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Electron Transfer. 116. Reductions by Trinuclear Aquamolybdenum(III)[1]

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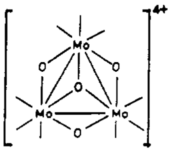
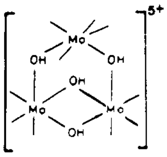
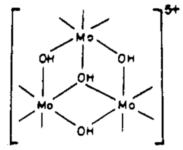
Received August 20, 1992

The red trinuclear cation of molybdenum(IV), $Mo_3O_4(OH_2)_9^{4+}$ (structure I), is reduced rapidly and quantitatively to a green trinuclear molybdenum(III) species, $(Mo^{III})_3$, using Zn–Hg in 2 M *p*-toluenesulfonic acid. This trimeric Mo(III) cation reacts readily with a series of $(NH_3)_5Co^{III}$ oxidants, first forming a 1e⁻ oxidation product, $Mo^{IV,III,III}$, which is further oxidized more slowly to the $(Mo^{IV})_3$ cation, I. In no case is there indication of the accumulation of a $Mo^{IV,IV,III}$ intermediate. Rate laws for the initial step indicate the operation of kinetic paths involving $(Mo^{III})_3$ as such (Red) and as its conjugate base (Red–OH). Reactions with $(NH_3)_5Co(OAc)^{2+}$ appear to involve the protonated ($Co–OAcH^{3+}$) form of this oxidant. Rate laws for the oxidation of $Mo^{IV,III,III}$ are more diverse, and there is kinetic evidence for the formation of complexes of the type Ox·Red with amide-substituted oxidants. The initial oxidations are taken to utilize outer-sphere paths exclusively, and the specific rates for the deprotonated reductant, Red–OH, are found to be proportional to the values of k_{Ru} pertaining to reactions of the outer-sphere reagent $Ru(NH_3)_6^{2+}$ for the same series of Co(III) oxidants. Comparison of the reactivities of $(Mo^{III})_3$ and $Ru(NH_3)_6^{2+}$ within the framework of the Marcus model leads to an estimated self-exchange rate of $10^{4.2\pm0.6}$ M^{-1} s^{-1} for $(Mo^{III})_3$/$Mo^{IV,III,III}$. This relatively high value is in accord with Richens' assignment of structure II to both the reactive $(Mo^{III})_3$ cation and (with an extra unit of positive charge) to $Mo^{IV,III,III}$ and rules out the possibility that major structural changes are associated with electron transfer in this trinuclear system. Although earlier studies suggest that cation II exists in equilibrium with larger concentrations of a second trinuclear complex (structure III) in 2 M CF_3SO_3H solutions which are allowed to age for more than 10 h, we find it to be the only kinetically detectable reductant in solutions which are used within 1 h after reduction in HTos.

No metal offers a more abundant variety in its patterns of redox behavior than does molybdenum. All oxidation states of that element between 2+ and 6+ are of importance, and these in turn form an array of dimeric and polymeric species, each with a distinctive chemistry.[2] Typically, recent studies have dealt with three different aqua complexes of Mo(III): (A) the yellow mononuclear cation, $Mo(H_2O)_3^{3+}$;[3] (B) a dinuclear derivative, which is formulated as a μ-dihydroxy complex, $Mo_2(OH)_2^{4+}$;[4] and (C) a green trinuclear aquamolybdenum(III) cation, which may be prepared by reduction of the trinuclear Mo(IV) ion, I. For the third of these Mo(III) ions, related structures II and III have been proposed[2e,5] (coordinated H_2O's are not shown).


I, $(Mo^{IV})_3$


II, $(Mo^{III})_3$


III, $(Mo^{III})_3$

Impelled both by our continuing interest in the redox chemistry of the lower oxidation states of molybdenum[6] and by the increased availability of the $(Mo^{IV})_3$ precursor, I,[6c] we have examined a number of oxidations of the trinuclear cation $(Mo^{III})_3$. The latter is an unusually facile reductant, and its reactions with several of the more sluggish Co(III) oxidants are best monitored using stop-flow methods. The resulting profiles yield information concerning the production and further oxidation of a one-electron intermediate, Mo(IV,III,III).

Experimental Section

Materials. *p*-Toluenesulfonic acid (HTos), trifluoromethanesulfonic acid (triflic acid) and its lithium salt (lithium triflate) (Aldrich products) were used as received.

Solutions of the red ion, $(Mo^{IV})_3$, (I) in 2 M HTos were prepared as described.[6c,7] The concentration of Mo(IV) was estimated at 505 nm (ε = 63 M^{-1} cm^{-1} per Mo). This was converted to the green cation, $(Mo^{III})_3$, by reduction with Zn–Hg under N_2,[5a] a reaction requiring 5 min at 25 °C in 2 M aqueous HTos. Maxima of the latter were at 821 (ε = 45 M^{-1} cm^{-1} per Mo) and 638 nm (87 M^{-1} cm^{-1}; lit:[5a] 825 (ε = 45) and 635 nm (80 M^{-1} cm^{-1}). Solutions of $(Mo^{III})_3$ were used within 1 h after preparation. In our hands, solutions of $(Mo^{III})_3$ prepared by reduction of $(Mo^{IV})_3$ with Eu(II)[2e] were less stable than those obtained from reaction with Zn-Hg and were generally not satisfactory for kinetic experiments. All operations involving both $(Mo^{IV})_3$ and $(Mo^{III})_3$ were carried out in de-ionized water that had been previously boiled for at least 1 h and then, after addition of supporting electrolyte, sparged with N_2 for 4 h.

Cobalt(III) complexes used as oxidants were available as their perchlorates from previous studies[8] or were prepared from aquopentaaminecobalt(III) perchlorate as described.[9,10]

Stoichiometric Studies. The stoichiometry of the reactions with three oxidants were determined, taking Co(III) in excess, by adding each oxidant to a known deficiency of $(Mo^{III})_3$, waiting for completion of the reaction,

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(1) Sponsorship of this work by the National Science Foundation (Grant 9019840) is gratefully acknowledged.

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Table I. Stoichiometries of the Oxidations of $(Mo^{III})_3$ with Co(III) Complexes[a]

oxidant	waiting period	$[(Mo^{III})_3]$, M × 10^3	$[Co^{III}]$, M × 10^3	$\Delta[(Mo^{III})_3]$, M × 10^3	$\Delta[Co^{III}]$, M × 10^3	$\Delta[Co^{III}]/\Delta[(Mo^{III})_3]$
$Co(NH_3)_5OAc^{2+}$	2 h	2.00	12.0		6.7	3.4
		2.00	9.0		6.7	3.4
		1.33	12.0		4.4	3.3
$Co(NH_3)_5Py^{3+}$	2 h	1.33	6.0		4.6	3.4
		1.33	8.0		4.4	3.3
		0.67	6.0		2.2	3.3
	4.5 min	0.67	0.25	0.23		1.08
		0.67	0.50	0.47		1.06
$Co(en)_3^{3+}$	2 h	2.00	12.0		6.8	3.4
		1.33	12.0		4.1	3.1
		2.00	9.0		5.5	2.8

[a] Reactions were carried out in 0.2–0.7 M *p*-toluenesulfonic acid. With Co(III) in excess, $\Delta[Co^{III}]$ was determined by measuring $[Co^{II}]$ in HCl at 692 nm; with $(Mo^{III})_3$ in excess, $\Delta[Mo^{III}]$ was estimated from absorbance change at 635 nm (see Experimental Section).

diluting the solution tenfold with con HCl, and measuring the absorbance of Co(II) at 692 nm (ϵ = 560).[11] In addition, the stoichiometry of the reaction with $(NH_3)_5Co(py)^{3+}$, taking $(Mo^{III})_3$ in excess, was estimated at 635 nm by adding a measured quantity of Co(III) to the reductant, waiting 90 s, then comparing the observed change in absorbance to that resulting from addition of a slight excess of Co(III). Results are summarized in Table I.

Additional Observations. Addition of the slowest of the Co(III) oxidants, $Co(en)_3^{3+}$ (2.0 mM) to $(Mo^{III})_3$ (0.67 mM) in 1 M HTos demonstrated that the overall reaction occurs in two separable steps. The first of these proceeded with an isosbestic point at 367 nm and produced an intermediate species with λ_{max} at 400 nm (ϵ = 227 M^{-1} cm^{-1} per Mo). In the second stage of reaction, this intermediate was consumed, yielding a product with a spectrum corresponding to that of $(Mo^{IV})_3$ (ϵ_{505}^{max} = 189 M^{-1} cm^{-1}).

Reaction of $(Mo^{III})_3$ with 0.05 M ClO_4^- (the largest concentration added in our kinetic runs) in the absence of Co(III) was found to negligibly slow under our experimental conditions.

Kinetic Studies. Reactions were generally monitored at 400 nm (λ_{max} for the reaction intermediate) by using either a Durrum-Gibson stopped-flow spectrophotometer interfaced with an OLIS computer system, or, for the slower reactions, a Beckman Model 5260 recording spectrophotometer. Acidity was regulated by adding *p*-toluenesulfonic or triflic acid, and the ionic strength was maintained at 1.0 M using either Na^+Tos^- or lithium triflate.[12] Reactions were usually carried out with the oxidant in excess, and concentrations were adjusted so that less than 10% of the oxidant was consumed during a run. In all cases, a rapid increase in absorbance, followed by larger decrease, was observed. Depending upon the oxidant taken, its concentration, and the acidity of the medium, peak absorbances occurred 3–300 s after mixing. In some cases, the components corresponded to two separate independent transformations, but in most instances curves were resolved into contributing pseudo-first order processes as described by Bose.[13]

Results and Discussion

The cation-exchange behavior of $(Mo^{III})_3$ is consistent with a net charge of +5 or greater,[5a,14] and the relatively easy electrochemical interconversions[5] between $(Mo^{III})_3$ and $(Mo^{IV})_3$ indicate that the lower state features the "triangulo" structural unit (I) recognized to be present in the upper.[15,7b] However, detailed electrochemical studies[5b] point to the coexistence of two $(Mo^{III})_3$ species in solutions which have been allowed to age, and O^{17}-NMR studies of such solutions[2e] support the assignment of structures II (with 10 bound H_2O's) and III (with 9 H_2O's), in a ratio near 1:2 in 1.3 M TosH. Paffett[5b] has noted that reduction of $(Mo^{IV})_3$ with Zn–Hg gives one of these ions initially, and that this is converted to an equilibrium mixture of the two components with $t_{1/2}$ approximately 10 h in 2 M triflic acid. Our preparations of $(Mo^{III})_3$, which were used immediately after its generation, by reduction, gave no indication of two kinetically distinct reducing species which are slowly interconverted on the time scale of our experiments.

Stoichiometries of the Co^{III}–$(Mo^{III})_3$ reactions are seen (Table I) to approach 3:1 with the oxidant in excess but lie near 1:1 with the reductant in excess, being thus in accord with reactions 1 and 2. Comparisons of the spectra of the oxidation products under

$$3Co^{III} + (Mo^{III})_3 \rightarrow 3Co^{II} + (Mo^{IV})_3 \qquad (1)$$

$$Co^{III} + (Mo^{III})_3 \rightarrow Co^{II} + Mo^{IV,III,III} \qquad (2)$$

the two sets of conditions with the reported spectra of the trinuclear Mo(IV) cation (I)[6c] and the mixed valence species[2e] confirm these formulations as the predominant transformations, but the observed positive departures from 3:1 stoichiometry suggest that limited further oxidation of $(Mo^{IV})_3$ (presumably to Mo^{VI})[6c] may be occurring with excess Co(III) at extended reaction times.

Each of our reactions, carried out at 400 nm (the reported[2e] maximum for $Mo^{IV,III,III}$) features the growth and decay of this species, but in no case is there indication of the accumulation of the $2e^-$ product, $Mo^{IV,IV,III}$.

Representative kinetic data, pertaining to oxidations by the aqua and acetato derivatives of $(NH_3)_5Co^{III}$, appear in Table II and include pseudo-first order specific rates for both the formation (k_f) and decay (k_d) of the $1e^-$ oxidation product. Formation is first order in Co(III) with both pentaammines, but variation of k_f with acidity is seen to be in opposing directions for the two oxidants. Consumption of the intermediate by $Co(NH_3)_5(H_2O)^{3+}$ is first order in Co(III), but that by the acetato complex is seen to exhibit kinetic saturation.

Rates for both components of the oxidation by $(NH_3)_5Co(H_2O)^{3+}$ conform to the two-term rate law (3),

$$(k_{obsd}) = (-d[Red]/dt)/[Red] = [Ox](k_0 + k'/[H^+]) \qquad (3)$$

indicating the operation of two paths, one of which (k_0) involves the redox partners in their predominant forms, with the second (k') utilizing one of these reactants as its conjugate base. Since

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(9) Gould, E. S.; Johnson, N. A.; Morland, R. B. *Inorg. Chem.* **1976**, *15*, 1929. Complex perchlorates derived from basic ligands (e.g. imidazole) were sometimes contaminated the ligand hydroperchlorate. Purification was achieved by carefully dissolving in 1 M aqueous tris(hydroxymethyl)aminomethane at room temperature, after which the desired complex was quickly precipitated by addition of aqueous $NaClO_4$.[10]

(10) Heh, J. C.-K.; Gould, E. S. *Inorg. Chem.* **1978**, *17*, 3138.

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(12) Solubility problems involving the Co(III) oxidants were much less frequently encountered in triflate than in tosylate systems.

(13) Bose, R. N.; Gould, E. S. *Inorg. Chem.* **1985**, *24*, 2832. Specific rates for rise and fall in absorbance for the $(Mo^{III})_3$–$Co(en)_3^{3+}$ reaction were very nearly equal. Treatment of reaction profiles for this system utilized eq 3 in footnote 16 of the cited contribution.

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Table II. Representative Kinetic Data for the Oxidations of $(Mo^{III})_3$ by $[Co(NH_3)_5(H_2O)]^{3+}$ and $[Co(NH_3)_5(OAc)]^{2+}$ [a]

$Co(NH_3)_5(H_2O)^{3+}$ reactions				$Co(NH_3)_5(OAc)^{2+}$ reactions			
[Ox], mM	[H⁺], M	k_f, s^{-1} [b]	10^2k_d, s^{-1} [b]	[Ox], mM	[H⁺], M	k_f, s^{-1} [b]	10^2k_d, s^{-1} [b]
24.0	1.0		18.6 (17.9)	10.0	1.00	1.49 (1.53)	6.0 (6.4)
12.0	1.0		8.8 (8.9)	7.5	1.00	1.14 (1.15)	
6.0	1.0		4.4 (4.5)	7.0	1.00		5.5 (5.5)
5.0	1.0	4.0 (3.9)	4.0 (3.7)	5.0	1.00	0.75 (0.76)	4.8 (4.6)
2.5	1.0	1.80 (1.93)		3.5	1.00		3.9 (3.8)
5.0	0.125	7.0 (7.3)	17.0 (16.4)	2.8	1.00	0.43 (0.43)	
5.0	0.25	5.6 (5.3)	9.8 (9.1)	2.5	1.00		2.8 (3.0)
5.0	0.37	5.0 (4.7)	6.5 (6.8)	5.0	0.11		8.9 (9.0)
5.0	0.50	4.3 (4.4)	4.9 (5.5)	5.0	0.18	0.63 (0.67)	
5.0	0.75	4.1 (4.0)	4.5 (4.3)	5.0	0.24		8.2 (8.1)
				5.0	0.30	0.70 (0.68)	
				5.0	0.36		7.4 (7.3)
				5.0	0.50	0.78 (0.71)	
				5.0	0.75	0.74 (0.74)	6.2 (5.7)

[a] Reactions were carried out at 22 °C, μ = 1.0 M (lithium triflate); $[(Mo^{III})_3]$ = 0.17–0.60 mM. [b] Pseudo-first order specific rates for formation (k_f) and decay (k_d) of le⁻ oxidation product; parenthetical values were calculated using rate laws 3, 4, and 7 and kinetic parameters in Tables III and IV.

Table III. Kinetic Parameters for the le⁻ Oxidations of $(Mo^{III})_3$ (k_f)[a]

$$(Mo^{III})_3 + Co^{III} \rightarrow Mo^{IV,III,III} + Co^{II}$$

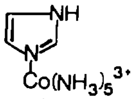
$$\text{rate} = [Ox][Red](k_o + k'[H^+]^{-1}) \tag{3}$$

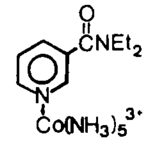
oxidant	[H⁺], M	k_o, M^{-1} s^{-1}	k', s^{-1}
$Co(en)_3^{3+}$	0.10–1.0		0.068 ± 0.003
$Co(NH_3)_5(imidazole)^{3+}$ (IV)	0.11–0.75	9.1 ± 1.1	2.5 ± 0.3
$Co(NH_3)_5(H_2O)^{3+}$	0.125–1.0	(6.8 ± 0.3) × 10^2	98 ± 11
$Co(NH_3)_5(pyridine)^{3+}$	0.080–1.0	143 ± 10	33 ± 4
$Co(NH_3)_5(diethylnicotinamide)^{3+}$ (V)	0.16–1.0	135 ± 38	156 ± 12
$Co(NH_3)_5(dimethylformamide)^{3+}$	0.20–1.0	106 ± 23	110 ± 13

[a] Reactions at 22 ± 1 °C, μ = 1.0 M (lithium triflate). Parameters k_o and k' were obtained from refinement of k_f values (measured at 400 nm) pertaining to generation of $Mo^{IV}Mo^{III}Mo^{III}$ in accordance with (3).

this inverse-acid term occurs with six oxidants in the present study whether or not these have acidic protons, it may reasonably attributed to deprotonation of the reductant. No approach to kinetic saturation with respect to [H⁺] is observed at the lowest acidities ([H⁺] = 0.08 M) compatible with our reagents, pointing to a $pK_a > 2$ for both $(Mo^{III})_3$ and its le⁻ oxidation product. Refinement of data for reaction with the aqua-substituted oxidant yields k_0 = (6.8 ± 0.3) × 10^2 M^{-1} s^{-1} and k' = 98 ± 11 s^{-1} for the initial le⁻ reduction, with k_0 = 3.8 ± 0.3 M^{-1} s^{-1} and k' = 3.6 ± 0.2 s^{-1} for consumption of the intermediate. The k' values correspond to lower limits of 10^4 and 4 × 10^2 M^{-1} s^{-1} for bimolecular rate constants pertaining to reaction of the deprotonated reductant (Red–OH). Rates calculated using (3) are compared with observed values in Table II.[16,17]

Kinetic parameters applicable to generation of $Mo^{IV,III,III}$ by reaction with other Co(III) oxidants, including the complexes of imidazole (IV) and *N′*,*N′*-diethylnicotinamide (V) are assembled in Table III.


IV


V

Oxidations by $(NH_3)_5Co(OAc)^{2+}$ are complicated by partial protonation of this cation ($OxH^+ \rightleftarrows Ox + H^+$; K_A^{OxH} = 4.0 at μ = 1.0 M)[18] in the range considered. Data for the initial le⁻ transformation are compatible with competing paths involving the protonated reductant (k_1) and its conjugate base (k_2), each with the (more reactive) protonated form of the oxidant, OxH, leading to rate law (4), where K_A^{Red} designates the acidity quotient for $(Mo^{III})_3$.

$$\text{rate} = [OxH](k_1[Red] + k_2[Red\text{–}OH]) = \frac{[Red]_{tot}[Ox]_{tot}(k_1[H^+] + k_2K_A^{Red})}{K_A^{OxH} + [H^+]} \tag{4}$$

Refinement in terms of (4) (using the reported[18] value for K_A^{OxH}) yields k_1 = (2.5 ± 0.3) × 10^2 M^{-1} s^{-1} and the product $k_2K_A^{Red}$ = (5.1 ± 0.2) × 10^2 s^{-1}.

Rate laws and kinetic parameters for consumption of the le⁻ oxidation product, $Mo^{IV,III,III}$, are summarized in Table IV. Patterns here feature rather more kinetic variety than those pertaining to its growth. The two-term expression (3) for the aqua- and pyridine-substituted oxidants corresponds to that observed for the initial reaction, whereas only the inverse-[H⁺] path is observable for the imidazole and $(en)_3$ derivatives.

Profiles for both amide-substituted cations exhibit kinetic saturation with respect to [Ox] (eq 6), pointing to the formation of a complex of the redox partners (Ox·Red). The form of this rate law is consistent with the sequence in eqs 8–10, Because no saturation with respect to [H⁺] is apparent, only the parameter product kK_A (rather than individual values of each) can be obtained.

The still more complicated expression (7) for reaction of $Mo^{IV,III,III}$ with the acetato oxidant is also in accord with reaction

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(16) The deprotonation of the aqua-substituted oxidant (pK_A = 6.2)[17] appears to play no part within the acidity range examined.

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(18) Barrett, M. B.; Swinehart, J. H.; Taube, H. *Inorg. Chem.* **1971**, *10*, 1983.

Table IV. Rate Laws and Kinetic Parameters for Oxidations of $Mo^{IV,III,III}$ [a]

$$Mo^{IV,III,III} + 2Co^{III} \rightarrow (Mo^{IV})_3 + 2Co^{II}$$

oxidant	rate law[b]	eq no.	parameters[c]
$Co(en)_3^{3+}$	$k[Ox][H^+]^{-1}$	5	$k = 0.068 \pm 0.003$ s^{-1} [d]
$Co(NH_3)_5(Im)^{3+}$ (IV)		5	$k = 1.01 \pm 0.04$ s^{-1}
$Co(NH_3)_5(H_2O)^{3+}$	$[Ox](k_o + k'[H^+]^{-1})$	3	$k_o = 3.8 \pm 0.3$ M^{-1} s^{-1}; $k' = 3.6 \pm 0.4$ s^{-1}
$Co(NH_3)_5(py)^{3+}$		3	$k_o = 2.8 \pm 0.6$ M^{-1} s^{-1}; $k' = 4.3 \pm 0.3$ s^{-1}
$Co(NH_3)_5(Et_2Nic)^{3+}$ (V)	$[Ox]kK_AQ^{OR}/[H^+](1 + Q^{OR}[Ox])$	6	$Q^{OR} = 97 \pm 20$ M^{-1}; $kK_A = 0.084 \pm 0.010$ M s^{-1}
$Co(NH_3)_5(DMF)^{3+}$		6	$Q^{OR} = 109 \pm 19$ M^{-1}; $kK_A = 0.092 \pm 0.008$ M s^{-1}
$Co(NH_3)_5(OAc)^{2+}$	$[Ox]kK_A^{Ox}K_A^{Red}Q^{OR}/[H^+](K_A^{Ox} + [H^+]) + K_A^{Ox}K_A^{Red}Q^{OR}[Ox]$	7	$k = 0.113 \pm 0.003$ s^{-1}; $K_A^{Ox} = 4.0$;[d] $K_A^{Red}Q^{OR} = (2.2 \pm 0.2) \times 10^2$

[a] Reactions at 22 °C; $\mu = 1.0$ M (lithium triflate). Ligand abbreviations: Im = imidizole; py = pyridine; Et_2Nic = *N′*,*N′*-diethylnicotinamide; DMF = *N*,*N*-dimethylformamide. [b] Rate laws describe $-d(\ln[Mo^{4.33}]/dt$. [c] Q^{OR} values pertain to the Ox·Red association quotient; K_A, K_A^{Ox}, and K_A^{Red} are deprotonation quotients. [d] Reference 18.

$$Ox + Red \rightleftharpoons Ox{\cdot}Red \qquad Q^{OR} \tag{8}$$

$$Ox{\cdot}Red \rightleftharpoons H^+ + Ox{\cdot}Red(OH) \qquad K_A \tag{9}$$

$$Ox{\cdot}Red(OH) \xrightarrow{k} \text{products} \tag{10}$$

through Ox·Red(OH), but further elaboration is necessary to accommodate partial protonation of Ox to OxH^+.[18]

Since there is no indication that an intermediate $Mo^{IV,IV,III}$ accumulates, conversions to $(Mo^{IV})_3$ may be taken to proceed through a pair of $1e^-$ steps, with the oxidation of $Mo^{IV,III,III}$ rate-determining.

To compare the reactivities of the oxidants taken, we may consider the initial oxidations of $(Mo^{III})_3$ (Table III), for which observed rate laws are closely analogous. The reactivity pattern brings to mind that encountered for reductions of the same set of oxidants by such reducing metal centers as V^{2+}, $Ru(NH_3)_6^{2+}$, and U^{3+}.[8,19] Values of log k', observed for all oxidants taken, are plotted against the analogous values of log k_{Ru} (pertaining to reductions by $Ru(NH_3)_6^{2+}$ at 25 °C in 0.50 M LiCl)[8b] in Figure 1. The slope of the resulting regression line (log k'_{Mo} = 1.08 log k_{Ru} + 1.71) is very nearly unity, telling us that specific rates for reductions by the deprotonated form of $(Mo^{III})_3$ are proportional to those for $Ru(NH_3)_6^{2+}$. Moreover, this proportionality extends to the corresponding rates for Cr^{2+}, Eu^{2+}, V^{2+}, and U^{3+}, since values for each of these reductants are in turn proportional to k_{Ru}.[8,19] The $1e^-$ oxidations of Red(OH) thus conform to the Marcus model,[20] in which differences in ΔG^* associated with changes in the ligand environment about the oxidizing center are nearly independent of the reductant.

Except for the aqua and acetato complexes, the structures of our oxidants dictate outer-sphere redox paths. The aqua point (aq) falls close to the $(Mo^{III})_3$–$Ru(NH_3)_6^{2+}$ regression line, and we find no evidence pointing to a kinetic contribution involving $Co(NH_3)_5(OH)^{2+}$ (for which a bridged path may be envisaged).[21] The initial $(Mo^{III})_3$–$Co(OAc)^{2+}$ reaction appears to proceed preponderantly through the protonated form of the oxidant, in which the basic-site of the bound acetato group is blocked off by attachment of H^+ and is not available for bridging.[22]

The apparent nonutilization of inner-sphere routes in the rapid $1e^-$ reactions of Red(OH) in the $(Mo^{III})_3$ system, and by implication, in the oxidations of the protonated form (k_0 terms) as well, is in accord with slow exchange of H_2O in the coordination sphere of this reductant, a feature which allows the appearance, in ^{17}O NMR spectra, of well-defined resonances attributable to Mo-bound water.[2e] Application of a mechanistic assignment to our oxidations of $Mo^{IV,III,III}$ is less certain, for these are generally much slower than those of $(Mo^{III})_3$ and proceed by more diverse rate laws.

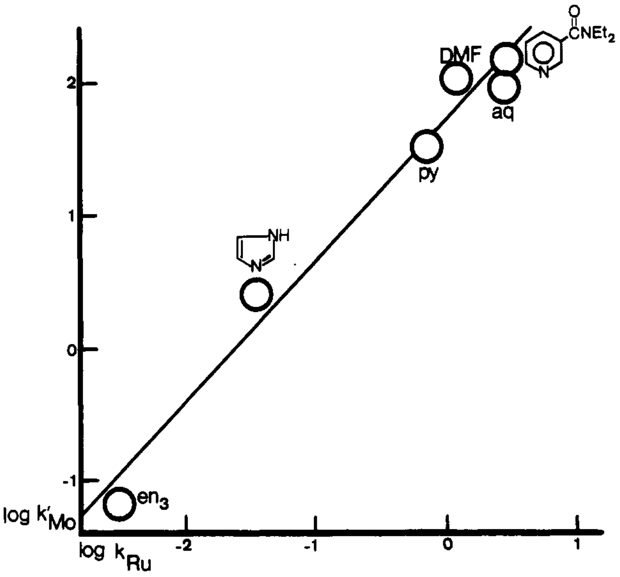

Figure 1. Log–log plot comparing $[H^+]^{-1}$-proportional specific rates, k'_{Mo}, for reductions of the cobalt(III) complexes, listed in Table II, by $(Mo^{III})_3$ (22 °C, μ = 1.0 M ($CF_3SO_3^-$)) and by $Ru(NH_3)_6^{2+}$ (k_{Ru}, 25 °C, μ = 0.5 M (Cl^-)). The least-squares line shown corresponds to the relationship log k'_{Mo} = (1.08 ± 0.08) log k_{Ru} + (1.72 ± 0.10).

The relative reactivities of $(Mo^{III})_3$ and $Ru(NH_3)_6^{2+}$ in conjunction with the reported formal potential (−0.175 V vs. NHE)[2e] of the trimeric reductant, allow us to calculate an electron self-exchange rate for $(Mo^{III})_3/Mo^{IV,III,III}$. Values of k_0 for $(Mo^{III})_3$ (adjusted to 25 °C) pertaining to the oxidants at hand exceed those for k_{Ru} by an average factor of $10^{2.3\pm0.3}$. In terms of the simplified Marcus model,[20] this difference stems almost entirely from the 0.242 V difference in formal potentials associated with the two reductants,[23-25] which then may be assigned very similar self-exchange rates. Despite the approximate nature of this treatment, the rate so estimated, $10^{4.2\pm0.6}$ M^{-1} s^{-1}, for $(Mo^{III})_3$ may be considered great enough to rule out the possibility that major changes in bond connectivity and/or molecular geometry occur prior to the electron transfer act in this trinuclear system.

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(23) The reported formal potential and self-exchange rate for $Ru(NH_3)_6^{2+/3+}$ are +0.067 V[24] and $10^{3.6}$ M^{-1} s^{-1}.[25] Note that the indicated difference in potentials for the two reductants corresponds[20] to a reactivity ratio of $10^{2.05}$.

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Our observations are in accord with Richens' assignment of structure II to both the readily oxidized $(\mathrm{Mo^{III}})_3$ cation and (with an extra unit of positive charge) to $\mathrm{Mo^{IV,III,III}}$.[2e] However, in contrast to his view that II is formed slowly, and in minor amount (36%), when solutions of the alternate $(\mathrm{Mo^{III}})_3$ species (structure III) are allowed to equilibrate in triflic acid, we find our reductant to be generated rapidly and quantitatively on reduction of $(\mathrm{Mo^{IV}})_3$. We suspect then that transformation of the initially formed trinuclear reductant to the equilibrium mixture described both by Richens[2e] and by Paffett[5b] entails a net conversion of II to III, rather than the reverse. Further examination of this system may be informative.[26]

Acknowledgment. The authors are grateful to Dr. M. C. Ghosh for valuable discussions and to Ms. Arla McPherson for technical assistance.

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(26) A reviewer inquires as to the fate of the $\mathrm{Mo^{IV,IV,III}}$ intermediate which necessarily intervenes when $\mathrm{Mo^{IV,III,III}}$ is oxidized to $(\mathrm{Mo^{IV}})_3$ but is observed neither in the present work nor in the related study by Richens and Sykes[5c] dealing with electrolytic and air oxidations of $(\mathrm{Mo^{III}})_3$. These authors present evidence that disproportionation of this intermediate ($2\mathrm{Mo^{IV,IV,III}} \rightarrow \mathrm{Mo^{IV,III,III}} + (\mathrm{Mo^{IV}})_3$) is highly favored thermodynamically at $[\mathrm{H^+}] = 0.5$–4.0 M but becomes much less so at lower acidities. We suspect that both disproportionation and rapid oxidation of this intermediate by $\mathrm{Co^{III}}$ are occurring in our systems, with the latter becoming more important at low $[\mathrm{H^+}]$. Our experiments do not allow us to gauge the relative importance of the two processes, both of which are consistent with the observed stoichiometries.