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Kinetics and Mechanism of the Oxidation of Bis(μ-hydroxo)bis[aqua(1,4,7-triazacyclononane)molybdenum(III)](4+) by Perchlorate. Acid–Base-Catalyzed Trans → Cis Isomerization of Bis(μ-oxo)-*trans*-dioxobis[(1,4,7-triazacyclononane)molybdenum(V)](2+)

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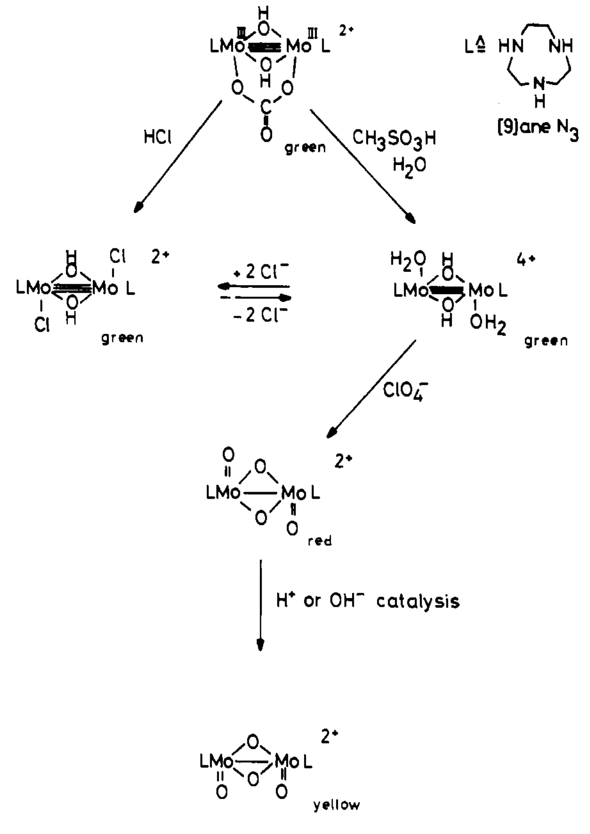
The kinetics of the 1:1 reactions of $[L_2Mo_2(H_2O)_2(\mu\text{-}OH)_2]^{4+}$, where L = 1,4,7-triazacyclononane, with chloride and perchlorate have been investigated spectrophotometrically in methanesulfonate media (I = 1.0 M ($LiSO_3CH_3$)) and found to be independent of $[H^+]$ in the range of 0.05–1.0 M. Pseudo-first-order rate constants for the equilibration of the Mo(III) dimer with Cl^- may be expressed as $k_{eq} = k_1[Cl^-] + k_{-1}$. The Mo^{III}_2 dimer reacts with ClO_4^- to give the red bis(μ-oxo)-*trans*-dioxobis[(1,4,7-triazacyclononane)molybdenum(V)](2+) cation and Cl^-. Pseudo-first-order rate constants may be expressed as $k_{obsd} = k[ClO_4^-]$ with $k = 2.0 \times 10^{-3}$ M^{-1} s^{-1} at 294 K. It is proposed that substitution of ClO_4^- into the coordination sphere of the Mo^{III}_2 dimer is the rate-determining step. *trans*-$[L_2Mo_2O_4]^{2+}$ is irreversibly converted to the yellow *cis*-$[L_2Mo_2O_4]^{2+}$ via acid–base catalysis. The kinetics of these reactions are reported, and mechanisms are proposed. The slightly greater thermodynamic stability of the cis isomer as compared to the trans isomer is explained from structural data in terms of slightly increased nonbonding O···O distances within the MoN_3O_3 octahedron of the cis isomer. The sum of three O–Mo–O bond angles is greater for the cis than for the trans isomer.

Introduction

We have recently reported the syntheses and structural characterization of a series of binuclear complexes of molybdenum(III) and molybdenum(V) containing the facially coordinated triamine 1,4,7-triazacyclononane.[1,2] The μ-carbonato complex, $[Mo_2([9]aneN_3)_2(\mu\text{-}OH)_2(\mu\text{-}CO_3)]^{2+}$ proved to be a useful starting material for the preparation of Mo^{III}_2 dimers and Mo^V_2 dimers (Scheme I). One of the interesting results has been the preparation of a genuine bis(μ-oxo)-*trans*-dioxobis[(1,4,7-triazacyclononane)molybdenum(V)](2+) complex and its thermodynamically more stable cis isomer. The kinetics of the irreversible trans → cis isomerization are reported here.

The reduction of perchlorate by transition-metal ions has been of interest for some time, but available kinetic data are rather scarce.[3] The hypothesis has been proposed that metal ions, which are capable of forming strong M=O bonds, should be more suitable reductants for ClO_4^- than those that do not form "yl" ions. Kinetically labile complexes of Mo(III) or Mo(IV) should potentially be good candidates for the ClO_4^- reduction because Mo(V) and Mo(VI) complexes form very stable Mo=O bonds. We here report the first kinetic study of such a reaction with a binuclear complex of molybdenum(III) as reductant.

Scheme I



Experimental Section

The complexes $[Mo_2([9]aneN_3)_2(\mu\text{-}OH)_2(\mu\text{-}CO_3)]I_2{\cdot}H_2O$ and $[Mo_2([9]aneN_3)_2(H_2O)_2(\mu\text{-}OH)_2]I_4$ were prepared as described.[1,2] The iodide salts were converted to the corresponding tetrafluoroborate salts by precipitation from oxygen-free aqueous solutions after the addition of $NaBF_4$. Anal. Calcd for $[Mo_2([9]aneN_3)_2(\mu\text{-}OH)_2(\mu\text{-}CO_3)](BF_4)_2{\cdot}2H_2O$ (green): C, 20.71; H, 4.81; N, 11.15; Mo, 25.49. Found: C, 20.7; H, 5.1; N, 11.1; Mo, 25.2. Anal. Calcd for $[Mo_2([9]aneN_3)_2(\mu\text{-}OH)_2(OH_2)_2](BF_4)_4$ (green): C, 16.61; H, 4.18; N, 9.69; Mo, 22.12. Found: C, 16.4; H, 3.9; N, 9.5; Mo, 21.9.

These tetrafluoroborate and iodide salts were used for kinetic measurements, which were made on a Unicam SP 1700 spectrophotometer interfaced to a Commodore PET 4001 computer for data acquisition and analysis. All reactions were run under pseudo-first-order conditions under an argon atmosphere. Pseudo-first-order rate constants were calculated with a least-squares program[4] where the absorptions at the beginning (t = 0) and after the completed reaction ($t = \infty$) were treated as variables. The observed and calculated values differed only within the uncertainty of the last digit of the readings of the instrument. The UV–visible spectra of all complexes have been reported.[1,2]

Results

The green molybdenum(III) dimer (μ-carbonato)bis(μ-hydroxo)bis[(1,4,7-triazacyclononane)molybdenum(III)](2+)[1] reacts with hydrochloric acid under rigorous oxygen-free conditions to form the green dimer bis(μ-hydroxo)bis[chlo-

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(1) Wieghardt, K.; Hahn, M.; Swiridoff, W.; Weiss, J. *Angew. Chem.* **1983**, *95*, 499; *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 491; *Angew. Chem. Suppl.* **1983**, 583.

(2) Wieghardt, K.; Hahn, M.; Swiridoff, W.; Weiss, J. *Inorg. Chem.* **1984**, *23*, 94.

(3) Taube, H. In "Mechanistic Aspects of Inorganic Reactions"; (Editors: Rorabacher, D. B., Endicott, J. F., Eds.; American Chemical Society: Washington, D.C., 1982; ACS Symp. Ser. No. 198.

(4) DeTar, D. F. *Comput. Chem.* **1978**, *2*, 99.

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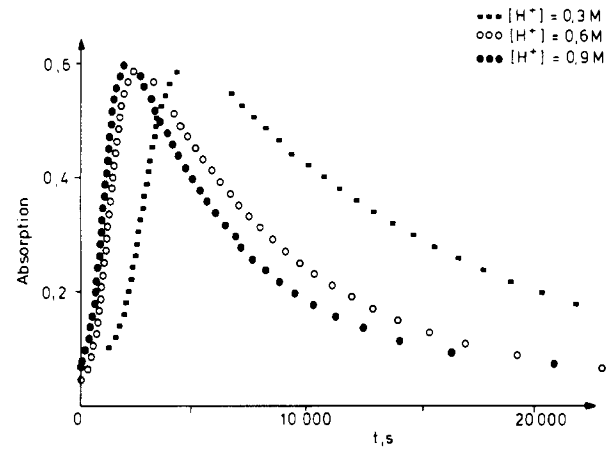


Figure 1. Multiphasic reaction of (μ-carbonato)bis(μ-hydroxo)bis-[(1,4,7-triazacyclononane)molybdenum(III)](2+) with perchloric acid at 31 °C (λ = 525 nm; [ClO_4^-] = 0.5 M; [$Mo^{III}{}_2$] = 1.6 × 10^{-3} M).

ro(1,4,7-triazacyclononane)molybdenum(III)](2+)[2] (Scheme I). The same complex is generated from the very oxygen-sensitive bis(μ-hydroxo)bis[(aqua(1,4,7-triazacyclononane)-molybdenum(III)](4+) complex and chloride ions. The latter complex is formed by reacting the μ-carbonato complex with noncoordinating acids such as methanesulfonic acid. The bis(μ-hydroxo)-*trans*-diaquabis[(1,4,7-triazacyclononane)-molybdenum(III)](4+) complex is readily oxidized by air and, interestingly, by perchlorate ions in aqueous solutions to form quantitatively the red bis(μ-oxo)-*trans*-dioxobis[(1,4,7-triazacyclononane)molybdenum(V)](2+) cation. The latter red molybdenum(V) dimer, which contains two terminal oxo groups in the unusual trans position with respect to each other, undergoes an acid–base-catalyzed isomerization to form a yellow molybdenum(V) dimer with the well-known cis arrangement of the two terminal oxo groups.[1] The kinetics and mechanisms of these reactions will be described now.

Preliminary Kinetic Experiments. A series of three preliminary kinetic experiments of the reaction of the μ-carbonato dimer with perchloric acid is shown in Figure 1 ([H^+] = 0.3, 0.6, 0.9 M; [ClO_4^-] constant at 0.5 M; [Mo_2] = 2.5 × 10^{-4} M). The change in absorbance at 525 nm is monitored as a function of time. Clearly, three stages are detectable: (1) A rapid induction period within the first few minutes decreases with increasing H^+ concentration. This step shows only a small change in absorbance at 525 nm. (2) The second stage is accompanied by a large increase in absorbance. This step is independent of [H^+] (0.3–0.9 M). (3) The final stage exhibits a slow decrease of absorbance. This step is dependent on [H^+]. The green color of the starting complex changes to red and finally to yellow during the course of the reaction. When the same set of experiments was performed with the bis(μ-hydroxo)-*trans*-diaquabis[(1,4,7-triazacyclononane)molybdenum(III)] cation instead of the μ-carbonato dimer, only the induction period, i.e. the first of the above steps, is not observed. When the μ-carbonato dimer is reacted with a nonoxidizing acid (methanesulfonic acid), only the first step is observed and no green to red to yellow color changes are detected. And finally, when the red bis(μ-oxo)-*trans*-dioxobis[(1,4,7-triazacyclononane)molybdenum(V)] dimer is treated with H^+, only the red to yellow change of color is observed, i.e. the last slow stage of the reaction sequence in Figure 1. These observations are in agreement with the following assignment of reaction steps: (1) The μ-carbonato dimer of molybdenum(III) undergoes rapid acid-catalyzed decarboxylation to produce the *trans*-diaqua dimer of molybdenum(III). (2) This species is then oxidized by perchlorate ions to give the red *trans*-dioxo dimer of molybdenum(V), which in the final step 3 is trans → cis isomerized by acid catalysis.

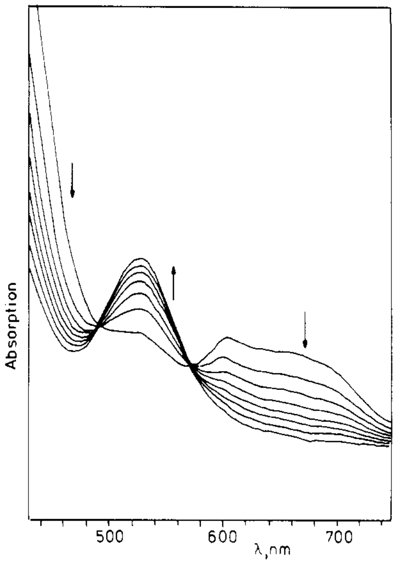


Figure 2. Scan spectrum of the oxidation of [$([9]aneN_3)_2Mo_2(OH_2)_2(\mu\text{-}OH)_2]^{4+}$ by perchlorate (scans after 2, 4, 6, 8, 10, 12, and 15 min; [H^+] = 0.1 M; [$Mo^{III}{}_2$] = 8 × 10^{-4} M; [ClO_4^-] = 0.5 M; T = 30 °C).

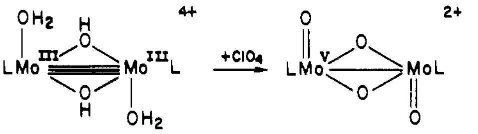
Table I. Pseudo-First-Order Rate Constants for the Reaction of [$([9]aneN_3)_2Mo_2(OH_2)_2(\mu\text{-}OH)_2]^{4+}$ with ClO_4^- [a]

T, K	[ClO_4^-], M	10^3 × k_{obsd}, s^{-1}	T, K	[ClO_4^-], M	10^3 × k_{obsd}, s^{-1}
294	0.3	0.59	303	0.5	2.18
294	0.5	1.07	303	0.7	2.86
294	0.7	1.38	303	0.9	4.30
294	0.9	1.81	314	0.3	3.67
303	0.1	0.72	314	0.5	4.59
303	0.3	1.38	314	0.7	7.46
303	0.4	1.85	314	0.9	11.25

[a] [$Mo^{III}{}_2$] = 3.5 × 10^{-4} M; [H^+] = 0.1 M; I = 1.0 M.

We decided to study the oxidation and the following isomerization steps in more detail with the bis(μ-hydroxo)-*trans*-diaquabis[(1,4,7-triazacyclononane)molybdenum(III)](4+) complex as starting material. The decarboxylation reaction of the μ-carbonato dimer has not been studied.

Kinetics of the Oxidation of Bis(μ-hydroxo)-*trans*-diaquabis[(1,4,7-triazacyclononane)molybdenum(III)](4+) by Perchlorate. Figure 2 shows a scan spectrum of the reaction of the *trans*-diaqua dimer of molybdenum(III) with perchloric acid ([H^+] = 0.1 M; [ClO_4^-] = 0.5 M; [$Mo^{III}{}_2$] = 8 × 10^{-4} M) at 30 °C (eq 1). Two isosbestic points are observed at



(1)

λ = 490 nm and 570 nm. The color changes from green to red within 20 min, during which time the red bis(μ-oxo)-*trans*-dioxobis[(1,4,7-triazacyclononane)molybdenum(V)](2+) species is generated quantitatively. The final spectrum is identical with that reported for the red Mo(V) dimer.[1] Perchlorate is reduced to chloride. The rate of this reaction was studied at 525 nm with perchlorate in large excess of [$Mo^{III}{}_2$]. Plots of absorbance changes, log ($A_t - A_\infty$), against time, t, were linear for at least 4 half-lives. First-order rate constants obtained, k_{obsd}, are listed in Table I. The rate was found to be independent of [H^+] = 0.05–1.0 M. The linear dependence of k_{obsd} on [ClO_4^-] is shown in Figure 3 (eq 2). Values of

$$k_{obsd} = k[ClO_4^-] \qquad (2)$$

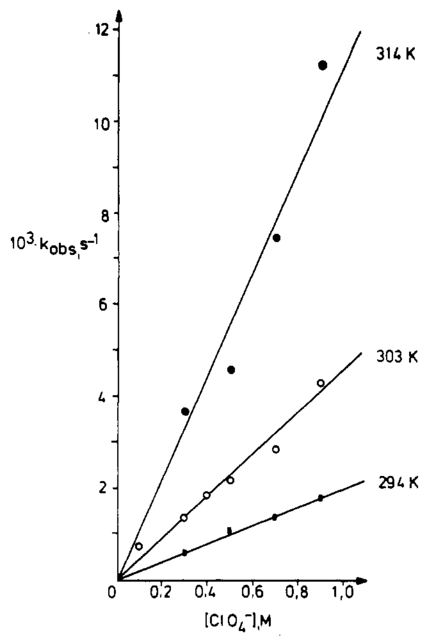


Figure 3. Kinetics of the oxidation of $[([9]aneN_3)_2Mo_2(OH_2)_2(\mu\text{-}OH)_2]^{4+}$ by perchlorate ($[H^+]$ = 0.1 M; I = 1.0 M ($LiCH_3SO_3$)).

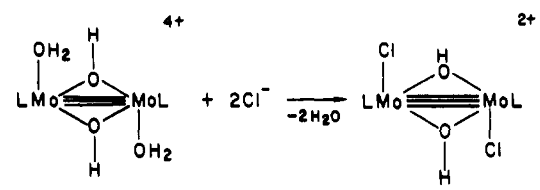
Table II. Pseudo-First-Order Rate Constants for the Equilibrium Kinetics of $[([9]aneN_3)_2Mo_2(OH_2)_2(\mu\text{-}OH)_2]^{4+}$ with Cl^- [a]

T, K	$[Cl^-]$, M	k_{eq}, s^{-1}	T, K	$[Cl^-]$, M	k_{eq}, s^{-1}
286	0.05	0.007	293	0.3	0.045
286	0.1	0.011	293	0.4	0.054
286	0.2	0.016	293	0.5	0.066
286	0.3	0.024	300	0.05	0.023
286	0.4	0.028	300	0.1	0.032
289	0.1	0.017	300	0.15	0.036
289	0.2	0.026	300	0.2	0.050
289	0.3	0.033	300	0.25	0.074
289	0.4	0.044	300	0.3	0.59
293	0.1	0.021	300	0.4	0.087
293	0.2	0.033			

[a] $[Mo^{III}_2]$ = 1.6 × 10^{-3} M; $[H^+]$ = 0.1 M; I = 1.0 M ($LiSO_3CH_3$).

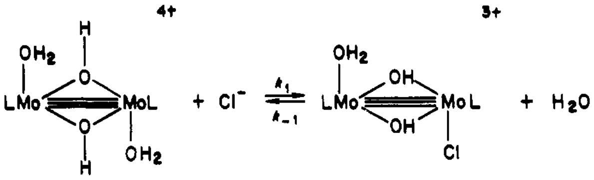
k (M^{-1} s^{-1}) obtained by a least-squares treatment are 2.0 × 10^{-3} (294 K), 4.7 × 10^{-3} (303 K), and 11.3 × 10^{-3} (314 K). Activation parameters for k are $\Delta H^* = 64 \pm 2$ kJ mol^{-1} and $\Delta S = -80 \pm 6$ J mol^{-1} K^{-1}.

Kinetics of the Equilibration of Bis(μ-Hydroxo)-*trans*-diaquabis[(1,4,7-triazacyclononane)molybdenum(III)](4+) with Chloride. The reaction of bis(μ-hydroxo)-*trans*-diaquabis[(1,4,7-triazacyclononane)molybdenum(III)] with chloride in very high concentrations under strictly oxygen-free conditions yields the bis(μ-hydroxo)-*trans*-dichlorobis[(1,4,7-triazacyclononane)molybdenum(III)](2+) cation[2] (eq 3). The kinetics



(3)

of the 1:1 reaction have been studied (eq 4) at λ = 550 nm



(4)

with chloride in at least 50-fold excess of Mo^{III}_2 in methanesulfonic acid media. Plots of log ($A_t - A_\infty$) against time were linear to at least 90% of reaction. First-order rate constants, k_{eq}, obtained are listed in Table II. No dependence on $[H^+]$ in the range 0.1–0.8 M was observed. The dependence of rate constants, k_{eq}, on Cl^- (Figure 4) is described by eq 5. Reaction of the first chloride ion with the Mo(III) dimer

$$k_{eq} = k_1[Cl^-] + k_{-1} \qquad (5)$$

is thought to be rate determining in the forward reaction and dissociation of this chloro ligand in the back-reaction. k_1 and k_{-1} correspond to forward and back reactions in eq 5. From this data, activation parameters $\Delta H_1^* = 51 \pm 4$ kJ mol^{-1}, $\Delta S_1^* = -88 \pm 13$ J mol^{-1} K^{-1}, and $\Delta H_{-1}^* = 54 \pm 17$ kJ mol^{-1}, $\Delta S_{-1}^* = -92 \pm 50$ J mol^{-1} K^{-1} were calculated. Values of k_1 and k_{-1} are summarized in Table III.

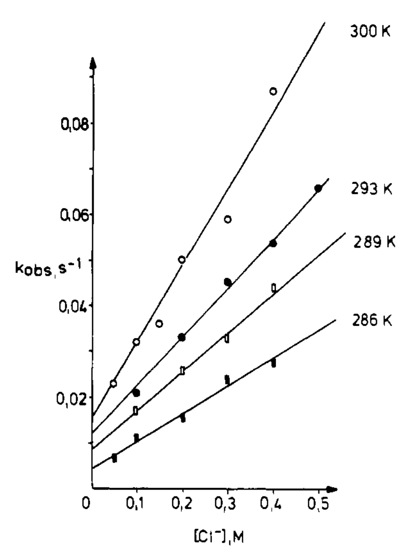


Figure 4. Equilibrium kinetics for the reaction of $[([9]aneN_3)_2Mo_2(OH_2)_2(\mu\text{-}OH)_2]^{4+}$ with chloride ($[H^+]$ = 0.1 M; I = 1.0 M ($LiCH_3SO_3$)).

Table III. Summary of Rate Constants for the Equilibration of $[([9]aneN_3)_2Mo_2(OH_2)_2(\mu\text{-}OH)_2]^{4+}$ with Cl^-

T, K	k_1, M^{-1} s^{-1}	k_{-1}, s^{-1}	T, K	k_1, M^{-1} s^{-1}	k_{-1}, s^{-1}
286	0.061	0.0045	293	0.108	0.012
289	0.084	0.009	300	0.178	0.016

Kinetics of the Trans → Cis Isomerization of Bis(μ-oxo)-*trans*-dioxobis[(1,4,7-triazacyclononane)molybdenum(V)](2+). Aqueous solutions of the red bis(μ-oxo)-*trans*-dioxobis[(1,4,7-triazacyclononane)molybdenum(V)](2+) cation are stable at 25 °C for at least 2 days. Upon addition of methanesulfonic acid or sodium hydroxide, the yellow isomer bis(μ-oxo)-*cis*-dioxobis[(1,4,7-triazacyclononane)molybdenum(V)](2+) is formed quantitatively. The difference of absorption spectra of these two species (the trans isomer has a characteristic absorption maximum at λ = 527 nm (ε = 380 L mol^{-1} cm^{-1}); in the cis isomer this maximum is shifted to λ = 378 nm (ε 455)) enabled the spectrophotometric measurement of the kinetics of this acid–base-catalyzed process at λ = 527 nm. The rate of isomerization was studied with $[H^+]$ or $[OH^-]$ in large excess of red $[([9]aneN_3)_2Mo_2O_4]^{2+}$. Plots of absorbance changes, log ($A_t - A_\infty$), against time, t, were linear to at least 5 half-lives of the reaction. First-order rate constants are listed in Tables IV and V. The dependence of rate constants, k_{obsd}, on $[H^+]$ and $[OH^-]$, respectively, can be summarized by eq 6 and 7. In accord with eq 6 and 7

$$k_{obsd} = k_a(1 + K_a[H^+]^{-1})^{-1} \qquad (6)$$

$$k_{obsd} = k_b(1 + K_b[OH^-]^{-1})^{-1} \qquad (7)$$

Table IV. Pseudo-First-Order Rate Constants for the Proton-Catalyzed Trans → Cis Isomerization of $[([9]\mathrm{aneN_3})_2\mathrm{Mo_2O_4}]^{2+\,a}$

T, K	[H$^+$], M	10^5k_{obsd}, s^{-1}	T, K	[H$^+$], M	10^5k_{obsd}, s^{-1}
294	0.1	1.82	303	0.5	9.78
294	0.3	2.80	303	0.6	11.06
294	0.5	4.15	303	0.7	12.38
294	0.7	5.43	303	0.8	14.67
294	0.9	7.16	303	0.9	15.94
303	0.05	1.25	303	1.0	16.46
303	0.15	3.36	314	0.1	8.62
303	0.2	3.96	314	0.3	23.3
303	0.25	5.34	314	0.5	31.7
303	0.3	7.10	314	0.7	43.0
303	0.4	7.91	314	0.9	52.4

[a] $[\mathrm{Mo^V}_2] = 3.5 \times 10^{-4}$ M; $I = 1.0$ M.

Table V. Pseudo-First-Order Rate Constants for the Hydroxide-Catalyzed Trans → Cis Isomerization of $[([9]\mathrm{aneN_3})_2\mathrm{Mo_2O_4}]^{2+\,a}$

T, K	[OH$^-$], M	10^3k_{obsd}, s^{-1}	T, K	[OH$^-$], M	10^3k_{obsd}, s^{-1}
283	0.04	1.12	295	0.2	9.25
283	0.06	1.89	304	0.01	1.76
283	0.1	2.29	304	0.013	2.38
283	0.14	2.62	304	0.016	3.01
283	0.18	2.96	304	0.02	3.80
283	0.2	2.84	304	0.04	7.38
295	0.02	2.28	304	0.06	9.41
295	0.04	4.19	304	0.1	13.53
295	0.06	5.46	304	0.14	15.59
295	0.1	7.31	304	0.18	17.30
295	0.14	8.00	304	0.2	17.70
295	0.18	8.57			

[a] $[\mathrm{Mo^V}_2] = 3.5 \times 10^{-4}$ M; $I = 1.0$ M.

Table VI. Summary of Rate Constants and Activation Parameters for the Acid–Base-Catalyzed Trans → Cis Isomerization of Red $[([9]\mathrm{aneN_3})_2\mathrm{Mo_2O_4}]^{2+\,a}$

T, K	10^4k_{a}, M^{-1} s^{-1}	K_{a}, M	k_{b}, M^{-1} s^{-1}	K_{b}, M	$\Delta H^{\ddagger}$, kJ mol^{-1}	$\Delta S^{\ddagger}$, J mol^{-1} K^{-1}
			(a) Acid Catalysis			
294	2.4	2.3			64 ± 8	−96 ± 25
303	6.4	2.8				
314	14	1.5				
			(b) Base Catalysis			
283			0.0036	0.05	77 ± 2	−18.5 ± 8
295			0.015	0.11		
304			0.036	0.16		

[a] $I = 1.0$ M ($\mathrm{LiO_3SCH_3}$).

Figures 5 and 6 show linear dependences of k_{obsd}^{-1} vs. $[\mathrm{H^+}]^{-1}$ and $[\mathrm{OH^-}]^{-1}$, respectively. Values for k_{a}, k_{b}, K_{a}, and K_{b} are summarized in Table VI along with the respective activation parameters.

Discussion

Kinetic data on the substitution of aqua ligands coordinated to molybdenum(III) centers are rather scarce. The kinetics of the complexing of chloride and thiocyanate to the monomeric, yellow aqua ion, $\mathrm{Mo(OH_2)_6}^{3+}$, have been studied, and evidence for a mechanism exhibiting $\mathrm{S_N2}$ character has been presented.[5,6] At 25 °C second-order rate constants for these processes, $k_{\mathrm{Cl^-}} = 4.6 \times 10^{-3}$ M^{-1} s^{-1} and $k_{\mathrm{NCS^-}} = 0.27$ M^{-1} s^{-1}, have been reported. The rate of substitution of coordinated H$_2$O of the dimeric $[([9]\mathrm{aneN_3})_2\mathrm{Mo_2(OH_2)_2}(\mu\text{-OH})_2]^{4+}$ cation for chloride, as was investigated here, falls into the same range ($k_1 = 0.11$ M^{-1} s^{-1} at 25 °C). the observed small enthalpy of activation ($\Delta H^{\ddagger} = 51$ kJ mol^{-1}) together with a negative entropy of activation ($\Delta S^{\ddagger} = -88$ J mol^{-1}) may be taken as an indication that the substitution reaction of the dimer is also associative in character.

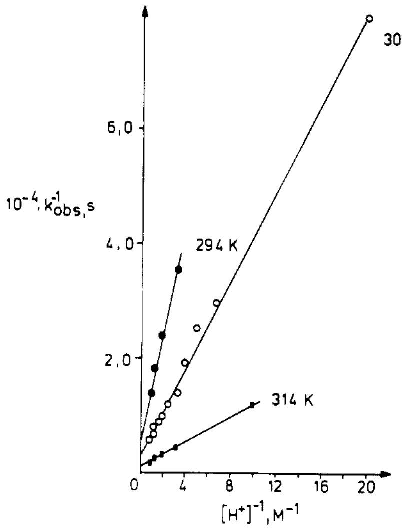


Figure 5. Plot of k_{obsd}^{-1} vs. $[\mathrm{H^+}]^{-1}$ for the acid-catalyzed trans → cis isomerization of $[([9]\mathrm{aneN_3})_2\mathrm{Mo_2O_4}]^{2+}$ ($I = 1.0$ M).

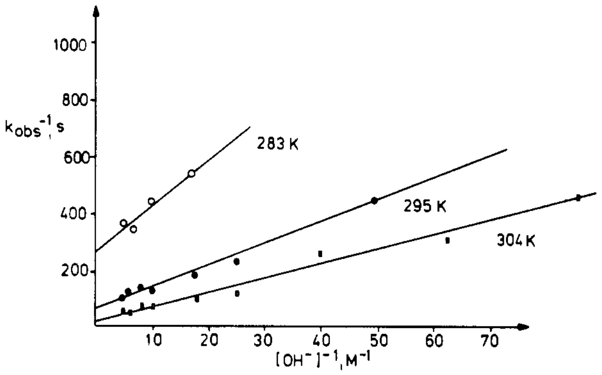


Figure 6. Kinetics of the hydroxide-catalyzed trans → cis isomerization of $[([9]\mathrm{aneN_3})_2\mathrm{Mo_2O_4}]^{2+}$ ($I = 1.0$ M).

Table VII. Summary of Second-Order Rate Constants for $\mathrm{ClO_4}^-$ Reductions by Metal Ions at 25 °C

complex	k,[a] M^{-1} s^{-1}	ref
$\mathrm{V(OH_2)_6}^{2+}$	5.3×10^{-7}	7
$\mathrm{Cr(OH_2)_6}^{2+}$	$<10^{-8}$	3
$\mathrm{Ti(OH_2)_6}^{2+}$	1.9×10^{-4}	8
$\mathrm{Ru(OH_2)_6}^{2+}$	3.2×10^{-3}	9
$[\mathrm{Ru(NH_3)_5H_2O}]^{2+}$	2.6×10^{-2}	10
$[([9]\mathrm{aneN_3})_2\mathrm{Mo_2(OH_2)_2}(\mu\text{-OH})_2]^{4+}$	2.0×10^{-3}	this work

[a] rate = $k[\mathrm{ClO_4}^-]$[complex].

The most interesting facet of the present study is the facile oxidation of the $[([9]\mathrm{aneN_3})_2\mathrm{Mo_2(OH_2)_2}(\mu\text{-OH})_2]^{4+}$ dimer by perchlorate to yield the red bis(μ-oxo)-*trans*-dioxobis[(1,4,7-triazacyclononane)molybdenum(V)](2+) cation and chloride. The reduction of $\mathrm{ClO_4}^-$ by metal ions has recently been discussed by Taube.[3] There appears to be a discrepancy of slow rates of reduction observed for same strong reductants such as $\mathrm{Cr(OH_2)_6}^{2+}$ or $\mathrm{Eu(OH_2)_6}^{2+}$ on the one hand, and more rapid rates of reduction for weaker reductants, e.g. $\mathrm{Ti(OH_2)_6}^{3+}$, on the other hand (Table VII).[7-10] Taube has proposed that

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the formation of a stable bond to O^{2-} be formed by the oxidized product (formation of "yl" species) is responsible for this observation. The available data seem to support this idea. The chemistry of molybdenum in its higher oxidation states (>4+) in aqueous solution is dominated by species containing at least one very stable terminal oxo ligand. Therefore, kinetically labile complexes of molybdenum(IV) have been suggested as potentially powerful reductants for ClO_4^-,[3] but no detailed kinetic study has been reported to date. Haight has shown that Sn(II) reduces ClO_4^- in the presence of catalytic amounts of molybdenum(IV).[11] Species such as $MoCl_4(SnCl_3)_2^{2-}$ are thought to mediate electron transfer from Sn(II) to ClO_4^-.[12] There are some hints in the literature that monomeric $Mo(OH_2)_6^{3+}$ reduces perchlorate, generating a molybdenum(V) dimer although no kinetic study has been reported to date.[5,6]

The present investigation appears to be the first kinetic report on the perchlorate reduction by a dinuclear complex of molybdenum(III). The rate of reduction is rather rapid and independent of $[H^+]$. The observed second-order rate constant falls into the same range expected for the substitution of coordinated H_2O by ClO_4^-. We propose therefore that this substitution reaction is the rate-determining step for the reduction of ClO_4^-. This is bolstered by the fact that ClO_4^- is not reduced by the (μ-acetato)bis(μ-hydroxo)bis[(1,4,7-triazacyclononane)molybdenum(III)](3+) cation. This complex is a green dimer of molybdenum(III) that does not contain labile aqua ligands.[2] It is noted that the above statement requires that the μ-acetato complex is as strong a reducing agent as the aqua dimer. Preliminary electrochemical investigations seem to support this view. Since chloride ions are the final products of ClO_4^- reduction, ClO_3^- and ClO_2^- are most probably intermediates, if the reduction of coordinated ClO_4^- occurs via oxygen atom transfer. The present investigation does not provide experimental evidence for this hypothesis.

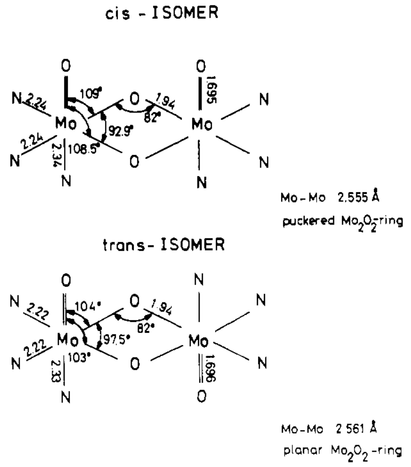
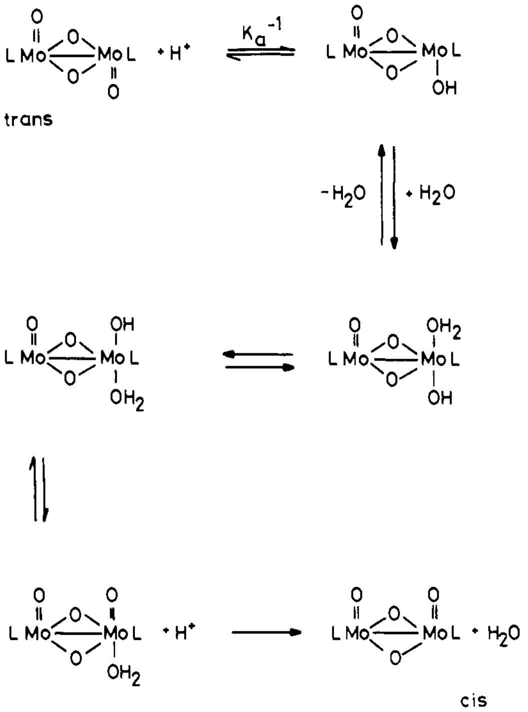


Figure 7. Crystallographic data of the trans and cis isomers of the $[([9]aneN_3)_2Mo_2O_4]^{2+}$ cation.[1]

Scheme II



In good agreement with the above conclusion are the activation parameters for the ClO_4^- reduction, which are very similar to those observed for the Cl^- substitution. The ratio of second-order rate constants, $k_{Cl^-}/k_{ClO_4^-}$, of 73 at 298 K indicates the associative character of the substitution process. If this mechanistic interpretation is correct, this would suggest that Cl^- and ClO_4^- are comparable nucleophiles. On the other hand, a dissociative mechanism would also be in accord with these data although the rather low enthalpy of activation is more in favor of an I_a mechanism. Compounds containing the $Mo^V{}_2O_4^{2+}$ central unit are well-known[13] and are well characterized from a series of X-ray determinations.[14-18] Generally, the $Mo(\mu\text{-}O)_2Mo$ four-membered ring was found to be strongly puckered, and the terminal oxo ligands were found to occupy exclusively cis positions with respect to each other. The Mo–Mo distances are in the range 2.54–2.58 Å, which together with the observed diamagnetism of these compounds has been interpreted in terms of a Mo–Mo metal bond of bond order 1. It was therefore of great interest that the oxidation of bis(μ-hydroxo)-*trans*-diaquabis[(1,4,7-triazacyclononane)molybdenum(III)](4+) by oxygen or ClO_4^- yields—kinetically controlled—the thermodynamically slightly more unstable bis(μ-oxo)-*trans*-dioxobis[(1,4,7-triazacyclononane)molybdenum(V)](2+) and that this species undergoes irreversible isomerization to the stable bis(μ-oxo)-*cis*-dioxodimolybdenum(V) complex.[1] A comparison of the X-ray structures of the two cations sheds some light on the question "why is the cis isomer more stable than the trans isomer?" In Figure 7 some relevant data of both structures are given (both of which have been determined on the *same* diffractometer[1]). The most obvious difference appears to be a planar Mo_2O_2 ring for the trans isomer whereas the cis isomer has the usual puckered Mo_2O_2 ring. Interestingly, this does *not* lead to significantly different Mo–Mo bond lengths (Δd(Mo–Mo) = 0.006 Å), although in the cis isomer the shorter distance is observed. The Mo–N, Mo–O, and Mo=O bond lengths are identical within experimental error for both isomers as are the Mo–O–Mo bond angles of the Mo_2O_2 ring (82°). A significant difference between the structures emerges when the O–Mo–O bond angles are compared. This is most clearly demonstrated when the sum of the three O–Mo–O bond angles

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of a distorted *fac*-$\mathrm{Mo^VN_3O_3}$ octahedron is taken into consideration. For the trans isomer this sum is calculated to be 304.5° whereas for the cis isomer a value of 310.4° is found. It is noted that for bis(2-thiopyrimidinato)bis(pyridine)-*cis*-dioxobis(μ-oxo)dimolybdenum(V) a value of 314.7° is observed;[16] for two other *cis*-$\mathrm{Mo_2O_4}$ units[15,16] this sum is ~310°; and for the monomeric [dien$\mathrm{Mo^{VI}O_3}$] the sum of three O–Mo–O angles equals 319°.[19] The Mo–$\mathrm{O_b}$ and Mo═$\mathrm{O_t}$ bond distances are nearly identical in both structures. This leads to a slightly *increased* nonbonding overall distance between the oxygen atoms of the $\mathrm{LMoO_3}$ moieties of the cis isomer $\sum_1^3 d(\mathrm{O\cdots O})$ = 8.646 Å for the cis isomer and 8.750 Å for the trans isomer), although the nonbonding $\mathrm{O_b\cdots O_b}$ distance of the oxo bridges in the cis isomer is shorter (puckered $\mathrm{Mo_2O_2}$ ring!) than in the trans isomer (planar $\mathrm{Mo_2O_2}$!) by 0.10 Å. Thus, the three oxygen atoms of the $\mathrm{MoN_3O_3}$ octahedron are farther apart from each other by 0.104 Å in the cis isomer. This small difference may acount for the enhanced thermodynamic stability of the cis isomer.

The rate law for the acid-catalyzed trans → cis isomerization is in accord with a mechanism where the protonated form of the trans isomer reacts in the rate-determining step (eq 8–10).

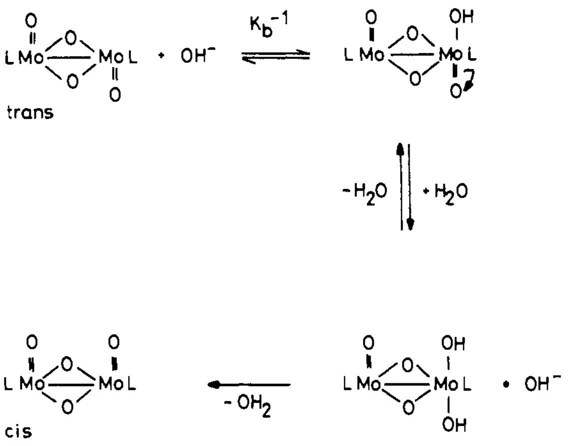
$$trans\text{-}[\mathrm{L_2Mo_2O_4}]^{2+} + \mathrm{H^+} \underset{}{\overset{K_a^{-1}}{\rightleftharpoons}} trans\text{-}[\mathrm{L_2Mo_2O_4H}]^{3+} \quad (8)$$

$$trans\text{-}[\mathrm{L_2Mo_2O_4H}]^{3+} \xrightarrow{k_a} cis\text{-}[\mathrm{L_2Mo_2O_4H}]^{3+} \quad (9)$$

$$cis\text{-}[\mathrm{L_2Mo_2O_4H}]^{3+} \xrightarrow{\text{fast}} cis\text{-}[\mathrm{L_2Mo_2O_4}]^{2+} + \mathrm{H^+} \quad (10)$$

Values for the dissociation constant and for k_a are given in Table VI. Although the actual point of protonation is not known, we consider one of the terminal oxo groups to be most susceptible for an electrophilic attack, which leads to a weakening of the Mo═OH bond. It is then conceivable that an addition of an $\mathrm{H_2O}$ molecule takes place, trans to the protonated Mo═OH group. Further protonation of this moiety gives a coordinated $\mathrm{H_2O}$ that dissociates with concomitant deprotonation of the incoming $\mathrm{H_2O}$ molecule, thereby producing the cis isomer (Scheme II). A different scheme involving protonation of an oxo bridge and Mo–O bond fission is considered to be less likely. The base-catalyzed trans → cis isomerization may then be explained by a very similar mechanism. Nucleophilic attack of $\mathrm{OH^-}$ at one Mo(V) center trans to a Mo═O unit generates an intermediate species that may be converted to the cis isomer via a reaction sequence depicted in Scheme III. Equations 11 and 12 are in accord with the rate law (7). Values for K_b and k_b are given in Table VI.

Scheme III



$$trans\text{-}[\mathrm{L_2Mo_2O_4}]^{2+} + \mathrm{OH^-} \overset{K_b^{-1}}{\rightleftharpoons} [\mathrm{L_2Mo_2O_4(OH)}]^+ \quad (11)$$

$$[\mathrm{L_2Mo_2O_4(OH)}]^+ \xrightarrow{k_b} cis\text{-}[\mathrm{L_2Mo_2O_4}]^{2+} + \mathrm{OH^-} \quad (12)$$

The common feature of both mechanisms is the irreversible substitution of a terminal oxo ligand via nucleophilic attack of $\mathrm{OH_2}$ or $\mathrm{OH^-}$ at a molybdenum(V) center at a position trans to the original oxo ligand. Kinetic studies using $^{18}\mathrm{O}$-labeled starting materials should prove the proposed mechanism. Interestingly, Murmann has reported[20] that no oxygen exchange in acidic or basic solutions has been observed for the [(edta)$\mathrm{Mo_2O_4}$]$^{2-}$ anion, which contains the *cis*-$\mathrm{Mo_2O_4}$ moiety. This is in agreement with our observation that the isomerization is irreversible trans → cis.

Acknowledgment. Financial support of this research by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowledged.

Registry No. $[\mathrm{L_2Mo_2(H_2O)_2(\mu\text{-}OH)_2}]^{4+}$, 92542-35-3; *trans*-$[\mathrm{L_2Mo_2O_4}]^{2+}$, 92542-34-2; $[\mathrm{Mo_2([9]aneN_3)_2(\mu\text{-}OH)_2(\mu\text{-}CO_3)}](\mathrm{BF_4})_2$, 92489-86-6; $[\mathrm{Mo_2([9]aneN_3)_2(\mu\text{-}OH)_2(OH_2)_2}](\mathrm{BF_4})_4$, 92542-36-4; $\mathrm{Cl^-}$, 16887-00-6; $\mathrm{ClO_4^-}$, 14797-73-0; bis(μ-hydroxo)-*trans*-bis[chloro(1,4,7-triazacyclononane)molybdenum(III)](2+), 92542-37-5.

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