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Preparation and electrochemistry of six-coordinate monooxo molybdenum(VI) complexes containing bidentate catecholate and tridentate NOS-donor Schiff base ligands

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Abstract

The preparation, characterization and electrochemical properties are reported for monooxo Mo(VI) complexes, MoO(cat)(ssp), containing bidentate catecholate (cat²⁻ = 3,5-di-tert-butylcatecholate, naphthalene-1,2-diolate, phenanthrene-9,10-diolate) and tridentate NOS-donor Schiff base (ssp²⁻ = *N*-salicylidene-2-aminobenzenethiolate) ligands. The intensely colored compounds are formed by oxo abstraction from MoO₂(ssp) with EtPh₂P in THF followed by oxidative addition of the appropriate quinone. Oxo abstraction leads to a mixture of MoO(ssp) and Mo₂O₃(ssp)₂ rather than either of these single products under the experimental conditions. The six-coordinet: MoO⁴⁺ species exhibit reversible Mo(VI/V) electrochemistry at a potential ~0.1 V more positive than that for analogous complexes with the NOO'-donor Schiff base ligand *N*-salicylidene-2-aminophenolate (sap²⁻). © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Electrochemistry; Molybdenum complexes, Oxo complexes; Catecholate complexes; Schiff base complexes

1. Introduction

Oxomolybdenum(VI) complexes are of interest as models for the active sites of oxotransferase enzymes [1-3]. The cisdioxo MoO_2^{2+} unit, which is found in oxidized sulfite oxidase and analogously in a *cis*-oxothio $MoOS^{2+}$ format in oxidized xanthine oxidase, is a common structural feature in Mo(VI) coordination chemistry [4-6]. Thus, recent discovery of a monooxo Mo(VI) center in the oxidized form of dimethylsulfoxide (DMSO) reductase [7.8] is unexpected. Although MoO^{4+} complexes exist, they are less numerous than MoO_2^{2+} species and almost always exhibit a coordination number of seven. The molybdenum coordination number in oxidized DMSO reductase is thought to be five or six [7,8]. Recently, we reported the preparation and characterization of several six-coordinate MoO⁴⁺ complexes containing a bidentate catecholate (cat²⁻) and a tridentate Schiff base ligand with an NOO' donor atom set [9]. An interesting property of these species is their ability to sustain reversible Mo(VI/V) electrochemistry [10,11]. By contrast, sevencoordinate MoO⁴⁺ complexes undergo irreversible metalligand bond cleavage reactions in conjunction with electron transfer [12], and the electrochemistry of six-coordinate MoO_3^{2+} species generally is not reversible [5]. Because sulfur is an important component of molybdenum's biological coordination environment [13], its influence on the electron transfer properties of monooxo Mo(VI) centers is of interest. The present paper reports the preparation and electrochemical characterization of several six-coordinate MoO(cat)(ssp) complexes (Fig. 1) containing the NOS-donor Schiff base ligand *N*-salicylidene-2-aminobenzenethiolate (ssp²⁻, 1a) and a comparison of their properties with analogous MoO(cat)(sap) (sap²⁻ = *N*-salicylidene-2-aminophenolate, 1b) complexes.

2. Experimental

2.1. General procedures

Synthetic procedures were performed under inert atmosphere using standard Schlenk techniques. Solvents were dried by standard methods and purged with nitrogen gas prior to use. Tetrahydrofuran (THF) was distilled from sodium/benzophenone, CH_2Cl_2 from P_4O_{10} and acetonitrile and hexane

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2c phencat²⁻ Fig. 1. Structures of ligands and complexes.

from CaH₂. The H₂ssp ligand and its *cis*-dioxo Mo(VI) complex, MoO₂(ssp), were prepared as described by Topich and Lyon [14]. Other synthetic reagents were purchased commercially and used without further purification. IR spectra were recorded in KBr pellets on a Bruker IFS 55 spectrometer. UV-Vis spectra were recorded in CH₂Cl₂ solution using a Beckman DU 640 spectrophotometer. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

Cyclic voltammetry measurements were carried out with a BAS-100A potentiostat employing a three-electrode cell configuration with a 0.071 cm² glassy carbon (GC) or 0.02 cm² Pt disk working electrode. The reference electrode was an aqueous Ag/AgCl half-cell, which was placed in a salt bridge containing the non-aqueous solvent and supporting electrolyte. Burdick and Jackson acetonitrile and Aldrich HPLC grade dichloromethane were used as received as electrochemical solvents. Tetra-*n*-butylammonium hexafluorophosphate (TBAPF₆) from SACHEM, Austin, TX was used as received as supporting electrolyte. The potential of the ferrocene/ferricenium couple (Fc^{+/0}) [15] was determined to be 0.421 V in CH₃CN (0.1 M TBAPF₆) and 0.487 V in CH₂Cl₂ (0.1 M TBAPF₆).

2.2. Syntheses

2.2.1. MoO(dtbcat)(ssp)

To 0.80 g (2.25 mmol) of $MoO_2(ssp)$ in 100 ml hot THF were added 2.0 ml (9.78 mmol) of $EtPh_2P$ in 30 ml THF. The mixture was refluxed for 1.5 h during which time the color of the solution changed from brown to reddish brown. The solution was allowed to cool, and a dark red-brown solid was collected by filtration. This solid was washed with THF and dried under vacuum. To a hot solution containing 0.40 g of the above solid in 70 ml CH₂Cl₂ was added 0.25 g (1.13 mmol) of 3,5-di-tert-butyl-1,2-benzoquinone in 20 ml CH₂Cl₂. The reaction mixture was refluxed for 2.0 h during which time its color changed from red-brown to deep purple. A light brown solid was identified as $Mo_2O_3(ssp)_2$ by elemental analysis. Anal. Calc. for $C_{26}H_{18}N_2O_3S_2Mo_2$: C, 44.97; H, 2.61; N, 4.03. Found: C, 43.46; H, 2.87; N, 4.03%. This was separated by filtration, and the purple solution was layered with hexane. After 3 days, 0.24 g of purple MoO(dtbcat)(ssp) was collected by filtration.

2.2.2. MoO(1,2-naphcat)(ssp) and MoO(phencat)(ssp)

These compounds were prepared following the method described for MoO(dtbcat)(ssp) employing 1,2-naphthoquinone and 9,10-phenanthrenequinone respectively. The compounds were recrystallized from CH_2Cl_2 /hexane as blue and burgundy solids respectively.

3. Results and discussion

3.1. Preparation and spectroscopic properties

MoO(cat)(ssp) complexes with catecholate ligands 2a-2c were prepared by oxo abstraction from MoO₂(ssp) with EtPh₂P in THF followed by oxidative addition of the appropriate quinone.

Table 1	
Analytical and spectroscopic data for MoO(cat)(ssp) complexes

Compound	Anal. Calc. (found) (%)			IR	UV-Vis*
	C	Н	N	ν _{Mo=O} (cm)	λ_{\max} (nm) (ε (M ⁻¹ cm ⁻¹))
MoO(dtbcat)(ssp)	57.96 (57.08)	5.22 (5.56)	2.50 (2.36)	922	552 (8000) 470sh (5400) 352 (17500)
MoO(1,2-naphcat)(ssp)	55.54 (53.21)	3.04 (2.77)	2.82 (2.47)	940	620 (9900) 472 (8400) 328 (17000)
MoO(phencat)(ssp)	59.23 (59.07)	3.13 (3.34)	2.56 (2.29)	947	612 (15000) 478 (8300) 352 (21300)

In CH₂Cl₂ solution.

$$Mo^{Vl}O_2(ssp) + EtPh_2P \rightarrow Mo^{V}O(ssp) + EtPh_2PO$$
 (1)

 $Mo^{V}O(ssp) + Mo^{V}O_2(ssp) \rightarrow Mo_2^VO_3(ssp)_2$ (2)

$$Mo^{IV}O(ssp) + Q \rightarrow Mo^{VI}O(cat)(ssp)$$
 (3)

The product of the oxo abstraction reaction was a reddish brown solid which did not give a satisfactory elemental analysis for MoO(ssp) or Mo₂O₃(ssp)₂ and was assumed to be a mixture of these two species. When quinone was added to this material in refluxing CH₂Cl₂, a light brown solid formed. The solid was separated by filtration and identified by elemental analysis to be Mo₂O₃(ssp)₂. The filtrate yielded purple MoO(dtbcat)(ssp), blue MoO(1,2-naphcat)(ssp) and burgundy MoO(phencat)(ssp) when layered with hexane.

Eqs. (1)-(3) are of interest with regard to the observations of Topich and Lyon [16] suggesting that the rate constant of Eq. (2) is very small compared with that of Eq. (1) which results in the formation of MoO(ssp) as the only product. In contrast, the work of Holm and coworkers [17] demonstrates that $Mo_2O_3(ssp)_2$ is formed stoichiometrically by the sum of Eqs. (1) and (2) from MoO₂(ssp) and MePh₂P in DMF. In our work, which differs from that of Topich and Lyon and of Holm and coworkers with regard to solvent, phosphine substituent and reactant ratio, we observe that the product of Eqs. (1) and (2) is a non-stoichiometric mixture of MoO(ssp) and $Mo_2O_3(ssp)_2$. We conclude that some MoO(ssp) must be produced by reaction of $MoO_2(ssp)$ with EtPh₂P under our conditions to afford the formation of MoO(cat)(ssp) via oxidative addition. This is consistent with the idea that Eq. (2) goes to equilibrium [18] allowing isolation of a mixture of MoO(ssp) and Mo₂O₃(ssp)₂. Oxidative addition (Eq. (3)) has been used previously to prepare MoO⁴⁺-catecholate species from o-quinones and oxomolybdenum(IV) complexes [19]. An alternative route to these compounds is neutralization of an MoO_2^{2+} center with protonated catechol [19,20]. This approach was followed in preparing MoO(cat)(sap) [9], but was not successful in the synthesis of MoO(cat)(ssp).

Analytical and spectroscopic data for the compounds are collected in Table 1. MoO(cat)(ssp) complexes exhibit an IR absorption band between 922 and 947 cm⁻¹ which is assigned to the Mo=O stretching vibration. This absorption falls at similar energies (930 to 939 cm⁻¹) in six-coordinate MoO(cat)(sap) complexes [9] and is slightly higher than the range of values (906 to 931 cm⁻¹) found in seven-coordinate MoO⁴⁺ species [19,20]. The MoO(cat)(ssp) complexes also exhibit a series of three electronic absorptions, among which the intermediate transition is the one of lowest intensity. The intense long-wavelength absorption at 552 to 620 nm parallels the observation of a similar feature ($\lambda_{max} \ge 500$ nm) in other MoO⁴⁺-catecholate complexes which has been attributed to catechol-to-Mo charge transfer [9,19,20].

3.2. Electrochemistry

The cyclic voltammetric behavior of MoO(cat)(ssp) complexes is illustrated in Fig. 2. In acetonitrile all three compounds exhibit a chemically reversible reduction at



Fig. 2. Cyclic voltammetric reductions at a GC electrode in CH₃CN/0.1 M TBAPF₆: (a) 0.50 mM MoO(dtbcat)(ssp), $\nu = 0.2 \text{ V s}^{-1}$; (b) 0.54 mM MoO(1,2-naphcat)(ssp), $\nu = 0.1 \text{ V s}^{-1}$. The voltammograms are plotted vs. an aqueous Ag/AgCl reference electrode, which exhibits a potential of -0.421 V vs. Fc^{+/0} under the experimental conditions.

Table 2			
Cyclic voltammetric data for	MoO(cat)(ssp)	and MoO(cat)(sap)	complexes a

Compound	Mo(VI/V)		Mo(V/IV)	cat ² /sq. E _{pa} (V)
	$E^{\circ\prime}$ (V) ($\Delta E_{\rm p}$ (mV))	i _{pa} /i _{pc}	$E_{\rm pc}$ (V)	
CHICN (0.1 M TBAPFA)				
MoO(dtbcat)(ssp)	-0.162 (74)	0.80 ^b	- 1.57	1.24
MoO(1.2-naphcat)(ssp)	-0.157 (75)	0.94	-1.03, -1.48	1.01
MoO(phencat)(ssp)	-0.240 (104)	0.88		0.91
MoO(dtbcat)(sap) ^c	-0.270 (68)	0.97	- 1.47	
CH ₂ Cl ₂ (0.1 M TBAPF ₆)				
MoO(dtbcat)(ssp)	-0.238 (78)	0.95		1.08 (150) ^a
MoO(1,2-naphcat)(ssp)	-0.194 (67)	0.90		1.11
MoO(phencat)(ssp)	-0.293 (86)	0.90		1.03

* Recorded at a GC (CH₃CN) or Pt (CH₂Cl₂) working electrode at v = 0.2 V s⁻¹.

^b Value influenced by reactant adsorption (see text).

^e Pt working electrode, from Ref. [9].

^d Reversible E° and ΔE_{p} .

 ~ -0.2 V versus Ag/AgCl which is assigned to Mo(VI/V) electron transfer and an irreversible oxidation at more positive potentials (not shown) which is attributed to removal of an electron from the coordinated catecholate ligand. MoO(dtbcat)(ssp) and MoO(1,2-naphcat)(ssp) also exhibit one or more quasi- to irreversible reductions at more negative potentials which are assigned to Mo(V/IV) electron transfer. These data are summarized in Table 2.

Plots of voltammetric peak current (i_p) versus square root of scan rate $(\nu^{1/2})$ for the first MoO(1,2-naphcat)(ssp) reduction in CH₃CN/0.1 M TBAPF₆ are linear and pass through the origin. The slope of these plots yields a peak current parameter of $i_{\rm p}/\nu^{1/2}AC = 870 \,\mu A \, {\rm s}^{1/2} \, {\rm V}^{-1/2} \, {\rm mM}^{-1}$ cm⁻², which is consistent with a one-electron transfer in this solvent [12]. In addition, the peak current ratio i_{pa}/i_{pc} is nearly equal to unity, and the peak potential separation of $\Delta E_{\rm p} = 75 \text{ mV}$ is only nominally larger than the 57 mV value anticipated for reversible one-electron transfer [21]. MoO(dtbcat)(ssp) and MoO(phencat)(ssp) exhibit similar behavior. For the former compound, values of $i_p/\nu^{1/2}AC$ increase and those of i_{pa}/i_{pc} decrease with increasing scan rate, results that are consistent with a small amount of reactant adsorption on the electrode surface [21]. Quantitative current data were not obtained for MoO(phencat)(ssp), which exhibits low solubility in CH₃CN. All three complexes are more soluble in CH₂Cl₂. A chemically reversible, one-electron transfer free of reactant adsorption is observed for the primary reduction of all three compounds in this solvent (Table 2).

The above results indicate that metal-centered reduction of MoO(cat)(ssp) complexes proceeds by the following oneelectron transfer:

$$Mo^{VO}(cat)(ssp) + e^{-} \Leftrightarrow Mo^{VO}(cat)(ssp)^{-}$$
 (4)

. . . .

In contrast to seven-coordinate MoO⁴⁺ complexes, this Mo(VI/V) electrode reaction exhibits a high degree of chemical and electrochemical reversibility. Molybdenum

 $4d_{xv}$ is the redox orbital for MoO^{4+/3+} electron transfer, and in the pseudo-octahedral geometry of MoO(cat)(ssp) and MoO(cat)(sap) (3, Fig. 1) partial filling of this orbital does not invoke destabilizing interactions with equatorial metalligand bonds. However, this occurs for seven-coordinate MoO⁴⁺ species which have pentagonal bipyramidal geometry [11]. Thus, the reversibility of electron transfer is influenced by the geometric disposition of ligands around the metal center.

The potential of Mo(VI/V) reduction is about 100 mV more positive for MoO(dtbcat)(ssp) than for MoO(dtbcat)-(sap) (Table 2). This result is in agreement with previous observations following replacement of O by S donors in transition metal compounds; positive shifts of $0.1-0.3 \vee in E^{\circ}$ are common [22-24]. The direction of the shift is consistent with greater stabilization of the lower oxidation state by S donor ligands.

Another effect of ligand composition on electrochemical behavior is illustrated in Fig. 2. Here, the initial electrode reaction of MoO(dtbcat)(ssp) is followed by a second electron transfer at a much more negative potential (Fig. 2(a)). This reaction is assigned to the irreversible one-electron reduction of MoO(dtbcat)(ssp)⁻:

$$Mo^{v}O(dtbcat)(ssp)^{-} + e^{-} \rightarrow Mo(IV)$$
 (5)

An analogous reaction is observed in the electrochemistry of MoO(cat)(sap) complexes [9,10]. However, Fig. 2(b) and Table 2 show that MoO(1,2-naphcat)(ssp)^{0/-} reduction is followed by two such waves, the first of which exhibits a degree of chemical reversibility. The current magnitude of each more negative wave is approximately one-half that of the initial one-electron reduction. An interpretation consistent with these observations is the formation in roughly equal proportions of two forms of Mo^VO(1,2-naphcat)(ssp)⁻ which are reduced at much different potentials. Although the additional wave could arise from an isomer of 3, a more plausible explanation is that the reaction at ~ -1.0 V in Fig. 2(b) corresponds to reduction of a species in which one donor atom has been detached or replaced by solvent. A 500 mV difference in reduction potentials is consistent with this structural change [12]. A similar process at about the same potential is discerned upon careful inspection of the MoO(dtbcat)(ssp) voltammogram. Thus, it is possible that the presence of an S donor ligand labilizes coordination reactions following reduction to Mo(V).

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