2Cl_2$ results in the transfer of 0.98 faraday/mol of Mo and produces a solution-stable olive green material whose properties are described below.

Table III. Voltammetric Data for Ligand-Centered Redox Processes of $MoO(cat)(S_2CNEt_2)_2$ Complexes and Their Corresponding Quinones[a]

		$MoO(cat)(S_2CNEt_2)_2$		
catechol	redox process	$E^{\circ\prime}$, (ΔE_p, mV) or E_{pa}, V	i_d/AC, $\mu A\ cm^{-2}\ mM^{-1}$	quinone $E^{\circ\prime}$, V
Cl_4cat	cat/SQ	+1.049 (86)	1070	−0.664
	SQ/Q	+1.602[c]		+0.085
Br_4cat	cat/SQ	+1.035 (84)	1030	−0.663
	SQ/Q	+1.594[c]		+0.090
NO_2cat	cat/SQ	+1.066 (81)	990	
	SQ/Q	+1.597[c]		
Phencat	cat/SQ	+0.362 (106)[b]	950	−1.305
	SQ/Q	+1.035[c]	920	−0.713
1,2-Naphcat	cat/SQ	+0.438 (90)	940	−1.242
	SQ/Q	+1.28[d]	1020	−0.632
2,3-Naphcat	cat/SQ	+0.832[c]		
Cat	cat/SQ	+0.719 (150)[b]	1240	−0.92[e]
	SQ/Q	+1.389[c]	1140	−0.31[e]
CH_3cat	cat/SQ	+0.623 (83)	1030	
	SQ/Q	+1.280[c]	1180	
DTBcat	cat/SQ	+0.550 (76)	1060	−1.28[f]
	SQ/Q	+1.303[c]	970	−0.636

[a] Recorded for solutions of complexes or free quinones in 0.1 M $[Bu_4]PF_6/CH_2Cl_2$. $E^{\circ\prime} = {}^1/_2(E_{pc} + E_{pa})$ and $\Delta E_p = E_{pa} - E_{pc}$ determined by cyclic voltammetry for reversible processes at 0.05 V s^{-1} except as noted. For irreversible processes, E_{pa} is reported. i_d/AC is the NPV current parameter for $MoO(cat)(S_2CNEt_2)_2$ oxidations. [b] 0.4 V s^{-1}. [c] E_{pa} at 0.05 V s^{-1}. [d] E_{pa} at 0.5 V s^{-1}. [e] Literature value in 0.1 M $[Et_4]ClO_4/CH_3CN$: Stallings, M. D.; Morrison, M. M.; Sawyer, D. T. *Inorg. Chem.* **1981**, *20*, 2655. [f] Irreversible electrode reaction, cathodic $E_{p/2}$ value at 0.05 V s^{-1}.

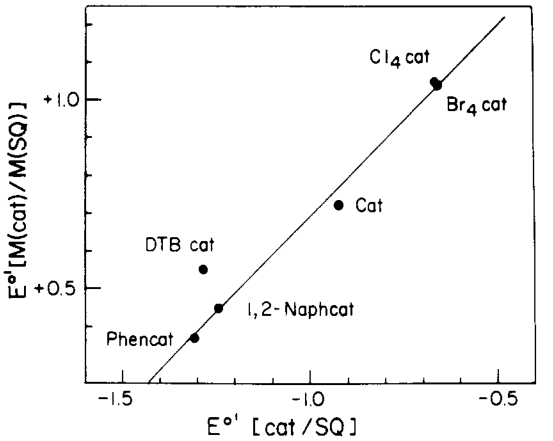

Figure 3. Potential of cat^{2-} to $SQ^{\bullet-}$ oxidation in $MoO(cat)(S_2CNEt_2)_2$ complexes plotted vs. that in isolated ligands (potentials in V vs. SCE recorded in 0.1 M $[Bu_4N]PF_6/CH_2Cl_2$). Data are from Table III. The straight line has the equation $y = 1.00x + 1.69$ V.

In Table III the potentials of reactions 9 and 10 are compared with those of the corresponding $cat^{2-}/SQ^{\bullet-}$ and $SQ^{\bullet-}/Q$ redox couples of the isolated ligands:

$$Q + e^- \rightleftharpoons SQ^{\bullet-} \quad E^{\circ\prime}(11) \qquad (11)$$

$$SQ^{\bullet-} + e^- \rightleftharpoons cat^{2-} \quad E^{\circ\prime}(12) \qquad (12)$$

The latter values were recorded for solutions of the free quinones in CH_2Cl_2. The $cat^{2-} \rightarrow SQ^{\bullet-}$ and $SQ^{\bullet-} \rightarrow Q$ oxidations occur at much more positive potentials in the $MoO(cat)(S_2CNEt_2)_2$ complexes. Figure 3 shows that an excellent correlation with unit slope exists between the potential of $cat^{2-} \rightarrow SQ^{\bullet-}$ oxidation in the complexes ($E^{\circ\prime}(9)$) and in the isolated ligands ($E^{\circ\prime}(12)$). A nearly equivalent correlation (not shown) exists between the potential of irreversible $SQ^{\bullet-} \rightarrow Q$ oxidation in the complexes ($E_{pa}(10)$) and that of the corresponding reversible couple of the ligands ($E^{\circ\prime}(11)$). These correlations support the assignment of

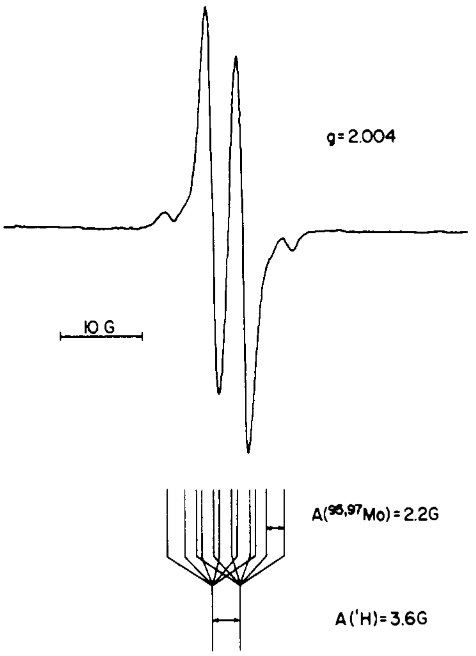

Figure 4. Room-temperature EPR spectrum of [MoO(DTBSQ)(S$_2$CNEt$_2$)$_2$]$^+$ in CH$_2$Cl$_2$.

ligand-centered electron transfer as does the observation of nearly equal spacing between the Q/SQ$^{\bullet-}$ and SQ$^{\bullet-}$/cat^{2-} potentials in the complexes (0.66 ± 0.11 V) and in the free ligands (0.66 ± 0.07 V, see Table III).

Similar ligand-centered oxidations have been reported for other metal–catecholate complexes, including M(cat)(CO)(Cl)(PR$_3$)$_2$ (M = Ir, Rh),[7] [Co(trien)(cat)]$^+$,[8,18a] and [Fe(salen)(cat)]$^-$ [11] (trien = triethylenetetramine; salen = ethylenebis(salicylaldimine)). In these cases complexation shifts the potentials of cat^{2-}/SQ$^{\bullet-}$ and SQ$^{\bullet-}$/Q oxidation by 1.1–1.6 V in the positive direction. In Table III the cat^{2-} → SQ$^{\bullet-}$ and SQ$^{\bullet-}$ → Q oxidations in the complexes are shifted positively by +1.7 ± 0.1 and +1.7 ± 0.2 V, respectively, relative to the potentials of the free ligands. Differences of this magnitude indicate a very strong interaction between the catechol and the oxomolybdenum(VI) center.

EPR spectroscopy provides additional evidence for the ligand-centered character of the first oxidation wave. Oxidation of deep blue MoO(DTBcat)(S$_2$CNEt$_2$)$_2$ by controlled-potential coulometry as described above or by reaction with a stoichiometric quantity of NOBF$_4$ in CH$_2$Cl$_2$ (eq 13) produces an olive green

$$\mathrm{MoO(DTBcat)(S_2CNEt_2)_2 + NOBF_4 \rightarrow [MoO(DTBSQ)(S_2CNEt_2)_2]^+ + BF_4^- + NO} \quad (13)$$

solution (λ_{max} = 405 nm, ϵ = 10 100 M^{-1} cm^{-1}) that exhibits the EPR spectrum shown in Figure 4. A cyclic voltammogram of this solution exhibits $E^{\circ\prime}$ and $i_p/v^{1/2}AC$ values identical with those of the starting complex indicating, together with the coulometry data, that the EPR-active substance derives from the reversible one-electron oxidation of MoO(DTBcat)(S$_2$CNEt$_2$)$_2$. The principal feature of the EPR spectrum is a doublet at g = 2.004 with a coupling constant of 3.6 G. These spectral parameters are nearly identical with those of free 3,5-di-*tert*-butyl-*o*-benzosemiquinone[2,40] and of 3,5-DTBSQ coordinated to other metal centers and result from strong interaction of unpaired electron spin density with the ring proton at C-4.[41] Electron spin interaction with the $I = {}^5/_2$ ^{95}Mo and ^{97}Mo nuclei (25.4% abundance) produces additional splitting of the doublet spectrum. Only the outermost 4 of the 12 expected lines of this interaction are detected, but their positions and spacings are consistent with a coupling constant of 2.2 G to the metal. The large ring proton interaction and this unusually small Mo coupling constant are further evidence that the product of reactions 9 and 13 is the coordinated semiquinone, [MoO(DTBSQ)(S$_2$CNEt$_2$)$_2$]$^+$.

Solutions of [MoO(DTBSQ)(S$_2$CNEt$_2$)$_2$]$^+$ in CH$_2$Cl$_2$ are stable for at least several hours on the basis of constant visible absorption spectrum and NPV current parameter for this length of time. Although isolation was tried with a variety of counter ions and solvents, we could not obtain a pure sample of this material in solid form. Our best attempt resulted from reaction of NOBF$_4$ with MoO(DTBcat)(S$_2$CNEt$_2$)$_2$ in CH$_2$Cl$_2$, which afforded a sample of [MoO(DTBSQ)(S$_C$NEt$_2$)$_2$]BF$_4$ that was ca. 80% pure on the basis of its NPV current parameter. Isolated salts of [MoO(DTBSQ)(S$_2$CNEt$_2$)$_2$]$^+$ appeared to decompose when stored in vacuo or under argon.

Energetics of Complex Formation. The strength of interaction between the catecholate ligand and the Mo(VI) center is of interest with regard to the energetics of the oxidative-addition reaction (eq 1) by which five of the complexes are formed. Consideration of potentials for reduction of the free quinones to SQ$^{\bullet-}$ and cat^{2-} (eq 11 and 12) and for oxidation of the Mo(IV) complex to Mo(V) and Mo(VI) (eq 14 and 15) leads to the conclusion that the

$$\mathrm{MoO(S_2CNEt_2)_2 \rightleftharpoons [MoO(S_2CNEt_2)]^+ + e^-} \quad E^{\circ\prime}(14) \quad (14)$$

$$\mathrm{[MoO(S_2CNEt_2)_2]^+ \rightleftharpoons [MoO(S_2CNEt_2)_2]^{2+} + e^-} \quad E^{\circ\prime}(15) \quad (15)$$

electron-transfer component of oxidative addition (eq 16) is un-

$$\mathrm{MoO(S_2CNEt_2)_2 + Q \rightleftharpoons [MoO(S_2CNEt_2)_2]^{2+} + cat^{2-}} \quad K_{16} \quad (16)$$

favorable by ca. 3.6 V for Q = DTBQ, PhenQ, and 1,2-NaphQ. This unfavorable driving force is estimated as the sum of electrode potentials for reactions 11 and 12 minus those for reactions 14 and 15, viz. $\Delta E = [E^{\circ\prime}(11) + E^{\circ\prime}(12)] - [E^{\circ\prime}(14) + E^{\circ\prime}(15)]$.[42] We have determined that $E^{\circ\prime}(14) = +0.5$ V by fast-sweep-rate cyclic voltammetry of MoO(S$_2$CNEt$_2$)$_2$ in CH$_3$CN/0.1 M tetraethylammonium tetrafluoroborate.[26] We estimate that $E^{\circ\prime}(15) = +1.3$ V on the basis of the ca. +0.8 V separation between the potentials of M(V) → M(VI) oxidation and M(V) → M(IV) reduction in the analogous [MO(SPh)$_4$]$^-$ (M = Mo, W) complexes.[43] Thus, from the data in Table III $\Delta E \cong -0.6 - 1.2 - (+0.5 + 1.3) = -3.6$ V for Q = DTBQ, PhenQ, and 1,2-NaphQ.

A strong bonding interaction between the catecholate dianion and the electropositive Mo(VI) center apparently compensates for the unfavorable energetics of reaction 16 and drives formation of the MoO(cat)(S$_2$CNEt$_2$)$_2$ complexes to completion.

$$\mathrm{[MoO(S_2CNEt_2)_2]^{2+} + cat^{2-} \rightleftharpoons MoO(cat)(S_2CNEt_2)_2} \quad K_{17} \quad (17)$$

In order for reaction 1 to be energetically favorable, the equilibrium constant of reaction 17 must be greater than that for the reverse of reaction 16, i.e., $K_{17} > 1/K_{16}$. We have not attempted to evaluate K_{17} experimentally. However, its magnitude may be appreciated by comparing the potentials of reactions 9 and 10 with those of reactions 11 and 12. From the data in Table III, $E^{\circ\prime}(9) - E^{\circ\prime}(12) = 0.059 \log (K_{17}/K_{18}) = +1.7 \pm 0.1$ V, where K_{18} is the formation constant of the Mo(VI)–semiquinone complex:

$$\mathrm{[MoO(S_2CNEt_2)_2]^{2+} + SQ^{\bullet-} \rightleftharpoons [MoO(SQ)(S_2CNEt_2)_2]^+} \quad K_{18} \quad (18)$$

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(40) (a) Ryba, O.; Pilar, J.; Petranek, J. *Collect. Czech. Chem. Commun.* **1968**, *33*, 26. (b) Trapp, C.; Tyson, C. A.; Giacometti, G. *J. Am. Chem. Soc.* **1968**, *90*, 1394. (c) Felix, C. C.; Sealy, R. C. *J. Am. Chem. Soc.* **1982**, *104*, 1555.

(41) The strength of this interaction derives from the fact that unpaired spin density in *o*-semiquinones is concentrated at positions on the aromatic ring that are most removed from the chelating portion of the molecule. Additional smaller (ca. 0.3-G) couplings to the ring proton at C-6 and to the *tert*-butyl protons at C-5 have been detected for 3,5-DTBSQ species[2,40] but were not observed in our experiment.

(42) Thermochemical cycles such as this have been used to estimate reaction energetics in similar circumstances, for example, in the reaction of dioxygen with Co(II)-tetraphenylporphyrin: Walker, F. A.; Beroiz, D.; Kadish, K. M. *J. Am. Chem. Soc.* **1976**, *98*, 3484.

(43) Bradbury, J. R.; Masters, A. F.; McDonnell, A. C.; Brunette, A. A.; Bond, A. M.; Wedd, A. G. *J. Am. Chem. Soc.* **1981**, *103*, 1959.

Likewise, $E_{pa}(10) - E^{\circ\prime}(11) = 0.059 \log (K_{18}/K_{19}) = +1.7 \pm 0.2$ V,[44] where K_{19} is the formation constant of the Mo(VI)–quinone complex:

$$[MoO(S_2CNEt_2)_2]^{2+} + Q \rightleftharpoons [MoO(Q)(S_2CNEt_2)_2]^{2+} \quad K_{19} \tag{19}$$

Thus, each increment of negative charge on the quinone ligand increases its tendency to bind to the Mo(VI) center by a factor of $\sim 10^{29}$. Combination of these results gives $E^{\circ\prime}(9) + E_{pa}(10) - E^{\circ\prime}(11) - E^{\circ\prime}(12) = 0.059 \log (K_{17}/K_{19}) = 3.4$ V. If the Mo(VI)–quinone formation constant, K_{19}, is ≥ 1, then $K_{17} \geq 10^{58}$. Clearly, an equilibrium constant of at least this order of magnitude is needed to drive the oxidative-addition reaction to completion in the face of its highly unfavorable electron-transfer energetics (i.e., $K_{16} \approx 10^{-60}$).

For Cl_4Q and Br_4Q reaction 16 is not quite as unfavorable ($\Delta E = -2.2$ V, $K_{16} = 10^{-37}$) as for the other three quinones. However, the potentials of these $Q/SQ^{\bullet-}$ and $SQ^{\bullet-}/cat^{2-}$ redox couples are still shifted in the positive direction by 1.5–1.7 V by complexation (Table III). Thus, either oxidative addition (eq 1) is inherently more favorable for Cl_4Q and Br_4Q or the magnitude of Mo(VI)–quinone interaction (K_{19}) is smaller for these compounds.

Other metal–catecholate and –semiquinone complexes that have been formed by oxidative addition also exhibit large positive shifts in $Q/SQ^{\bullet-}$ and $SQ^{\bullet-}/cat^{2-}$ redox potentials.[7b,c,11,18c,20a] These reports apparently represent further instances in which strong metal–ligand interactions facilitate oxidative addition by overcoming unfavorable electron-transfer thermodynamics. The balance between complexation and electron-transfer reactivity may be a finely established one, because Balch[7a] has noted that certain potential oxidative-addition reactions (e.g., $Ir(CO)(Cl)(PPh_3)_2$ reacted with PhenQ or 1,2-NaphQ and $Pt(PPh_3)_2(Cl)_2$ reacted with Cl_4Q) yield no product. Likewise, we observe that acenaphthenequinone fails to react with $MoO(S_2CNEt_2)_2$. Further understanding in this area will require more thorough examination of the relative contributions of complexation and electron-transfer energetics to oxidative-addition reactions.

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[44] Because reaction 10 is irreversible, we have used the anodic peak potential, $E_{pa}(10)$, rather than the thermodynamic $E^{\circ\prime}$ value in this calculation. This irreversibility appears to derive from a rapid chemical reaction following reversible electron transfer rather than slow charge-transfer kinetics. We estimate that $E_{pa}(10)$ differs from $E^{\circ\prime}(10)$ by no more than 0.1–0.2 V on the basis of the observation that a nearly equal spacing (0.66 ± 0.1 V) exists between the $Q/SQ^{\bullet-}$ and $SQ^{\bullet-}/cat^{2-}$ potentials in the complexes (eq 10 minus eq 9) and in the free ligands (eq 11 minus eq 12) (cf. Table III).

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Reversible Intramolecular Isomerization Associated with the Electron-Transfer Reactions of Mixed-Carbonyl-Isocyanide-Phosphine Complexes of Molybdenum of the Type $[Mo(CO)_2(CNR)_2(PR'_3)_2]^{+/0}$

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Neutral species of the type $Mo(CO)_2(CNR)_2(PR'_3)_2$ (R = methyl, isopropyl, *tert*-butyl, cyclohexyl, *p*-tolyl, xylyl, mesityl, 2,4,6-tri-*tert*-butylphenyl; $PR'_3 = PEt_3$, $P\text{-}n\text{-}Pr_3$, PEt_2Ph, $PMePh_2$, PPh_3) have been synthesized and found to exist as a single isomer with a trans disposition of phosphine ligands and cis arrangements of the pairs of CO and RNC groups in the case of R = alkyl and PR'_3 = any phosphine except (in some instances) PPh_3. For the analogous aryl isocyanide complexes, spectroscopic evidence (IR and ^1H and $^{31}P\{^1H\}$ NMR) suggests that a mixture of isomers is present. In all instances (i.e., R = alkyl and aryl) electrochemical and chemical oxidations afford the paramagnetic 17-electron all-trans cations $[Mo(CO)_2(CNR)_2(PR'_3)_2]^+$, which have been isolated as their PF_6^- salts in a few cases. The monocations have been characterized by IR and X-band ESR spectroscopies. Rereduction of these cations results in a very rapid reisomerization to the isomer or equilibrium mixture of isomers that are present in the parent neutral complexes, except in the cases of $Mo(CO)_2(CNxylyl)_2(PEt_2Ph)_2$, $Mo(CO)_2(CN(t\text{-}Bu_3Ph))_2(PMePh_2)_2$, and $Mo(CO)_2(CN(t\text{-}Bu_3Ph))_2(P\text{-}n\text{-}Pr_3)_2$. For these three complexes rereduction affords solutions of the neutral all-trans isomers, which can be characterized spectroscopically before they slowly reisomerize to the mixtures of isomers that contain cis CO groups. From cyclic voltammetric measurements on solutions of these complexes in 0.1 M $n\text{-}Bu_4NPF_6/CH_2Cl_2$, the equilibrium constants for the redox cross-reactions $trans^0 + cis^+ \rightleftharpoons trans^+ + cis^0$ show that these equilibria lie far to the right; this is attributable to the high thermodynamic stability of the $trans^+$ and cis^0 species. The homogeneous chemical rate constants for the cis–trans isomerizations of $Mo(CO)_2(CNR)_2(PR'_3)_2$ have been evaluated. For the processes

$$cis^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} trans^+ \qquad trans^0 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} cis^0$$

it is clear that $k_1 > k_2$. The intramolecular isomerizations can be interpreted in terms of sequential trigonal twists.

Introduction

One of the premises of the theoretical treatment for heterogeneous electron-transfer rates is that smaller rate constants can be expected for redox couples that have greater structural differences between the oxidized and reduced forms than for those in which there is little or no structural change accompanying electron transfer.[1,2] However, the assumption that structural inferences can be made on the basis of reversibility, or lack of it, in electrochemical processes has been shown to be misleading when electrochemically induced isomerization is involved. When the mechanism shown in eq 1 holds, where O1 represents the reactant

$$O1 + e^- \rightleftharpoons R2 \tag{1}$$

in one structural form and R2 the reduced product having a

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[1] Weaver, M. J. *Inorganic Reactions and Methods*; Zuckerman, J., Ed.; Verlag Chemie: Weinheim, FRG, in press.

[2] Tulyathan, B.; Geiger, W. E. *J. Electroanal. Chem. Interfacial Electrochem.* **1980**, *109*, 325.