Contribution from the Department of Chemistry and Biochemistry, Utah State University, Logan, Utah 84322, and the Department of Chemistry, University of New Hampshire, Durham, New Hampshire 03824

Reduction of Nitrate by Monomeric Molybdenum(V) Complexes in Dimethylformamide[1]

R. D. TAYLOR,[2a] P. G. TODD,[2a] N. D. CHASTEEN,[2b] and J. T. SPENCE*[2a]

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As a model system for the molybdenum enzyme nitrate reductase, the reduction of NO_3^- by monomeric Mo(V) complexes of the formulas $MoOCl_3L$ (L = α,α'-bipyridyl, *o*-phenanthroline), $MoOClL_2$ (L = 8-hydroxyquinoline, 8-mercaptoquinoline), $MoOCl(CH_3OH)L$ (L = *o*-(salicylidenimino)phenol), and MoOClL (L = *o*-bis(salicylidenimino)benzene) has been investigated. The complexes, with the exception of MoOClL, reduce NO_3^- in a one-electron step with complex kinetics, producing NO_2 and the corresponding Mo(VI) compound. A general mechanism is proposed involving preliminary dissociation of a Cl^-, followed by intermediate formation of a molybdenum(V)–nitrate complex coordinated cis to the oxo group, which subsequently undergoes transfer of an oxo group. Possible applications to enzymatic nitrate reduction are discussed.

Introduction

The reduction of nitrate to nitrite by plants and microorganisms is catalyzed by a group of molybdenum enzymes, the nitrate reductases.[3] Recent ESR (electron spin resonance) studies of these enzymes have detected the presence of Mo(V) during the catalytic cycle, and this oxidation state appears a likely choice for the metal center of the reduced enzyme.[4,5]

Previous model studies have shown only monomeric Mo(V) is capable of nitrate reduction[6] and Mo(V) species exist primarily (>99%) as ESR-inactive dimers in aqueous solution.[7] Furthermore, reduction in aqueous solution proceeds to NO,[6] in contrast to the enzymatic process which produces nitrite. In aprotic solvents, however, monomeric Mo(V) complexes are stable, and recent work has shown NO_2, which disproportionates to NO_3^- and NO_2^- in the presence of water, is the reduction product in such solvents.[8,9]

As a possible model system for the nitrate reductases, we have recently reported the results of a kinetic study of the reduction of NO_3^- by $(NH_4)_2MoOCl_5$ in anhydrous dimethylformamide (DMF).[8] The reduction was found to be first order in each reactant and to be inhibited by Cl^-. A mechanism involving the formation of an intermediate $MoOCl_3(NO_3)^-$ complex, followed by intramolecular electron transfer, was developed to explain the results. In order to obtain more information concerning possible enzymatic mechanisms, the reduction of nitrate by the monomeric Mo(V) complexes $MoOCl_3L$ (L = α,α'-bipyridyl, *o*-phenanthroline), $MoOClL_2$ (L = 8-hydroxyquinoline, 8-mercaptoquinoline), $MoOCl(CH_3OH)L$ (L = *o*-(salicylidenimino)phenol), and MoOClL (L = *o*-bis(salicylidenimino)benzene) in anhydrous DMF has been investigated and the results are reported here.[10]

Experimental Section

Materials. $(NH_4)_2MoOCl_5$ was prepared as previously described.[11] α,α'-Bipyridyl and *o*-phenanthroline were obtained from Aldrich, 8-hydroxyquinoline, tetraethylammonium nitrate, and tetraethylammonium chloride were purchased from Eastman, *o*-(salicylidenimino)phenol was obtained from Pfaltz and Bauer, *o*-phenylenediamine and $Na_2MoO_4{\cdot}2H_2O$ were obtained from Baker, salicylaldehyde came from Brothers Chemicals, and 8-mercaptoquinoline hydrochloride was obtained from K & K Laboratories. All chemicals were reagent grade.

DMF was purified and dried as previously described[8] and dry ethanol was distilled from a mixture of magnesium turnings and absolute ethanol to which a small amount of iodine had been added. Prepurified N_2 (99.99%) was used for deaerating all solutions.

Preparation of Complexes. *trans*-**$MoOCl_3$(bpy) (Green).** This complex was prepared by the method of Saha and Halder[12] and a product giving a satisfactory C, H, N, and Cl analysis was obtained.

cis-**$MoOCl_3$(bpy) (Red).** This complex was prepared by adding 0.40 g of $(NH_4)_2MoOCl_5$ and 0.20 g of α,α'-bipyridyl to 30 mL of dry, deaerated DMF. After being stirred under N_2 for 1 h, the solution was cooled in an ice bath and filtered with vacuum under N_2 into 150 mL of cold 6 N HCl. A reddish pink solid precipitated immediately in the filter flask. The precipitate and filtrate were cooled in an ice bath, and the precipitate was collected on a sintered glass filter. Two grams of the precipitate was refluxed in 30 mL of 6 N HCl under N_2 for 24 h. The reddish pink mixture was cooled in an ice bath for 30 min, and the precipitate was collected on a sintered glass filter under vacuum, washed with 60 mL of cold 6 N deaerated HCl, and dried in vacuo over KOH. This procedure was found to give a considerably better product than the procedure described by Saha and Halder,[12] with a satisfactory C, H, N, and Cl analysis.

cis-**$MoOCl_3$(phen).** A synthesis of this complex has been described by Saha and Halder,[13] but it gave an impure product. A preparation giving a satisfactory C, H, N, and Cl analysis was obtained by mixing a deaerated solution of 1.00 g of $(NH_4)_2MoOCl_5$ in dry ethanol (40 mL) with a deaerated solution of 1.20 g of *o*-phenanthroline in 10 mL of dry ethanol. An immediate reddish brown precipitate was formed. After the mixture was allowed to stand under N_2 for 1 h, the precipitate was collected under vacuum on a sintered glass filter. Two grams of the precipitate was refluxed in 30 mL of 6 N HCl under N_2 for 24 h. The reddish pink mixture was cooled in an ice bath for 30 min, and the precipitate was collected on a sintered glass filter under vacuum, washed with 60 mL of cold 6 N deaerated HCl, and dried in vacuo over KOH.

trans-**MoOCl(ox)$_2$.** This complex was prepared by the method of Dutta and Chatterjee[14] and gave a product having a satisfactory C, H, N, and Cl analysis.

trans-**MoOCl(tox)$_2$.** This new complex was synthesized by adding 0.083 g of 8-mercaptoquinoline hydrochloride, in 10 mL of dry, dearated ethanol, to a filtered solution of 0.065 g of $(NH_4)_2MoOCl_5$ in 10 mL of dry, deaerated ethanol. After 1 h of stirring under N_2, the mixture was cooled in an ice bath for 2 h under N_2 and then filtered under vacuum on a sintered glass filter; the resulting dark brown-black product was dried in vacuo over KOH. Anal. Calcd for $MoOCl(C_{18}H_{12}N_2S_2)$: C, 46.21; H, 2.59; N, 5.99; Cl, 7.58; S, 13.71, Found: C, 46.38; H, 2.66; N, 5.95; Cl, 7.47; S, 13.86.

trans-**MoOCl(CH_3OH)(sip).** This complex was prepared by a procedure developed by Enemark and Yamanouchi[15] and gave a product with a satisfactory C, H, N, and Cl analysis.

cis-**MoOCl(sal$_2$phen).** A procedure modified from that reported by Dilworth et al.,[16] was used to prepare this complex. The dilithium salt of *o*-bis(salicylidenimino)benzene (obtained according to the method of Dilworth et al.[16]) was prepared by suspending 1.58 g of the ligand in 15 mL of dry ethanol and adding this to 17 mL of a solution of 0.15 g of lithium metal in dry ethanol. The ligand dissolved immediately, and shortly thereafter, the yellow dilithium salt precipitated. After 30 min of stirring, the precipitate was collected on a sintered glass filter under vacuum and dried over P_2O_5 in vacuo. The complex was prepared by suspending 1.64 g of the dilithium salt of the ligand in 80 mL of dry, deaerated ethanol and adding a filtered solution of 1.79 g of $(NH_4)_2MoOCl_5$ in 40 mL of dry, deaerated ethanol. The mixture turned brown immediately. After refluxing under N_2 for 30 min, the precipitate was collected on a sintered glass filter under vacuum, rinsed twice with small portions of dry ethanol and dry ether, and dried over P_2O_5 in vacuo. A product with a satisfactory analysis for C, H, N, and Cl was obtained.

MoO_2(ox)$_2$. This complex was prepared by the method of Fleck and Ward,[17] giving a product with a satisfactory analysis for C, H, and N.

MoO_2(tox)$_2$. This new complex was prepared by the method as described by Fleck and Ward for $MoO_2(ox)_2$,[17] using 8-mercapto-

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quinoline instead of 8-hydroxyquinoline. Anal. Calcd for $MoO_2(C_{18}H_{12}N_2S_2)$: C, 48.22; H, 2.70; N, 6.25; S, 14.30. Found: C, 49.31; H, 2.82; N, 6.44; S, 13.79.

MoO_2(sip). This new complex was synthesized by adding 0.53 g of *o*-(salicylidenimino)phenol to 60 mL of 2 M NaOH solution. $Na_2MoO_4 \cdot 2H_2O$, 0.70 g, dissolved in 20 mL of H_2O was then added to the ligand solution followed by dropwise addition of concentrated HCl until a yellow precipitate formed. After the solution was allowed to stand for a short time, the yellow precipitate was collected on a sintered glass filter under vacuum, washed with water, and dried in vacuo over P_2O_5. Anal. Calcd for $MoO_2(C_{13}H_9NO_2)$: C, 46.04; H, 2.67; N, 4.13. Found: C, 46.78; H, 2.97; N, 4.46.

ESR Measurements. Quantitative ESR measurements were made of DMF solutions of complexes (5.00×10^{-4}–1.00×10^{-3} M) at −195 °C to determine the monomeric content of the complexes. ESR spectra, recorded on a Varian V-4500 spectrometer, were doubly integrated to determine spin concentrations. $K_3Mo(CN)_8$ was used as a standard for comparison. The average value for the complexes was found to be 98 ± 12% monomer, a satisfactory result considering the errors inherent in this technique.

For structural determination, the ESR spectra of $MoOCl(ox)_2$ in DMF was recorded at both X-band (9.2 GHz) and Q-band (35 GHz) frequencies using Varian E-4 and E-9 spectrometers, respectively. Spectra of frozen solutions (77 and 110 K for X- and Q-band spectra, respectively) were simulated on a DEC-10 computer using a modified version of the program described by White and Belford.[18] This program uses perturbation formulas and has the provision for two noncoincident principal axes of the **g** and nuclear hyperfine tensors, g_z and A_z being coincident.[19]

Methods. Product analysis was accomplished by comparing the electronic spectra of the reaction mixtures at t_∞ with spectra of authentic samples of the corresponding Mo(VI) complexes, $MoO_2(ox)_2$, $MoO_2(tox)_2$, and MoO_2(sip). Since attempts to synthesize the MoO_2Cl_2L complexes were unsuccessful, solutions containing MoO_2Cl_2 and the appropriate ligand were prepared and used for identification in these cases.

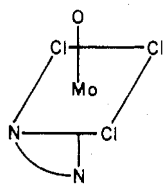
The general techniques and nitrite analysis have been previously described.[8] Kinetic measurements were made by following the decrease in absorbance of the Mo(V) complex at an appropriate wavelength using a recording spectrophotometer. Extreme care was exercised to prevent absorption of O_2 or H_2O by stock solutions, reaction mixtures, and solvents, since these species react with the Mo(V) complexes, giving irreproducible results.

All kinetic data were treated with appropriate programs on a PDP-8 computer to obtain best values of rate constants.

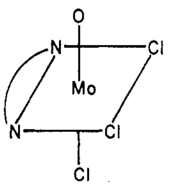
Results

Structures of the Complexes. All but one of the complexes ($MoOCl(sal_2phen)$) can exist in two geometrical isomers with respect to the species coordinated in the position trans to the MoO (oxo) group. Since the rate and mechanism of the reaction with NO_3^- appear to depend on this geometry, attempts were made to obtain unambiguous proof of structure.

$MoOCl_3$(bpy) (green), $MoOCl_3$(bpy) (red), and $MoOCl_3$(phen) (red) have been assigned trans, cis, and cis geometries (structures **1** and **2**), respectively, by Saha and Halder on the basis of conductivity and reactivity measurements[12,13] (cis and trans refer to the position of the chelate ligand with respect to the oxo group). We have repeated their conductivity work and our results are in good agreement with theirs. The green $MoOCl_3$(bpy) has recently been shown by X-ray crystallography to have the trans structure[15] (**1**). It is highly probable the red isomers have, therefore, the cis geometry (**2**), although attempts to grow suitable crystals for X-ray analysis of these compounds have as yet been unsuccessful (Saha and Halder also prepared a green $MoOCl_3$(phen) isomer[13]).



1
trans-$MoOCl_3$(bpy)



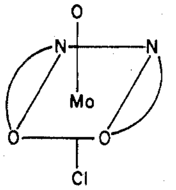
2
cis-$MoOCl_3$L
(L = bpy, phen)

Table I. ESR Parameters for $MoOCl(ox)_2$[a]

g_x	1.971 ± 0.001	A_x	51.4 (2.0)
g_y	1.953 ± 0.001	A_y	10.0 (1.0)
g_z	1.940 ± 0.001	A_z	80.6 (1.0)
g_0[b]	1.955 ± 0.001	A_0[b]	47.4 ± 1.4
g'_0[c]	1.953 ± 0.001	A'_0[c]	47.4 ± 0.1

[a] Hyperfine splitting (A) in gauss. [b] $g_0 = (g_x + g_y + g_z)/3$; $g_0A_0 = (g_xA_x + g_yA_y + g_zA_z)/3$. [c] g'_0 and A'_0 are measured values (X band, room temperature).

Evidence for the structure of $MoOCl(ox)_2$ comes primarily from ESR measurements. With frozen-solution samples, Q-band measurements have the advantage of being more sensitive to **g** anisotropy and noncoincident axes of **g** and nuclear hyperfine tensors than those at X-band. A detailed analysis of the spectra at the two frequencies with the assistance of computer simulation techniques indicates that none of the principal magnetic axes, g_x, and A_x, g_y and A_y, or g_z and A_z, are coincident for $MoOCl(ox)_2$. The principal g values (Table I) can be reliably obtained from the Q-band lines of the ^{96}Mo (I = 0) isotope present in 75% abundance. The nuclear hyperfine parameters of the $I = {}^5/_2$ isotopes (Table I) were derived from the X-band spectrum where the effects of noncoincidence are minimal. Agreement between calculated and measured isotropic coupling constants, A_0 and A'_0, is good (Table I). The presence of completely noncoincident magnetic tensors requires that the complex can have no mirror planes or rotation axes. For the two possible cis isomers (**3** and **4**), **3** has a mirror plane and **4** has a C_2 rotation axis, making them unlikely structures. Of the four possible trans isomers, **5** is perhaps the most probable, since the corresponding Mo(VI) dioxo complex has this arrangement, as determined by X-ray crystallography.[20] For consideration of the mechanism, it is necessary, however, to know only whether the complex is cis or trans.



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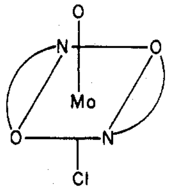

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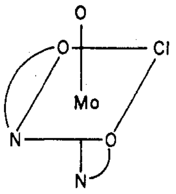
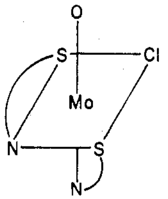


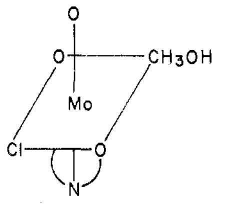
5

The $MoOCl(tox)_2$ complex has recently been shown by X-ray crystallography to have structure **6**, with the two S atoms in a trans arrangement.[15]



6

The electronic and ESR spectra, and the cyclic voltammogram in DMF for $MoOCl(CH_3OH)$(sip) are identical with the spectra and cyclic voltammogram of $Et_4NMoOCl_2$(sip), which has been shown by X-ray crystallography to be the trans isomer, with the two Cl atoms cis to the oxo group and trans to each other.[15] It is, therefore, highly likely $MoOCl(CH_3OH)$(sip) has the same geometry, with a Cl^- replaced by CH_3OH (**7**).



7

For MoOCl(sal$_2$phen) only one structure (cis) is possible, due to the rigid planar structure of the tetradentate ligand, with Cl$^-$ trans to the oxo group.[16]

Stoichiometry of the Reaction with NO$_3^-$. The stoichiometry was determined by allowing the reactions (in anhydrous DMF) to go essentially to completion, as measured by the decrease in absorbance of the Mo(V) complex, under conditions in which NO$_2$ was not removed by purging with N$_2$. The reaction mixtures were then analyzed for nitrite, which is formed by disproportionation of NO$_2$ in acidic aqueous solution:

$$H_2O + 2NO_2 \rightleftharpoons HNO_2 + NO_3^- + H^+$$

The ratio of Mo(V) complex reacted to HNO$_2$ formed, for six of the seven complexes, was found to be 2.22 ± 0.14. An almost identical result was found for the reduction of NO$_3^-$ by (NH$_4$)$_2$MoOCl$_5$.[8]

The stoichiometric equations may thus be written

$$MoOCl_3L + NO_3^- \rightarrow MoO_2Cl_2L + NO_2 + Cl^-$$

$$MoOClL_2 + NO_3^- \rightarrow MoO_2L_2 + NO_2 + Cl^-$$

$$MoOCl(CH_3OH)(sip) + NO_3^- \rightarrow MoO_2(sip) + NO_2 + CH_3OH + Cl^-$$

(It is likely a solvent DMF is also coordinated to MoO$_2$(sip). Preparation of this complex in H$_2$O, however, gives the five-coordinate species.)

Kinetics. MoOCl$_3$(bpy), MoOCl$_3$(*o*-phen), and MoOCl(ox)$_2$. In the presence of excess NO$_3^-$, plots of ln absorbance (A) vs. time (t) for the disappearance of the Mo(V) complexes show some departure from linearity with a decreasing slope; this departure is greatest for the two trans complexes (*trans*-MoOCl$_3$(bpy) and *trans*-MoOCl(ox)$_2$) and is barely discernible for *cis*-MoOCl$_3$(bpy). Furthermore, this departure increases for each complex with increasing [Mo(V)]/[NO$_3^-$] ratio. As the NO$_3^-$ concentration is increased, the rates increase, but not linearly.

In the presence of added Cl$^-$ (excess) and excess NO$_3^-$, excellent plots of ln A vs. t are obtained for at least 3 half-lives, and the rates decrease with increasing Cl$^-$ concentration, indicating Cl$^-$ is an inhibitor. These results may be expressed by the rate law

$$-d[Mo(V)]/dt = a[NO_3^-][Mo(V)]/(b[Cl^-] + [NO_3^-])$$

In the absence of added Cl$^-$, the first term in the denominator is not constant (see stoichiometry) accounting for the deviation in the ln A vs. t plots. In the presence of added Cl$^-$ (excess) and excess NO$_3^-$, this expression becomes an ordinary first-order rate expression:

$$-d[Mo(V)]/dt = k_{obsd}[Mo(V)]$$

$$k_{obsd} = a[NO_3^-]/(b[Cl^-] + [NO_3^-])$$

If the rate expression is correct, a plot of $1/k_{obsd}$ vs. [Cl$^-$] at constant NO$_3^-$ concentration should be a straight line, from the slope and intercept of which the values of a and b may be obtained:

$$1/k_{obsd} = b[Cl^-]/a[NO_3^-] + 1/a$$

Figure 1 shows this is indeed the case, and the values of a and b, obtained from the plots, are found in Table II.

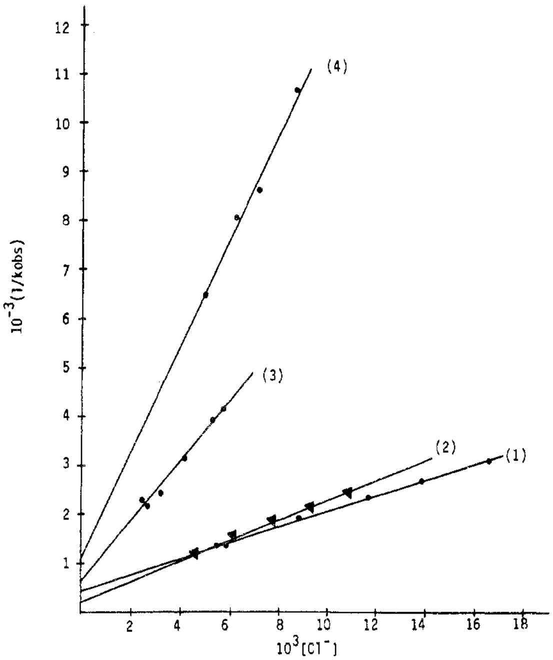


Figure 1. Reduction of NO$_3^-$ by Mo(V) complexes in presence of excess [Cl$^-$]. Plots of $1/k_{obsd}$ vs. [Cl$^-$] (25.0 °C, DMF): (1) *cis*-MoOCl$_3$(bpy), [NO$_3^-$] = 5.05 × 10^{-2} M, [Mo(V)]$_0$ = 3.51 × 10^{-4} M; (2) *cis*-MoOCl$_3$(phen), [NO$_3^-$] = 5.03 × 10^{-2} M, [Mo(V)]$_0$ = 4.72 × 10^{-4} M; (3) *trans*-MoOCl(ox)$_2$, [NO$_3^-$] = 5.00 × 10^{-2} M, [Mo(V)]$_0$ = 4.45 × 10^{-4} M; (4) *trans*-MoOCl$_3$(bpy), [NO$_3^-$] = 5.16 × 10^{-2} M, [Mo(V)]$_0$ = 2.16 × 10^{-4} M.

Table II. Values of a and b for the Rate Expression $-d[Mo(V)]/dt = a[Mo(V)][NO_3^-]/(b[Cl^-] + NO_3^-)$[a]

	excess [Cl$^-$] present[b]		from integrated rate expression[c]	
complex	a, s^{-1} × 10^3	b	a, s^{-1} × 10^3	b
cis-MoOCl$_3$(phen)	3.52 ± 0.43	35.2 ± 4.3	4.94 ± 1.54[d]	115 ± 95[d]
cis-MoOCl$_3$(bpy)	2.44 ± 0.24	20.3 ± 2.0	2.53 ± 0.82[e]	57.5 ± 53.3[e]
trans-MoOCl$_3$(bpy)	0.99 ± 0.40	56.6 ± 23.2	0.71 ± 0.23[f]	37.3 ± 26.1[f]
trans-MoOCl(ox)$_2$	1.62 ± 0.44	50.4 ± 14.1	1.71 ± 0.41[g]	92.7 ± 41.9[g]

[a] 25.0 °C, DMF. [b] From Figure 1 where $1/k_{obsd}$ is plotted vs. [Cl$^-$]. $k_{obsd} = a[NO_3^-]/(b[Cl^-] + [NO_3^-])$. [c] ln ([Mo(V)]$_0$/[Mo(V)])/([Mo(V)] − [Mo(V)]$_0$) is plotted vs. t/([Mo(V)] − [Mo(V)]$_0$). [d] 30 runs; [Mo(V)]$_0$ = (0.343–5.99) × 10^{-4} M, [NO$_3^-$] = (1.04–5.15) × 10^{-2} M. [e] 23 runs; [Mo(V)]$_0$ = (0.120–1.27) × 10^{-3} M, [NO$_3^-$] = (1.76–5.29) × 10^{-2} M. [f] 20 runs; [Mo(V)]$_0$ = (0.374–3.81) × 10^{-3} M, [NO$_3^-$] = (0.608–6.23) × 10^{-2} M. [g] 34 runs, [Mo(V)]$_0$ = (0.111–1.13) × 10^{-3} M, [NO$_3^-$] = (0.563–5.08) × 10^{-2} M.

In the absence of added Cl$^-$, with NO$_3^-$ in excess and [Cl$^-$] = [Mo(V)]$_0$ − [Mo(V)], the integrated form of the rate expression is

$$\ln([Mo(V)]_0/[Mo(V)])/([Mo(V)] - [Mo(V)]_0) = at[NO_3^-]/(b[Mo(V)]_0 + [NO_3^-])([Mo(V)] - [Mo(V)]_0) - b/(b[Mo(V)]_0 + [NO_3^-])$$

Plots of the left side of this equation vs. t/([Mo(V)] − [Mo(V)]$_0$) give excellent straight lines for at least 3 half-lives, and the values of a and b were obtained from the slopes (S) and intercepts (I):

$$a = S/(1 + I[\mathrm{Mo(V)}]_0)$$

$$b = -I[\mathrm{NO_3^-}]/(1 + I[\mathrm{Mo(V)}]_0)$$

As seen in Table II, the agreement between these values of a and those obtained from Figure 1 (excess $\mathrm{Cl^-}$) is good. The large uncertainty in the values of b (which depends directly on I) is due to the lengthy extrapolation necessary to obtain I from the plots and reflects the fact the first term in the denominator of the rate expression is small with respect to $[\mathrm{NO_3^-}]$ (this is particularly evident for the two cis complexes).

$\mathrm{MoOCl(CH_3OH)(sip)}$. This complex reacts considerably more rapidly with $\mathrm{NO_3^-}$ than the other complexes. Again, plots of ln A vs. t in the presence of excess $\mathrm{NO_3^-}$ show significant departure from linearity, but the rate appears to increase linearly with $\mathrm{NO_3^-}$ concentration. These results may be expressed by the rate expression

$$-\mathrm{d}[\mathrm{Mo(V)}]/\mathrm{d}t = k_{\mathrm{obsd}}[\mathrm{Mo(V)}][\mathrm{NO_3^-}]/[\mathrm{Cl^-}]$$

Chloride concentration in the denominator is not constant (see stoichiometry), accounting for the deviation from linearity of the ln A vs. t plots. The integrated form of his expression is

$$[\mathrm{Mo(V)}] + [\mathrm{Mo(V)}]_0 \ln ([\mathrm{Mo(V)}_0]/[\mathrm{Mo(V)}]) = k_{\mathrm{obsd}}[\mathrm{NO_3^-}]t + [\mathrm{Mo(V)}]_0$$

Plots of the left side of this equation vs. time are linear for at least 3 half-lives and the value of $k_{\mathrm{obsd}}/[\mathrm{NO_3^-}]$ for 12 runs over a range of $\mathrm{NO_3^-}$ concentrations from 0.811×10^{-2} M to 2.59×10^{-2} M was found to be $(1.58 \pm 0.17) \times 10^{-4}\ \mathrm{s^{-1}}$.

$\mathrm{MoOCl(tox)_2}$. This complex reacts considerably more slowly with $\mathrm{NO_3^-}$ than those discussed above; furthermore, the first-order plots of ln A vs. t in the presence of excess $\mathrm{NO_3^-}$ show essentially no deviation from linearity, and the rates are independent of $\mathrm{NO_3^-}$ concentration. The observed first-order rate constant for this complex for 26 runs with a range of $\mathrm{NO_3^-}$ concentrations from 1.04×10^{-2} M to 5.15×10^{-2} M was found to be $(1.86 \pm 0.20) \times 10^{-4}\ \mathrm{s^{-1}}$. At high excess $\mathrm{Cl^-}$ concentrations, the reaction appears to be inhibited. The rates under these conditions, however, are too low for useful measurements, since some oxidation and/or dimerization of the complex occurs in the long time periods required due to traces of $\mathrm{O_2}$ or $\mathrm{H_2O}$ in the system, precluding reproducible results.

Discussion

$\mathrm{MoOCl_3L}$, $\mathrm{MoOCl(ox)_2}$, and $\mathrm{MoOCl(CH_3OH)(sip)}$. The mechanism of eq 1–3 is proposed to explain the kinetic results for these complexes. (Only the relevant parts of the complexes

$$\mathrm{Mo^VOCl} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{Mo^VO^+} + \mathrm{Cl^-} \tag{1}$$

$$\mathrm{Mo^VO^+} + \mathrm{NO_3^-} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \mathrm{Mo^VO(NO_3)} \tag{2}$$

$$\mathrm{Mo^VO(NO_3)} \xrightarrow{k_3} \mathrm{Mo^{VI}O_2} + \mathrm{NO_2} \tag{3}$$

are written. For the bipyridyl complexes, e.g., the four species involved are $\mathrm{MoOCl_3(bpy)}$, $\mathrm{MoOCl_2(bpy)^+}$, $\mathrm{MoOCl_2(NO_3)(byp)}$, and $\mathrm{MoO_2Cl_2(bpy)}$.) Initial dissociation of a $\mathrm{Cl^-}$ (1) is followed by formation of an intermediate nitrato complex (2), which subsequently undergoes intramolecular transfer of an oxo group to produce products (3). Application of the steady-state assumption to both the initial dissociation product ($\mathrm{Mo^VO^+}$) and the intermediate nitrate complex ($\mathrm{Mo^VO(NO_3)}$) gives the rate expression

$$-\mathrm{d}[\mathrm{Mo(V)}]/\mathrm{d}t = k_1k_2k_3[\mathrm{Mo(V)}][\mathrm{NO_3^-}]/\{k_{-1}(k_{-2} + k_3)[\mathrm{Cl^-}] + k_2k_3[\mathrm{NO_3^-}]\}$$

$$\mathrm{Mo(V)} = \mathrm{MoOCl_3(bpy)},\ \mathrm{MoOCl_3(phen)},\ \text{or}\ \mathrm{MoOCl(ox)_2}$$

Table III. First-Order Rate Constants Obtained from Linear Sections of ln A vs. t Plots[a]

complex	k_1, $\mathrm{s^{-1}} \times 10^3$
cis-$\mathrm{MoOCl_3(phen)}$	4.45 ± 0.03
cis-$\mathrm{MoOCl_3(bpy)}$	2.39 ± 0.04 (2.07 ± 0.34)[b]
trans-$\mathrm{MoOCl_3(bpy)}$	0.80 ± 0.04
trans-$\mathrm{MoOCl(ox)_2}$	1.73 ± 0.09

[a] 25.0 °C, DMF. [b] From entire ln A vs. t plot.

This is identical with the experimental rate law observed for the $\mathrm{MoOCl_3L}$ and $\mathrm{MoOCl(ox)_2}$ complexes, with a = k_1 and $b = k_{-1}(k_{-2} + k_3)/k_2k_3$. At low $[\mathrm{Mo(V)}]/[\mathrm{NO_3^-}]$ ratios, in the absence of added $\mathrm{Cl^-}$, plots of ln A vs. t are linear for more than 1 half-life, since, as is seen from the values of b, the first term in the denominator is quite small with respect to the second term (Table II), and the rate expression approaches first order (excess nitrate). For *cis*-$\mathrm{MoOCl_3(bpy)}$, plots of ln A vs. t are almost as linear as plots of the integrated rate expression involving $\mathrm{Cl^-}$ inhibition (Table III). Under these conditions (low $[\mathrm{Mo(V)}]/[\mathrm{NO_3^-}]$) $k_{\mathrm{obsd}} \simeq k_1$ (Table III) (k_{obsd} was obtained from the linear section of the first-order plots).

The two cis compounds (*cis*-$\mathrm{MoOCl_3(bpy)}$ and *cis*-$\mathrm{MoOCl_3(phen)}$) react more rapidly than the two trans compounds (*trans*-$\mathrm{MoOCl_3(bpy)}$ and *trans*-$\mathrm{MoOCl(ox)_2}$), as is seen by a comparison of k_{obsd} at the same $\mathrm{Cl^-}$ concentration (Figure 1) or k_1. The larger values of k_1 for the cis complexes are most likely due to the well-known trans effect of the oxo group, which weakens the trans Mo–Cl bond.[21]

In the case of $\mathrm{MoOCl(CH_3OH)(sip)}$, the same mechanism applies, provided the second term in the denominator of the rate expression is negligible with respect to the first term, i.e., $k_{-1}(k_{-2} + k_3)[\mathrm{Cl^-}] >> k_2k_3[\mathrm{NO_3^-}]$:

$$-\mathrm{d}[\mathrm{Mo(V)}]/\mathrm{d}t = k_1k_2k_3[\mathrm{Mo(V)}][\mathrm{NO_3^-}]/k_{-1}(k_{-2} + k_3)[\mathrm{Cl^-}]$$

There are two limiting cases for this expression:

$$k_{-2} >> k_3 \qquad k_{\mathrm{obsd}} = k_1k_2k_3/k_{-1}k_{-2} = K_1K_2k_3$$

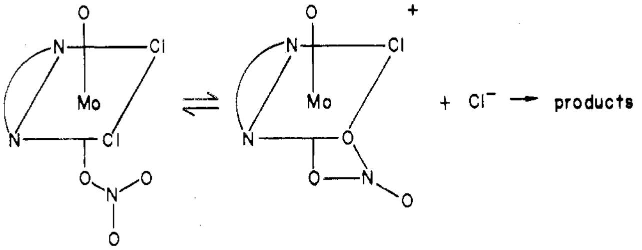
$$k_{-2} << k_3 \qquad k_{\mathrm{obsd}} = k_1k_2/k_{-1} = K_1k_2$$

In the first, reactions 1 and 2 are equilibria and the rate-controlling step is the oxo-transfer step (3). In the second, reaction 1 is an equilibrium and the rate-controlling step is reaction 2, formation of the nitrato complex. In either case, k_{-1} must be considerably larger than k_2 or k_3, in contrast to the complexes discussed above. This might arise from the fact the $\mathrm{Cl^-}$ dissociated in reaction 1 for this complex is in a position trans to the weakly coordinating $\mathrm{CH_3OH}$ (or solvent DMF), rather than the much more strongly bonded O, N, or S of the other complexes. The result of this should be a stronger $\mathrm{Cl^-}$ bond as reflected in a larger k_{-1} value.

$\mathrm{MoOCl(tox)_2}$. This complex reacts considerably more slowly than the complexes discussed above and follows good first-order kinetics for more than 3 half-lives. Furthermore, the rate is independent of $\mathrm{NO_3^-}$ concentration. The same mechanism developed for the other complexes gives this kinetic behavior, if the first term in the denominator is negligible with respect to the second term. The rate constant k_1 is almost 1 order of magnitude smaller than k_1 for $\mathrm{MoOCl(ox)_2}$.

***cis*-$\mathrm{MoOCl(sal_2phen)}$.** This complex, which does not reduce $\mathrm{NO_3^-}$ under the conditions used, has a structure which prevents coordination of $\mathrm{NO_3^-}$ in a position cis to the oxo group (the planar ligand precludes rearrangement to a trans structure[16]). Moreover, the Mo(VI) product would require a trans dioxo group, a structure as yet not reported for the $\mathrm{MoO_2}$ unit.[21]

The results may be interpreted by the proposal of Garner et al.,[22] which requires $\mathrm{NO_3^-}$ to coordinate to the Mo(V) center with an oxygen cis to the MoO group in order for proper overlap of the Mo(V) d_{xy} orbital (which contains the electron) and the nitrate oxygen π orbital for electron transfer. In the cases of the *cis*-$MoOCl_3$(bpy) and *cis*-$MoOCl_3$(phen) complexes, initial coordination of NO_3^- at the trans position must then be followed by rapid rearrangement or rapid formation of an intermediate chelate nitrato complex:



It was anticipated the reduction of NO_3^- by MoOCl(CH_3OH)(sip) would be rapid and would not exhibit Cl^- inhibition, since a coordination site cis to the oxo group is occupied by a weakly bound CH_3OH (or solvent DMF), which should be easily replaced by NO_3^-. While this complex does indeed react more rapidly than the others, the reduction appears still to proceed by a preliminary loss of Cl^-, suggesting the formation of a negatively charged intermediate nitrato complex, $MoOCl(NO_3)(sip)^-$, is not favorable.

Finally, the lack of reduction of NO_3^- by MoOCl(sal_2phen) may be due either to the impossibility of forming an intermediate nitrato complex with the correct orbital overlap or to the thermodynamic instability of the trans Mo(VI) dioxo structure required of the product.[16,22]

The results suggest a possible mechanism for the enzymatic reduction of NO_3^-: NO_3^- is initially bound at a nonaqueous Mo(V) site at an open coordination position or, by displacement of a weakly coordinated ligand, cis to the oxo group, accompanied by dissociation of a second negatively charged group (sulfhydryl or tyrosyl, e.g.), to maintain the original charge at the site (binding might occur at the trans position, followed by rapid rearrangement to the cis structure, but this seems less likely with the protein). After transfer of an oxo group, NO_2 is released and disproportionates in an aqueous region to NO_3^- and NO_2^-. The Mo center subsequently is reduced by the flavin or iron cofactors of the enzyme,[3] with the oxygen forming H_2O or OH^-. Appropriate enzymatic experiments using ^{18}O-labeled NO_3^- and H_2O would provide a possible test of the hypothesis.

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Registry No. *cis*-$MoOCl_3$(phen), 38237-92-2; *cis*-$MoOCl_3$(bpy), 35408-53-8; *trans*-$MoOCl_3$(bpy), 35408-54-9; *trans*-$MoOCl(ox)_2$, 67650-70-8; *trans*-$MoOCl(tox)_2$, 67650-71-9; *cis*-MoOCl(sal_2phen), 64085-34-3; *trans*-MoOCl(CH_3OH)(sip), 68081-62-9; $MoO_2(tox)_2$, 17926-52-2; MoO_2(sip), 67598-36-1; $(NH_4)_2MoOCl_5$, 17927-44-5; Na_2MoO_4, 7631-95-0; NO_3^-, 14797-55-8.

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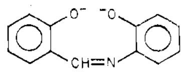
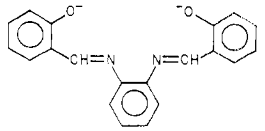
(10) Abbreviations used: bpy = α,α'-bipyridyl; phen = *o*-phenanthroline; ox = 8-hydroxyquinoline (oxine); tox = 8-mercaptoquinoline (thiooxine); sip = *o*-(salicylidenimino)phenol



sal_2phen = *o*-bis(salicylidenimino)benzene



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Contribution from the Department of Chemistry,
University of Massachusetts, Amherst, Massachusetts 01003

Three Classes of Seven-Coordinate Tungsten(II) Chelates with Both Hard and Soft Donors

WILLIAM H. BATSCHELET, RONALD D. ARCHER,* and DAVID R. WHITCOMB

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Three types of mixed-ligand tungsten(II) chelates have been isolated with simultaneous coordination of hard phenolato oxygen, borderline heterocyclic nitrogen, and soft carbonyl and phosphine donors. The complexes are $W(CO)_2(PPh_3)(dcq)_2$, $W(CO)_3(PPh_3)(dcq)Cl$, and $W(CO)_2(PPh_3)_2(dcq)Cl$, where Ph = C_6H_5 and dcq^- = 5,7-dichloro-8-quinolinolato. A strong base (e.g., proton sponge) is necessary to prepare the bis-dcq^- chelate from $W(CO)_3(PPh_3)_2Cl_2$ and Hdcq. The physical and chemical properties of the diamagnetic chelates are consistent with seven-coordinate geometries.

Introduction

We have been interested in the synthesis of seven-coordinate tungsten(II) complexes of the general form $W(CO)_2(PPh_3)L_2$, where L is an anion of 8-quinolinol, picolinic acid, or related derivative. These complexes might then serve as starting materials for the synthesis of mixed-ligand tungsten(IV)

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