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New Molybdenum(IV) Complexes. Syntheses and Properties

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Received January 16, 1980

The molybdenum enzymes xanthine oxidase, sulfite oxidase, and nitrate reductase catalyze the transfer of electrons between an electron donor or acceptor and substrate.[1,2] Current evidence suggests the molybdenum center undergoes an overall two-electron redox reaction, involving the +6 and +4 oxidation states.[1,3,4]

As part of a study of molybdenum complexes as models for these enzymes, we have recently reported the syntheses and properties of a number of molybdenum(VI)–dioxo and monomeric molybdenum(V)–oxo complexes.[5-7] We report here the synthesis and properties of molybdenum(IV)–oxo complexes with some of the same ligands, and a new nonoxo molybdenum(IV) complex.

Results and Discussion

Syntheses and Properties. As starting material, $MoOCl_2(MePPH_2)_3$ was used.[8] This leaves one $MePPh_2$ ligand in the product; this ligand, however, appears to be easily displaced by solvent and has little influence on the solution properties of the complexes. These Mo(IV) complexes are very sensitive to O_2 and H_2O in solution and must be carefully handled to prevent oxidation and decomposition. Except for the 8-mercaptoquinoline complex, they are reasonably stable in the solid state; storage for periods longer than a few days, however, should be under vacuum.

Molybdenum(V)–oxo complexes are readily reduced in a one-electron reduction to Mo(IV) complexes at a platinum cathode in DMF.[6] The visible electronic spectra of these reduction products have been reported.[6] The molybdenum(IV)–oxo complexes prepared here differ in color in the solid state from the solutions of the products obtained in the electrochemical reduction of the corresponding Mo(V) complexes; upon solution in DMF, however, their visible electronic spectra are identical with the spectra of the products obtained upon reduction of the Mo(V) complexes.[6] This change in color is likely due to the loss of the weakly bound $MePPh_2$ ligand, possibly with replacement by DMF. Furthermore, rapid coulometric oxidation to Mo(V) followed by rereduction to Mo(IV) also gives solutions with visible spectra identical with those obtained by reduction of the corresponding Mo(V) complexes.[6]

Attempts to synthesize $(Et_4N)MoO(tdt)_2$[9] resulted in the formation of the nonoxo complex $(Et_4N)_2Mo(tdt)_3$. Similar results have been reported for the Mo(VI) complex of *o*-aminobenzenethiol.[10]

Table I. Properties of Complexes

complex	E_{p_a}[a]	E_{p_c}[b]	ΔE[c]	n[d]	ν(MoO), cm^{-1}
$MoOCl_2(bpy)(MePPh_2)$	−0.220	−0.290	0.070	0.95	959
$MoOCl_2(phen)(MePPh_2)$	−0.200	−0.275	0.075	0.96	962
$MoO(ox)_2(MePPh_2)$	−0.435	−0.510	0.075	0.88	928
$MoO(tox)_2(MePPh_2)$	−0.410	+0.255	0.665	1.04	990
$(Et_4N)_2Mo(tdt)_3$	−0.345	−0.405	0.060	0.92	-

[a] Oxidation peak; cyclic voltammogram; V vs. SCE; standard deviation ±0.015 V. 0.10 M Et_4NCl in DMF; scan rate 0.100 V/s. [b] Reduction peak. [c] Difference between E_{p_a} and E_{p_c}, V. [d] Electrons/molecule for oxidation; average of two or more determinations; standard deviation ±0.05.

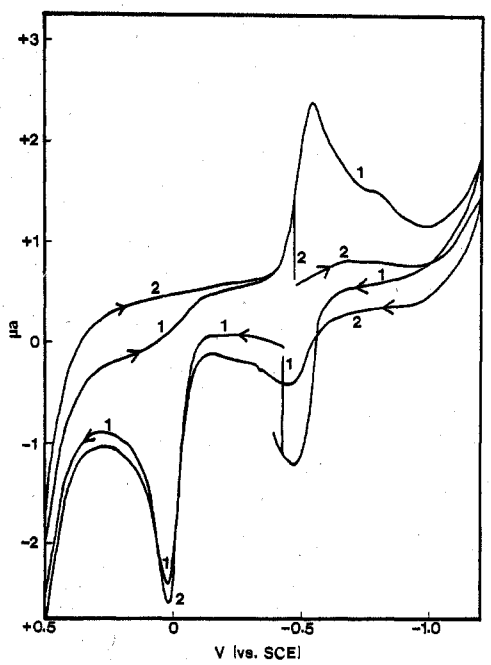

Figure 1. Cyclic voltammogram of $MoO(ox_2)(MePPh_2)$ (5.00×10^{-4} M in DMF, 0.10 M Et_4NCl): (1) anodic scan, beginning at −0.400 V; (2) cathodic scan, beginning at −0.450 V. The scan rate is 0.100 V/s.

Electrochemistry. Cyclic voltammograms show an oxidation peak when scanned in an anodic direction and a reduction peak coupled to the oxidation peak when scanned in the cathodic direction after anodic scanning. Initial cathodic scans show no reduction peaks. With the exception of $MoO(ox)_2(MePPh_2)$,[9] the potentials of the peaks are identical within experimental error to the potentials reported for the corresponding Mo(V) complexes,[6] and controlled coulometric oxidation at potentials slightly more positive than the oxidation peaks indicates the oxidations are one-electron processes.[6] It should be noted three of the oxo complexes undergo essentially reversible electron transfer (Table I). As with the Mo(V) complexes,[6] no oxidation to Mo(VI) complexes was observed in the voltage range used. These Mo(IV) complexes appear to be identical in all respects in solution to the reduction products of corresponding Mo(V) complexes and are oxidized electrochemically to identical Mo(V) complexes.[6]

Immediately upon solution, $MoO(ox)_2(MePPh_2)$ gives a cyclic voltammogram with two oxidation peaks but only one reduction peak (Figure 1). The reduction peak at −0.510 V is coupled to the oxidation peak at −0.435 V. When the

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(9) Ligand abbreviations: phen = *o*-phenanthroline; bpy = α,α'-bipyridyl; ox = 8-hydroxyquinoline; tox = 8-mercaptoquinoline; tdt = 3,4-dimercaptotoluene.
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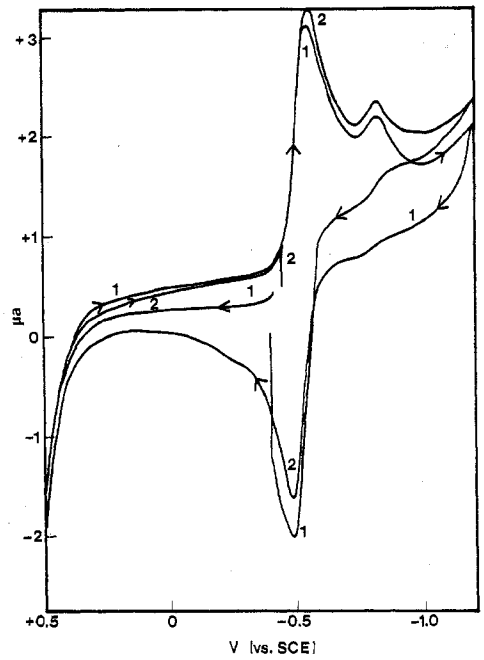

Figure 2. Cyclic voltammogram of $MoO(ox)_2(MePPh_2)$, after one-electron oxidation at +0.07 V (5.00×10^{-4} M in DMF, 0.10 M Et_4NCl): (1) anodic scan, beginning at −0.400 V; (2) cathodic scan, beginning at −0.450 V.

solution is allowed to stand, the oxidation peak at 0.037 V decreases in height at the expense of the oxidation peak at −0.435 V. After one-electron coulometric oxidation at 0.070 V, only the oxidation peak at −0.435 V remains (Figure 2); this peak and the reduction peak at −0.510 V are identical with those of $MoOCl(ox)_2$.[6] This is most likely due to the slow loss of the coordinated $MePPh_2$ ligand. Oxidation to the Mo(V) complex produces $MoOCl(ox)_2$, and subsequent rereduction gives only the Mo(IV) complex without $MePPh_2$. The changes in the cyclic voltammogram correspond in time to the changes noted above in the visible electronic spectrum for $MoO(ox)_2(MePPh_2)$ upon solution in DMF. For the other Mo(IV) complexes, the loss of coordinated $MePPh_2$ is apparently too rapid to observe during cyclic voltammetry.

Infrared Spectra. The infrared absorption frequencies for the MoO bands are found in the Table I. They occur at somewhat higher frequencies than the MoO bands of the molybdenum(V)–oxo or molybdenum(VI)–dioxo complexes.[11]

The $MoOCl_2L(MePPh_2)$ and $MoOL_2(MePPh_2)$ complexes described here form electron-transfer couples with the corresponding molybdenum(V)–oxo complexes $MoOCl_3L$ and $MoOClL_2$. The results are in agreement with the hypothesis of molybdenum(IV)–oxo and molybdenum(V))–oxo complexes being involved in rapid electron transfer at the molybdenum center of the molybdenum oxidases and nitrate reductase.[1-3]

Experimental Section

Materials. All solvents were spectrograde or were distilled before use. Et_3N, 8-aminoquinoline, Et_4NCl, and 8-hydroxyquinoline were purchased from Eastman, α,α'-bipyridyl and *o*-phenanthroline were from Aldrich, and $MePPh_2$ was purchased from Strem Chemicals.

Syntheses. C_9H_7NS·HCl (8-Mercaptoquinoline Hydrochloride). This ligand was synthesized according to the method of Kealey and Freiser.[12]

$MoOCl_2(bpy)(MePPh_2)$. This complex was prepared by addition of 0.50 g of α,α'-bipyridyl in 50.0 mL of dry EtOH to an equal volume of a hot solution equimolar in $MoOCl_2(MePPh_2)_3$ in dry EtOH, followed by gentle heating for 2 h under N_2. The solution was cooled and filtered, and the dark purple precipitate was washed with two 10-mL portions of pentane under N_2 and dried in vacuo overnight. Anal. Calcd for $MoC_{23}H_{21}Cl_2N_2OP$: C, 51,23; H, 3.93; Cl, 13.15; N, 5.19; P 5.74. Found: C, 50.73; H, 3.86; Cl, 13.28; N, 4.73; P, 5.36.

$MoOCl_2(phen)(MePPh_2)$. This complex was prepared in the same manner as $MoOCl_2(bpy)(MePPh_2)$. Anal. Calcd for $MoC_{25}H_{21}Cl_2N_2OP$: C, 53.51; H, 3.76; Cl, 12.59; N, 4.97; P, 5.50. Found: C, 52.48; H, 3.87; Cl, 12.30; N, 4.64; P, 5.84.

$MoO(ox)_2(MePPh_2)$. This complex was prepared by adding 25.0 mL of a dry EtOH slurry containing 1.70 g of $MoOCl_2(MePPh_2)_2$ to 1.13 g of 8-hydroxyquinoline and 0.80 mL of Et_3N (distilled) in 35.0 mL of dry EtOH. After being heated at rapid reflux under N_2 for 12 h, the solution was cooled, the deep wine precipitate was filtered, washed with two 10-mL portions of anhydrous diethyl ether, and dried in vacuo overnight. Anal. Calcd for $MoC_{31}H_{25}N_2O_3P$: C, 62.01; H, 4.20; N, 4.67; P, 5.16. Found: C, 61.77; H, 4.24; N, 4.73; P, 4.97.

$MoO(tox)_2(MePPh_2)$. This complex was prepared by adding 50.0 mL of dry CH_3CN containing 0.93 g of C_9H_7NS·HCl and 1.00 mL of Et_3N (distilled) to a slurry of 1.38 g of $MoOCl_2(MePPh_2)_3$ in 35.0 mL of dry CH_3CN. After the solution was stirred for 12 h at room temperature under N_2, the black-green precipitate was removed by filtration, washed with two 10-mL portions of anydrous diethyl ether, and dried in vacuo for 2 h. Anal. Calcd for $MoC_{31}H_{25}N_2OPS_2$: C, 58.66; H, 3.98; N, 4.43; P, 4.90; S, 10.14. Found: C, 56.53; H, 3.93; N, 4.35; P, 4.59; S, 9.60. This compound is unstable and must be stored under vacuum.

$(Et_4N)_2Mo(tdt)_3$. This complex was prepared by addition of a slurry of 0.665 g of $MoOCl_2(MePPh_2)_3$ in 25.0 mL of dry CH_3CN to 50.0 mL of a solution containing 0.350 g of 3,4-dimercaptotoluene and 0.45 mL of Et_3N (distilled) in dry CH_3CN. The mixture was stirred overnight at room temperature under N_2, 0.27 g of Et_4NCl was added, and the stirring was continued for 1 h. The bright blue precipitate was filtered, rinsed with three 10-mL portions of anhydrous diethyl ether, and dried in vacuo overnight. Anal. Calcd for $MoC_{37}H_{58}N_2S_6$: C, 54.25; H, 7.14; N, 3.42; S, 23.48. Found: C, 53.44; H, 7.33; N, 3.40; S, 22.11.

Electrochemical Measurements. Cyclic voltammetry and controlled-potential coulometry were performed as described previously.[7]

Acknowledgment. This work was supported by Grant GM 08347, National Institutes of Health.

Registry No. $MoOCl_2(bpy)(MePPh_2)$, 73953-23-8; $MoOCl_2(phen)(MePPh_2)$, 73953-24-9; $MoO(ox)_2(MePPh_2)$, 73953-25-0; $MoO(tox)_2(MePPh_2)$, 73953-26-1; $(Et_4N)_2Mo(tdt)_3$, 73970-85-1; $MoOCl_2(MePPh_2)_3$, 30859-03-1.

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Synthesis of Methylhydrazine and 1,1-Dimethylhydrazine by the Reactions of Hydroxylamine-*O*-sulfonic Acid with Methyl- and Dimethylamine

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Received February 13, 1980

Interest in the synthesis of methylhydrazine and 1,1-dimethylhydrazine in nonaqueous solvents led us to investigate the reactions of hydroxylamine-*O*-sulfonic acid with methylamine and dimethylamine. Amination of primary and secondary amines by hydroxylamine-*O*-sulfonic acid forming the corresponding hydrazines is a known reaction.[1-3] Although there is apparently no report on the synthesis of 1,1-dimethylhydrazine by this method, methylhydrazine has been synthesized by the reaction of hydroxylamine-*O*-sulfonic acid

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