# Electrochemistry of Six- and Seven-coordinate MoO$^{4+}$ Complexes. A Dramatic Influence of Coordination Number on Electron Transfer Reversibility and Metal-centered Reduction Potential

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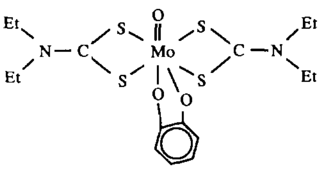
Changes in molecular structure can alter the electrochemical reactivity of transition metal complexes and thereby have important consequences on other properties of these materials. This is true particularly for compounds of molybdenum, whose oxo–metal functionalities occur in enzymatic [1] and industrial [2] catalysts carrying out atom and/or electron transfer reactions [3]. We wish to report an example in which a change in coordination number at the monooxomolybdenum(VI) (MoO$^{4+}$) center produces a dramatic influence on the electron transfer reversibility and reduction potential of Mo(VI) complexes.

We have described the preparation and electrochemistry of several series of MoO$^{4+}$ compounds [4], exemplified by MoO(cat)(S$_2$CNEt$_2$)$_2$ (1), which display seven-coordinate, pentagonal bipyramidal geometry. Mo(VI) to Mo(V) reduction of these species is irreversible, an observation we attribute to the fact that the Mo d$_{xy}$ orbital, which becomes singly occupied upon reduction to Mo(V), cannot orient its lobes among the five bonds in the equatorial plane of 1 without unfavorable electrostatic interaction. Consequently, metal–ligand bond cleavage accompanies electron transfer, causing reduction of the seven-coordinate MoO$^{4+}$ center to be irreversible.

We surmised that if an MoO$^{4+}$ complex could be prepared with four rather than five bonds in its equatorial plane, no change in coordination number need accompany electron transfer, and reversible Mo(VI)/Mo(V) electrochemistry would result. This structural requirement can be met by coordinating one tridentate plus one bidentate rather than three bidentate ligands to the monooxomolybdenum center. Thus, the six-coordinate complexes [MoO(cat)(Sap)] (Sap$^{2-}$ = *N*-salicylidene-2-aminophenolate; cat$^{2-}$ = Cat$^{2-}$ (2a), DTBcat$^{2-}$ (2b) and Naphcat$^{2-}$ (2c))[**] were prepared by reacting the molybdenum(VI) dimer [MoO$_2$(Sap)]$_2$ [5] with the appropriate catechol in chloroform, as shown in eqn. (1).



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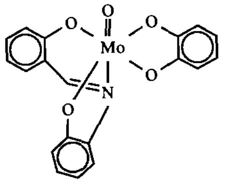

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$$[\mathrm{MoO_2(Sap)}]_2 + 2\mathrm{H_2cat} \longrightarrow 2[\mathrm{MoO(cat)(Sap)}] + 2\mathrm{H_2O} \qquad (1)$$

The synthesis and characterization of these complexes and the X-ray structural determination of the MoO(Naphcat)(Sap) derivative, confirming six-coordinate geometry about the MoO$^{4+}$ center, are being reported separately [6]. The present account describes how this change in coordination number influences the electrochemistry of the MoO$^{4+}$ center.

Figure 1a illustrates the cyclic voltammetric reduction of MoO(Cat)(S$_2$CNEt$_2$)$_2$ in acetonitrile. The metal-centered reduction at −1.28 V *versus* Fc$^+$/Fc is electrochemically irreversible by virtue of the fact that (a) no anodic peak is observed on the positive sweep, (b) the cathodic peak potential shifts in the negative direction with increasing sweep rate ($\Delta E_{\mathrm{pc}}/\Delta \log \nu = -85$ mV), and (c) the peak width ($E_{\mathrm{pc}} - E_{\mathrm{p/2}} = 135$ mV) is much greater than the value that is characteristic of reversible electron transfer. As detailed in ref. 4a and illustrated in Scheme 1, this behavior is attributed to the fact that cleavage of a metal–ligand bond and a concomitant change in coordination number accompany reduction of Mo(VI)[‡].

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[**] The catecholate ligands and their abbreviations are: Cat$^{2-}$ = catecholate, DTBcat$^{2-}$ = 3,5-di-tert-butylcatecholate and Naphcat$^{2-}$ = 2,3-naphthalene-2,3-diolate; cat$^{2-}$ is used as a general abbreviation for catecholate.

[‡] As further evidence of structural change accompanying electron transfer, we have recently reported [4c] heterogeneous electron transfer rates for reduction of [MoO(S$_2$CNEt$_2$)$_3$]$^+$ and four MoO(cat)(S$_2$CNEt$_2$)$_2$ complexes with variously substituted catecholate ligands. Rates of the MoO(cat)(S$_2$CNEt$_2$)$_2$ complexes are 10$^2$–10$^3$ times smaller than that of [MoO(S$_2$CNEt$_2$)$_3$]$^+$ and decrease as the electron donor strength of the catechol substituents increase. The need to distort (or cleave) successively stronger metal–ligand bonds in achieving the transition state of the electrode reaction apparently presents a larger activation energy barrier to electron transfer, thereby slowing the rate of the heterogeneous reaction. The circumstance is closely analogous to a recently reported example [7] involving electrochemical reduction of alkyl halides by dissociative electron transfer, where carbon–halogen bond-breaking accompanies electron transfer and the inner-shell activation energy of the electrode reaction can be correlated with the dissociation energy of the carbon–halogen bond.

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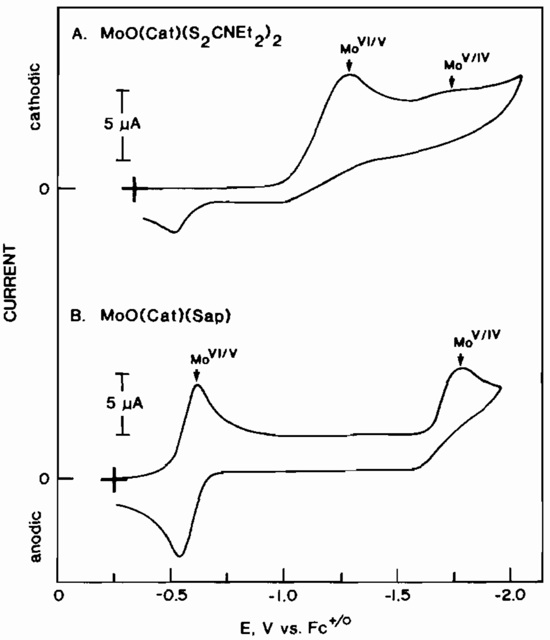


Fig. 1. Cyclic voltammograms recorded at 0.2 V $s^{-1}$ in 0.1 M $Bu_4NPF_6/CH_3CN$ at a Pt electrode: (a) 0.8 mM MoO(Cat)($S_2CNEt_2)_2$; (b) 0.7 mM MoO(Cat)(Sap).

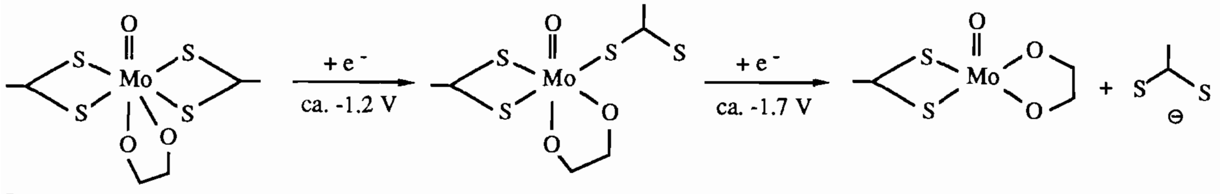
Cyclic voltammetric reduction of six-coordinate MoO(Cat)(Sap) exhibits dramatically different behavior (Fig. 1b). The metal-centered reduction at −0.58 V is chemically and electrochemically reversible: $E_{pc}$ is independent of sweep rate, $\Delta E_p = 66$ mV at $\nu = 0.2$ V $s^{-1}$, and $i_{pa}/i_{pc} = 0.98$. We attribute this behavior to the fact that no metal–ligand bonds need be broken in conjunction with electron transfer. The X-ray structure of MoO(Naphcat)(Sap) [6] confirms that Mo is six-coordinate and exists in a pseudo-octahedral environment. The four phenoxy groups of the $Naphcat^{2-}$ and $Sap^{2-}$ ligands define an equatorial plane from which the Mo(VI) atom is displaced by 0.29 Å toward the terminal oxo group. The bond angles in the equatorial $MoO_4$ set deviate from the ideal value of 90° because of ligand bite constraints, but the half-filled lobes of the Mo $d_{xy}$ orbital can now be oriented between the four Mo–O bonds without unfavorable interactions. Thus, our expectation that reversible metal-centered electrochemistry can be achieved by decreasing the coordination number of molybdenum is confirmed.

TABLE 1. $Mo^{VI/V}$ and $Mo^{V/IV}$ Reduction Potentials of MoO(cat)($S_2CNEt_2)_2$ and MoO(cat)(Sap) Complexes[a]

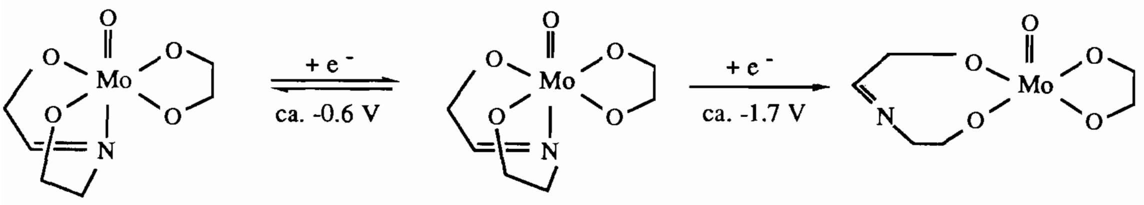
| Catecholate | MoO(cat)($S_2CNEt_2)_2$ | | MoO(cat)(Sap) | |
|---|---|---|---|---|
| | $Mo^{VI/V}$ [b] | $Mo^{V/IV}$ [b] | $Mo^{VI/V}$ [c] | $Mo^{V/IV}$ [b] |
| $Cat^{2-}$ | −1.28 | −1.73 | −0.58 | −1.79 |
| $Naphcat^{2-}$ | −1.09 | −1.44 | −0.51 | −1.65 |
| $DTBcat^{2-}$ | −1.24 | −1.56 | −0.69 | −1.89 |

[a] In V *vs.* $Fc^+/Fc$ measured by cyclic voltammetry in 0.1 M $Bu_4NPF_6/CH_3CN$ at a Pt electrode. [b] $E_{pc}$ at 0.2 V $s^{-1}$. [c] $E^{\circ\prime}$

A second clearly apparent effect of molecular structure on electrochemical properties is reflected in the potentials of the metal-centered redox steps. Table 1 compares the $Mo^{VI/V}$ reduction potentials of comparable MoO(cat)($S_2CNEt_2)_2$ and MoO(cat)(Sap) complexes. These occur at *ca.* −1.2 V *versus* $Fc^+/Fc$ for the seven-coordinate complexes and at *ca.* −0.6 V for the six-coordinate species. Ligands containing oxygen and nitrogen donor atoms are more electron donating than those containing sulfur and are known to produce substantial negative shifts in metal-centered reduction potentials [8]. However, the sulfur-rich MoO(cat)($S_2CNEt_2)_2$ complexes are



Scheme 1.



Scheme 2.

more difficult to reduce by *ca.* 0.6 V. Presumably, an even greater difference would result if the comparison could be made with complete parity of donor atoms. Therefore, we conclude that the decrease in coordination number from 7 to 6 also produces a significant positive shift in the Mo(VI) reduction potential.

Table 1 further compares potentials of $Mo^{V/IV}$ reduction for the $MoO(cat)(S_2CNEt_2)_2$ and MoO(cat)(Sap) species. As shown in Fig. 1 this reduction is irreversible for both complexes*. Since square-pyramidal geometry is the structural form most commonly associated with monooxomolybdenum(IV) [9], we have proposed [4a, b] that Mo(V) to Mo(IV) reduction proceeds with a change in coordination number from 6 to 5. This is illustrated in the second step of Schemes 1 and 2. Since six-coordinate species are reduced in both cases, approximately equal $Mo^{V/IV}$ redox potentials are observed. In fact, with equivalence of coordination number now achieved, slightly more negative values are observed for the MoO(cat)(Sap) derivatives in consonance with the greater O and N content of the donor atom set.

In conclusion, we have demonstrated that a difference in coordination number can have an important influence on the redox potential and electron transfer reversibility of oxomolybdenum centers. We believe this relationship may play an important role in regulating the electron transfer and catalytic propertires of such entities in enzymatic [1] and industrial [2] catalysts and in inorganic models [10] for such systems.

## Acknowledgement

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*The small size of the $Mo^{V/IV}$ reduction peak for $MoO(Cat)(S_2CNEt_2)_2$ is the result of a chemical reaction which consumes the Mo(V) electrode product following $Mo^{VI/V}$ reduction [4a]. A more prominent $Mo^{V/IV}$ reduction wave can be visualized by fast sweep rate cyclic voltammetry or normal pulse voltammetry.