data also indicate that formation of metal complexes of macrocyclic ligands containing pendent acetate arms involves a rapid preequilibrium established through coordination to a carboxylate group. The structure of $[Mg(H_2TETA)(H_2O)_4]\cdot 4H_2O$ reported here may be representative of this type of kinetic species.

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Supplementary Material Available: Tables listing anisotropic temperature factors, additional crystallographic information, and bond distances and angles for I and II (7 pages); tables of calculated and observed structure factors for I and II (21 pages). Ordering information is given on any current masthead page.

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Electron Transfer. 110. Oxidations of Trinuclear Aquomolybdenum(IV)

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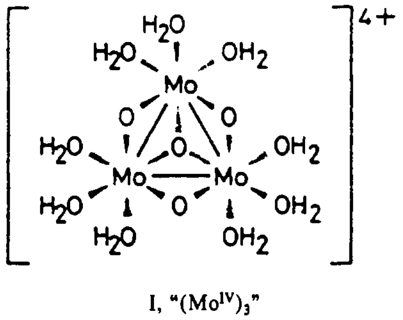
The trimeric cation of molybdenum(IV), $Mo_3O_4(OH_2)_9{}^{4+}$, (structure I) readily reacts with oxyhalogen species and metal-center oxidants in aqueous acid. Conversions are to Mo(VI), even with the oxidants in deficiency. Reductions of BrO_3^- and ClO_3^- are to the respective halide ions, whereas H_5IO_6 is reduced rapidly to IO_3^-, which is then reduced much more slowly. Kinetic patterns for oxidations by BrO_3^- and H_5IO_6 (rate law 6 in text) indicate that these reactions entail conversion of the reductant (pK_A = 0.7 at μ = 2.0 M) into its conjugate base, which forms a 1:1 complex with both oxyhalogens. Oxidation by V(V) appears to utilize two paths with transition states differing by a single H^+; an observed $[V(V)]^2$ dependency points to reaction via an unusually reactive vanadium(V) dimer. Oxidation by Fe(III) is unobservably slow in HTos or HCl but is markedly accelerated by thiocyanate, suggesting a specific bridging role for Fe(III)-bound NCS^-. Both $(Mo^{IV})_3$ and its anation product $(Mo^{IV})_3$–NCS are oxidized by $FeNCS^{2+}$, and both paths require loss of two protons. Oxidation by Cr(VI) is seen to pass through a strongly absorbing intermediate ($\epsilon_{530} = 3 \times 10^3\ M^{-1}\ cm^{-1}$ in 1 M HTos), which decays unimolecularly ($k = 1 \times 10^2\ s^{-1}$ at $[H^+]$ = 1.0 M). The behavior of this intermediate is consistent with its formulation as a complex of Cr(IV) associated with a partially oxidized molybdenum cluster (e.g. $Mo^{IV}Mo^{IV}Mo^{VI}$). Although all oxidations of $(Mo^{IV})_3$, by both 1e and 2e reagents, yield three Mo^{VI}'s (a net change of six units), rates are generally determined by the initial redox act. Succeeding electron transfers and breakup of partially oxidized Mo clusters proceed too rapidly to affect the kinetic picture.

Among the lower oxidation states of molybdenum,[1] there is continuing interest in Mo(IV), in part because of evidence that complexes of this state intervene in bioconversions catalyzed by the molybdoenzymes xanthine oxidase and xanthine dehydrogenase.[2] However, it is now recognized[3] that the aqueous chemistry of this state is dominated by the pink trinuclear ion $[Mo_3O_4(OH_2)_9]^{4+}$ (I). Although redox reactions involving aquomolybdenum species have been examined by a number of workers,[4] only scattered studies dealing with the transformations of "$(Mo^{IV})_3$" (I) have been described, possibly because preparations of this species from available materials require sequences of several steps. Reactions of $(Mo^{IV})_3$ with the strongly oxidizing 1e⁻ acceptors $IrCl_6^{2-}$, $Fe(phen)_3^{3+}$, and $Fe^{III}(aq)$ have been reported, and there are indications that both inner- and outer-sphere paths may operate.[5]



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

The present contribution deals with oxidations of the trinuclear molybdenum(IV) cation I using both oxyhalogen species and metal-center oxidants.

Experimental Section

Materials. Sodium chlorate (Baker and Adamson), sodium bromate (Sargent), sodium metaperiodate (MCB), sodium dichromate (MCB), ammonium metavanadate (Aldrich), iron(III) perchlorate (Alfa), and *p*-toluenesulfonic acid (HTos, Aldrich) were used as received. The sodium salt, Na^+Tos^- was prepared from the parent acid by neutralization with NaOH. The corresponding lithium salt was generated by treatment of the acid with Li_2CO_3 and then recrystallized twice from water. All solutions were prepared in distilled water that had been boiled for at least 1 h and then sparged with N_2 for 4 h.

To prepare solutions of $[Mo_3O_4(OH_2)_9]^{4+}$, the known Mo(III) complex $(NH_4)_2MoCl_5(OH_2)$[6] was treated with $Na_2MoO_4\cdot 2H_2O$ in 2 M HCl as described by Richens and Sykes.[3d,7] The resulting mixture of chloromolybdenum(IV) complexes, designated $Mo_3O_4Cl_n{}^{(4-n)+}$, was allowed to undergo aquation in aqueous 0.5 M HTos for 24 h under N_2. The preparation was then subjected to cation exchange chromatography under N_2, using Dowex 50W-X2. Impurities ($Mo_2O_4^{2+}$ and chloro complexes) were removed by washing successively with 0.5 and 1.0 M HTos, after which the desired aquo trimer, $(Mo^{IV})_3$, was eluted with 2.0 M HTos. The eluted solution was stored under N_2 at 0–4 °C and was found to be stable for 15 days under these conditions. Solutions were standardized spectrophotometrically at 505 nm; $\epsilon_{max} = 63\ M^{-1}\ cm^{-1}$ per Mo (189 per trimer).

Stoichiometric Studies. The stoichiometries of the reactions with the several oxo anions were determined, taking $(Mo^{IV})_3$ in excess, by adding a measured deficiency of the oxidant to $(Mo^{IV})_3$, waiting for completion

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Table I. Stoichiometries of the Reactions of $(Mo^{IV})_3$ with Oxyacids[a]

oxidant	$[H^+]$, M	waiting period, min	$[(Mo^{IV})_3]$, M × 10^4	[Ox], M × 10^4	$\Delta[(Mo^{IV})_3]$, M × 10^4	Δ[Ox], M × 10^4	$\Delta[(Mo^{IV})_3]/\Delta$[Ox]
BrO_3^-	0.18	5	6.7	3.0	2.9		0.97
			6.7	6.0	5.6		0.97
H_5IO_6	0.50	0.2	3.3	2.5	0.78		0.31
			5.0	3.8	1.50		0.39
			10.6	7.5	2.7		0.36
ClO_3^-	0.18	8	6.7	3.0	3.2		1.06
			6.7	6.0	6.1		1.02
Cr(VI)	0.61	2	32	30	15.6		0.52
			28	45	21		0.47
	0.0064		0.33	3.4		0.67	0.49
	0.0320		1.67	3.4		3.1	0.54
V(V)	0.38	8	10.0	20	3.3		0.165
			10.0	30	4.6		0.153
			10.0	60	9.5		0.158

[a] Reactions with $(Mo^V)_3$ in excess were followed at 505 nm; those with Cr^{VI} in excess were monitored at 350 nm.

of the reaction, and then measuring the decrease of absorbance at 505 nm. These changes were compared to those observed when $(Mo^{IV})_3$ was treated with excess oxidant. Results are summarized in Table I. In addition, the stoichiometry of the $(Mo^{IV})_3$–$Fe(SCN)^{2+}$ reaction was determined by spectrophotometric titration in 0.04 M $HClO_4$ at 505 nm. The latter gave a sharp "break-point" at $[Fe^{III}]:[Mo^{IV}] = 2.0$.

The chromium product from the reaction of Cr(VI) with excess $(Mo^{IV})_3$ was identified spectrally (after destruction of unreacted Mo^{IV} with $NaBrO_3$) as $Cr(H_2O)_6^{3+}$. Reaction with V(V) yielded VO^{2+}, $\epsilon_{max}^{760} = 17$.

Kinetic Studies. Rates were generally estimated from measurements of absorbance changes at 505 nm by using a Beckman 5260 recording spectrophotometer or (for very fast reactions) a Durrum-Gibson stopped-flow spectrophotometer. Since solutions of $(Mo^{IV})_3$ were found to undergo slow conversion to the characteristic blue isopolymolybdates at pH values above 1.5 (even under N_2), $[H^+]$ was kept between 0.030 and 2.0 M. Ionic strength was customarily maintained at 2.0 M by adding Na^+Tos^-. 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. Except as noted below, reactions yielded simple (psuedo-first-order) curves. Conversions were followed for at least 4 half-lives. Rate constants were evaluated by using either semilogarithmic plots of absorbance differences vs reaction times or nonlinear least-squares fittings to the relationship describing first-order decay. Specific rates for replicate runs using conventional mixing diverged by less than 8%, whereas stopped-flow experiments with each pair of master solutions were repeated until decay curves for three successive runs superimposed. Except for the reaction with Cr(VI), examination of kinetic profiles gave no indication of intermediates formed or destroyed on a time scale comparable to that for the disappearance of $(Mo^{IV})_3$.

The reactions with Cr(VI), which were monitored by using stopped-flow methods, did not yield the usual exponential decay curves. Kinetic profiles instead exhibited a small increase, followed by a large decrease in absorbance, with maximal absorbances occurring 20–30 ms after mixing. The indicated intermediate species absorbed most strongly at 530 nm. These biphasic kinetic traces were separated into contributing pseudo-first-order processes as described by Bose.[8]

Oxidations with iodate and with hypochlorous acid resulted in multiphasic profiles that could not be meaningfully disentangled. Reactions with ClO_2^- were characterized by erratic stoichiometry. Iron(III) did not oxidize $(Mo^{IV})_3$ at a measurable rate in ClO_4^- or Cl^- media, but reaction proceeded readily in the presence of NaSCN (see below). Reactions with Ce(IV) and Br_2 were complicated by reductions of these reagents by HTos in the supporting electrolyte; attempts to bypass the latter problem by carrying out the elution of $(Mo^{IV})_3$ from cation-exchange resin using CF_3SO_3H (in place of HTos) did not yield a satisfactory product.

Results and Discussion

Within the acidity range considered, BrO_3^- exists nearly completely as its nonprotonated form,[9] but I(VII) is converted largely to the weak acid H_5IO_6 (apparent $pK_A = 1.64$).[10a] The predominant form of V(V) under our conditions is VO_2^+,[11b] whereas Cr(VI) exists mainly as $HCrO_4^-$ ($pK_A = 5.8$).[11] A K_A value of 0.24 ($\mu = 2.0$ M) has been reported for $[Mo_3O_4(OH_2)_9]^{4+}$ by Richens and co-workers.[3d]

In no case did we observe measurable quantities of the dinuclear ion $[Mo_2O_4(H_2O)_6]^{2+}$, which is the stable form of Mo(V) under our conditions. All oxidations are then taken to proceed to the hexapositive state. Reactions of $(Mo^{IV})_3$ with BrO_3^- and ClO_3^- are seen (Table I) to consume nearly 1 mol of trimer (3 units of Mo^{IV}) per mole of oxidant. These oxyhalogens are then reduced to the 1– state (eq 1). The much lower stoichiometry seen with the more rapid oxidant, H_5IO_6 (2), indicates the formation of an intermediate state, an I(V) product (IO_3^-) which is then reduced so sluggishly that kinetic steps are readily separable. Stoichiometries of the reactions with Cr(VI), V(V), and $Fe(NCS)^{2+}$, in conjunction with the recognized states of the reduction products (Cr^{III}, V^{IV}, and Fe^{II}), are likewise in accord with oxidation of $(Mo^{IV})_3$ to Mo^{VI}.

$$(Mo^{IV})_3 + Hal^V \rightarrow 3Mo^{VI} + Hal^- \quad (Hal = Cl, Br) \tag{1}$$

$$(Mo^{IV})_3 + 3I^{VII} \rightarrow 3Mo^{VI} + 3I^V \tag{2}$$

$$(Mo^{IV})_3 + 2Cr^{VI} \rightarrow 3Mo^{VI} + 2Cr^{III} \tag{3}$$

$$(Mo^{IV})_3 + 6V^V \rightarrow 3Mo^{VI} + 6V^{IV} \tag{4}$$

$$(Mo^{IV})_3 + 6Fe^{III} \rightarrow 3Mo^{VI} + 6Fe^{II} \tag{5}$$

Kinetic data for two representative oxidants, BrO_3^- and V(V), are listed in Table II. Rates of both reactions increase with [oxidant], but the detailed dependencies are different. Variation of BrO_3^- rates is less steep than that corresponding to a direct proportionality, with an approach toward a limiting value seen at high $[Br^V]$. Rates with V(V) increase much more markedly, approaching a second-order dependence. Both reactions proceed more slowly at high acidities than at low acidities, but the V(V) reaction is again the more concentration sensitive. Rate laws describing the reactions of the four oxidants exhibiting exponential decay patterns are summarized in Table III. Also included are kinetic parameters resulting from least-squares refinements of observed rates in terms of these expressions. Specific rates calculated from these parameters are compared with observed rates in Table II.

Reactions with Oxyhalogens. Rate law (6), applying to the reactions of both Br(V) and I(VII), stipulates a limiting specific rate (k) at high [Ox] and low $[H^+]$, and is in accord with the formation of a 1:1 complex (association quotient K) between redox partners. It further points to the partition of one partner between two protonation levels (related by the acidity quotient K_A) with only the less protonated form reactive. The refined value of K_A, corresponding to a pK_A of 0.7, is the same for both systems and

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(10) (a) Kren, R. M.; Dodgen, H. W.; Nyman, C. J. *Can. J. Chem.* **1968**, *7*, 446. (b) Petterson, L.; Hedman, B.; Nenner, A.-M.; Andersson, I. *Acta Chem. Scand.* **1985**, *A39*, 499.

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Table II. Representative Kinetic Data for the Reaction of $(\mathrm{Mo^{IV}})_3$ with Bromate and Vanadium(V)[a]

$\mathrm{BrO_3^-}$ reactions				V(V) reactions			
$[(\mathrm{Mo^{IV}})_3]$, mM	$[\mathrm{Br^V}]$, mM	$[\mathrm{H^+}]$, M	10^2k,[b] $\mathrm{s^{-1}}$	$[(\mathrm{Mo^{IV}})_3]$, mM	$[\mathrm{V^V}]$, mM	$[\mathrm{H^+}]$, M	10^2k,[b] $\mathrm{s^{-1}}$
0.25	5.0	1.00	3.2 (3.3)	0.167	5.7	1.00	1.80 (1.74)
0.25	7.5		4.1 (4.6)	0.167	9.0		4.5 (4.3)
0.25	10.0		5.5 (5.8)	0.167	12.0		7.7 (7.7)
0.50	15.0		7.6 (7.9)	0.33	13.0		9.0 (9.0)
0.25	20		9.7 (9.7)	0.33	19.0		19.6 (19.3)
0.25	25		11.7 (11.2)	0.33	22		26 (26)
0.25	30		12.8 (12.5)	0.33	28		42 (42)
0.25	50		16.3 (16.0)	0.33	34		62 (62)
0.25	5.0	1.90	2.0 (1.95)	0.33	12.0	0.18	45 (47)
0.25	5.0	0.50	5.4 (5.1)	0.33	13.0	0.19	52 (52)
0.25	5.0	0.30	6.7 (6.7)	0.33	13.0	0.25	44 (39)
0.25	5.0	0.10	10.5 (9.8)	0.33	13.0	0.38	24 (25)
25	0.40	1.00	1.65 (1.69)	0.33	13.0	0.58	17.9 (16.0)
25	0.40	0.75	2.2 (2.1)	0.33	12.0	0.58	13.4 (13.6)
25	0.40	0.50	2.7 (2.8)	0.33	13.0	0.78	10.1 (11.7)
25	0.40	0.30	3.8 (3.8)				

[a] Reactions were carried out at 25 °C and monitored at 505 nm; $\mu = 2.0$ M ($\mathrm{Na^+Tos^-}$) for $\mathrm{BrO_3^-}$ reactions and 1.2 M ($\mathrm{Na^+Tos^-}$) for V(V) reactions. [b] Pseudo-first-order specific rates; parenthetical values were calculated by using the relationships and parameters in Table III.

Table III. Rate Laws and Kinetic Parameters for the Oxidations of Trimeric Molybdenum(IV)[a]

oxidant (Ox)	μ, M	rate law[b]	eq no.	parameters[c]
$\mathrm{BrO_3^-}$	2.0 ($\mathrm{Na^+Tos^-}$)	$kKK_A[\mathrm{Ox}]/(K_A + [\mathrm{H^+}] + KK_A[\mathrm{Ox}])$	6	$k = 0.29 \pm 0.03\ \mathrm{s^{-1}}$; $K = 150 \pm 20$; $K_A = 0.19 \pm 0.04$
$\mathrm{H_5IO_6}$	1.2 ($\mathrm{Li^+Tos^-}$)		6	$k = 44 \pm 2\ \mathrm{s^{-1}}$; $K = 70 \pm 8$; $K_A = 0.18 \pm 0.02$
V(V)	1.2 ($\mathrm{Na^+Tos^-}$)	$(kK_A + k'K_A[\mathrm{H^+}]^{-1})[\mathrm{Ox}]^2/(K_A + [\mathrm{H^+}])$	7	$k = (2.6 \pm 0.1) \times 10^3\ \mathrm{M^{-2}\ s^{-1}}$; $k' = 830 \pm 80\ \mathrm{M^{-1}\ s^{-1}}$; $K_A = 0.19$
$\mathrm{FeNCS^{2+}}$[d]	0.1 ($\mathrm{Na^+Tos^-}$)	$(k_1 + k_2K_{\mathrm{Mo}}[\mathrm{NCS^-}])[\mathrm{Red}]/$ $(1 + K_{\mathrm{Fe}}[\mathrm{NCS^-}])(1 + K_{\mathrm{Mo}}[\mathrm{NCS^-}])[\mathrm{H^+}]^2$	8	$k_1 = 0.192 \pm 0.008\ \mathrm{M^2\ s^{-1}}$; $k_2 = 0.138 \pm 0.007\ \mathrm{M^2\ s^{-1}}$; $K_{\mathrm{Mo}} = 300$;[e] $K_{\mathrm{Fe}} = 138$[f]

[a] Reactions were carried out at 25 °C and were monitored at 505 nm unless otherwise indicated. [b] Rate laws describe $-\mathrm{d}\ (\ln [(\mathrm{Mo^{IV}})_3])/\mathrm{d}t$. [c] K values pertain to the $(\mathrm{Mo^{IV}})_3$–Ox association quotient; K_A is a deprotonation quotient. [d] Reaction was monitored at 460 nm; rate law describes $-\mathrm{d}\ (\ln [\mathrm{Fe^{III}}])/\mathrm{d}t$. [e] Association quotient obtained by extrapolation of the data of Ooi and Sykes.[12] [f] K value reported by Carlyle and Espenson.[19]

is therefore considered to pertain to the reductant. It is in agreement with the value reported by Richens (0.62)[3d] but lies somewhat above that recorded by Ooi (0.4).[12] The indicated reaction sequence is thus given as (9)–(10) (only one of the nine

$$\underset{\mathrm{I}}{[(\mathrm{Mo^{IV}})_3\mathrm{OH_2}]^{4+}} \underset{K_A = 0.2}{\overset{-\mathrm{H^+}}{\rightleftharpoons}} [(\mathrm{Mo^{IV}})_3\mathrm{OH}]^{3+} \underset{K}{\overset{\mathrm{Ox}}{\rightleftharpoons}} (\mathrm{Mo^{IV}})_3\mathrm{OH(Ox)} \qquad (9)$$

$$(\mathrm{Mo^{IV}})_3\mathrm{OH(Ox)} \xrightarrow{k} \text{products} \qquad (10)$$

$\mathrm{H_2O}$'s associated with the reductant is shown). As expected, the association quotient, K, for the $\mathrm{BrO_3^-}$ anion is greater than that for the uncharged oxidant $\mathrm{H_5IO_6}$.[13]

Reaction with V(V). The rate expression for oxidation by V(V), (7), features a $[\mathrm{H^+}]^{-1}$-proportional term, pointing to participation of a doubly deprotonated (dispositive) $(\mathrm{Mo^{IV}})_3$ species, the formation of which is governed by an acidity constant (K_2) well below the $[\mathrm{H^+}]$ range examined. The specific rate associated with this form of the reductant, obtained by dividing k' by K_2, is at least 10^2k (which again pertains to $[\mathrm{Mo^{IV}}_3\mathrm{OH}]^{3+}$).

The perceived $[\mathrm{Ox}]^2$ dependence, implying the presence of two V(V)'s in the activated complex for both kinetic components, is unusual but not without precedent, for a $[\mathrm{V(V)}]^2$-proportional term has been noted with respect to the $\mathrm{VO^{2+}}/\mathrm{VO_2^+}$ self-exchange[14] and in the rate laws for the V(V) oxidations of Fe(II)[15] and the $(\mathrm{Ta_6Br_{12}})^{2+}$ cluster.[16a] The $[\mathrm{V(V)}]^2$ dependence in these oxidations has been interpreted alternatively in terms of (1) a preliminary equilibrium involving V(V) and the reductant prior to a rate-determining attack by a second V(V) or (2) a predominant path involving an unusually reactive $(\mathrm{V^V})_2$ species, present at small concentrations in these systems. In the present case, we favor the latter picture, which is in accord with the evidence of Madic and co-workers[16b] that V(V) is partially dimerized at very low pH values. Moreover, possible preequilibria such as (11) and (12), which might otherwise be considered, appear to be ruled

$$(\mathrm{Mo^{IV}})_3 + \mathrm{V^V} \rightleftharpoons \mathrm{V^{IV}} + \mathrm{Mo^{IV,IV,V}} \qquad (11)$$

$$(\mathrm{Mo^{IV}})_3 + \mathrm{V^V} \rightleftharpoons \mathrm{V^{III}} + \mathrm{Mo^{VI}} + (\mathrm{Mo^{IV}})_2 \qquad (12)$$

out by the absence of inhibition when either V(IV) (0.08 M) or Mo(VI) (0.03 M) is added to the reaction mixture.[17,18]

Reaction with $\mathrm{Fe(NCS)^{2+}}$. Among the oxidants considered, only Fe(III) unequivocally functions as a 1e⁻ reagent in its initial attack on $(\mathrm{Mo^{IV}})_3$. In our hands, reaction with $\mathrm{Fe^{III}}$(aq) is immeasurably slow, as is oxidation by $\mathrm{FeCl^{2+}}$ (to which $\mathrm{Fe^{III}}$ is partially converted in 0.02 M HCl). However, reactions in the presence of added $\mathrm{NCS^-}$ proceed readily and may be conveniently monitored by following the disappearance of the strongly absorbing $\mathrm{FeNCS^{2+}}$ cation. Although net conversion is to Mo(VI), we see no evidence that partially oxidized molybdenum species intervene, indicating that the first act of electron transfer from $(\mathrm{Mo^{IV}})_3$ is slower than all subsequent steps. This conclusion is in accord with that drawn for the $(\mathrm{Mo^{IV}})_3$–$\mathrm{Fe(phen)_3}^{3+}$ system by Diebler.[5c]

Within the range of $[\mathrm{NCS^-}]$ examined (0.005–0.020 M), both $\mathrm{Fe^{III}}$ and $(\mathrm{Mo^{IV}})_3$ are partially converted to mono-$\mathrm{SCN^-}$ com-

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(12) Ooi, B.-L.; Sykes, A. G. *Inorg. Chem.* **1988**, *27*, 310. This K_A was estimated at 25 °C, $\mu = 2.0$ M ($\mathrm{Li^+Tos^-}$).

(13) A preliminary kinetic examination of the $(\mathrm{Mo^{IV}})_3$–$\mathrm{ClO_3^-}$ reaction yields no indication of an acidity dependence within the $[\mathrm{H^+}]$ range 0.060–1.20 M ($\mu = 2.0$ M ($\mathrm{Li^+Tos^-}$)), suggesting that in this instance the reactivity of the deprotonated form of the reductant lies close to that of its parent cation, I. Why the selectivity of chlorate in this reaction is apparently much less marked than that of bromate remains a puzzling point.

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(17) The $[\mathrm{V(V)}]^2$ dependence also brings to mind the oxidation of $[\mathrm{Mo_2O_4(H_2O)_6}]^{2+}$ by $\mathrm{IO_3^-}$,[4d] which has been shown to entail anation of the Mo(V) center by one iodate prior to a redox act triggered by a second. Although the nature of this synergism is not yet clear, we cannot eliminate the possibility that V(V), like I(V), undergoes a change of two units, yielding V(III), which is then rapidly[18] oxidized by excess V(V) to the observed product, $\mathrm{VO^{2+}}$.

(18) See, for example: Daugherty, N. A.; Newton, T. W. *J. Phys. Chem.* **1964**, *68*, 612.

Table IV. Representative Kinetic Data for the Formation and Consumption of the Reaction Intermediate in the Oxidation of Trimeric Mo(IV) with Cr(VI)[a]

$[Cr^{VI}]$, M	$[H^+]$, M	k_1,[b] s^{-1}	k_2,[b] s^{-1}	$10^{-3}\epsilon_{int}$,[c] $M^{-1}\ cm^{-1}$
0.0080	1.00	1.40 (1.38)	112 (111)	4.2
0.0130	1.00	1.71 (1.76)	113 (111)	3.7
0.020	1.00	2.05 (2.08)	113 (111)	3.0
0.030	1.00	2.50 (2.35)	103 (111)	2.7
0.045	1.00	2.57 (2.58)	128 (111)	3.4
0.060	1.00	2.65 (2.70)	122 (111)	3.4
0.0080	0.16	1.46 (1.38)	34 (31)	1.5
0.0080	0.36	1.30 (1.38)	54 (58)	2.2
0.0080	0.56	1.33 (1.38)	82 (80)	3.3
0.0080	0.76	1.46 (1.38)	84 (96)	3.3

[a] Reactions were run at 22 °C; $\mu = 1.20$ M (Na^+Tos^-); $[(Mo^{IV})_3] = 6.6 \times 10^{-4}$ M throughout; $\lambda = 530$ nm. [b] Pseudo-first-order specific rates for formation and consumption of the intermediate. Values in parentheses were calculated from eqs 19 and 20 by using parameters in the text. [c] Extinction coefficient of the intermediate, obtained from refinement of biphasic kinetic curves.[8]

plexes, for which anation quotients of 138[19] and 300[20] may be assigned. Rate law (8) listed for the redox reaction features two binomial terms in the denominator, reflecting these partitions. The binomial in the numerator, $k_1 + k_2K_{Mo}[NCS^-]$, points to two reaction paths proceeding through activated complexes differing by one NCS^- unit, and the overall $[H^+]^{-2}$ dependence tells us that both paths require the loss of two protons.

The sequence shown as Scheme I, which appears to be consistent with the observed kinetic picture, applies only to the $(Mo^{IV})_3$ NCS path; an analogous sequence can be drawn up for the $(Mo^{IV})_3$(aq) component. The high reactivity of $Fe(NCS)^{2+}$ (as compared to Fe^{III}(aq) and $FeCl^{2+}$) in our Mo oxidations brings to mind a similar pattern observed for the oxidation of vitamin B_{12a} (cob(II)alamin) by these iron species[21] and suggests that NCS has assumed a specific bridging role analogous to that proposed for the cobalt(II)–corrin system. The $(Mo^{IV})_3$ center is represented as becoming attached to the "remote" (sulfur) end of the NCS bridge (in analogy to the preferred route for the $(NH_3)_5CoNCS^{2+}$–Cr^{2+} reaction),[22] with the act of electron transfer (eq 17) accompanied by migration of the bridging ligand. However, the rapid dissolution and/or subsequent oxidation of the initial redox product, "4,4,5", prevents our confirming these particulars.

Scheme I

$$Fe^{III}(aq) + NCS^- \xrightleftharpoons{K\,=\,138} Fe^{III}NCS\quad (Ox) \tag{13}$$

$$\underset{\text{I}}{(Mo^{IV})_3(aq)} + NCS^- \xrightleftharpoons{K\,=\,300} (Mo^{IV})_3NCS\quad (Red) \tag{14}$$

$$Ox + Red \xrightleftharpoons{K_P} \underset{Ox\cdot Red}{SCN(Mo^{IV})_3(SCN)Fe^{III}} \tag{15}$$

$$Ox\cdot Red \xrightleftharpoons{K_{2H}^{A}} \underset{Ox\cdot Red(OH)_2}{SCN(Mo^{IV})_3(SCN)Fe^{III}(OH)_2} + 2H^+ \tag{16}$$

$$Ox\cdot Red(OH)_2 \xrightarrow{k} \underset{\text{“4,4,5”}}{SCN(Mo^{IV,IV,V})SCN} + Fe^{II} \tag{17}$$

$$k_{obs} = kK_PK_{2H}^{A} = 0.14\ M\ s^{-1}$$

$$\text{“4,4,5”} + 5Fe^{III}NCS \rightarrow\rightarrow 3Mo^{VI} + 7NCS^- + 5Fe^{II}(\text{rapid}) \tag{18}$$

Reaction with Cr(VI). Kinetic patterns generated by the rapid reaction of $(Mo^{IV})_3$ with $HCrO_4^-$ feature the growth and disappearance of an intermediate species absorbing strongly at 530 nm. Representative kinetic parameters, obtained by resolution of the resulting curves into first-order components,[8] are listed in Table IV. The usual ambiguity attending the assignment of rate constants in such systems[23] is resolved here by comparing the dependencies on [oxidant] exhibited by the two contributions. Since only the lower rates are seen to increase with $[Cr^{VI}]$, we may attribute these to the generation of the observed transient, which then decays unimolecularly (specific rate k_2).

Treatment of k_1 values, which must take into account the acidity constant of $(Mo^{IV})_3$ ($K_A = 0.2$),[12] is in terms of eq 19, where [Int]

$$\text{rate} = \frac{d[Int]}{dt} = \frac{[(Mo^V)_3]KK_A[Ox]}{K_A + [H^+] + KK_A[Ox]}(k_0 + k_H[H^+]) \tag{19}$$

is the concentration of the observed intermediate and k_0 and k_H are the specific rates for the acid-independent and $[H^+]$-proportional components. Refinement of k_1 values yields $K = 573 \pm 67$, $k_0 = 5.1 \pm 0.3\ M^{-1}\ s^{-1}$, and $k_H = 4.4 \pm 0.4\ M^{-2}\ s^{-1}$. Values of k_2 are in accord with (20), with $k = (2.2 \pm 0.3) \times 10^2\ s^{-1}$ and $K_A = 0.99 \pm 0.25$.

$$\text{rate} = \frac{-d[Int]}{dt} = \frac{k[Int][H^+]}{K_A + [H^+]} \tag{20}$$

Rate laws (19) and (20) support the reaction sequence (21)–(25), in which the intermediate is generated by two routes, (22) and (23), but is consumed in a single protonated path (25).

$$[(Mo^{IV})_3OH_2]^{4+} \rightleftharpoons (Mo^{IV})_3OH + H^+ \qquad K_A = 0.2 \tag{9'}$$

$$\begin{gathered}(Mo^{IV})_3OH + Cr^{VI} \rightleftharpoons (Mo^{IV})_3OH{\cdot}Cr^{VI}\\ K = 6 \times 10^2\end{gathered} \tag{21}$$

$$(Mo^{IV})_3OH{\cdot}Cr^{VI} \rightarrow Int \qquad k_0 = 5\ M^{-1}\ s^{-1} \tag{22}$$

$$\begin{gathered}(Mo^{IV})_3OH{\cdot}Cr^{VI} \xrightleftharpoons[K_A']{H^+} (Mo^{IV})_3OH{\cdot}Cr^{VI}H^+ \xrightarrow{k'} Int\\ K_A'k' = 4\ M^{-2}\ s^{-1}\end{gathered} \tag{23}$$

$$Int + H^+ \rightleftharpoons IntH^+ \qquad K_{Int}^{A} = 1.0 \tag{24}$$

$$IntH^+ \xrightarrow{k_2} \text{products} \qquad k_2 = 2.2 \times 10^2\ s^{-1} \tag{25}$$

The observed variations, with acidity, of the extinction coefficient of the intermediate (Table IV) are likewise consistent with its partition into two protonation levels, but the estimated ϵ values are not precise enough to justify a supporting calculation of K_{Int}^{A}.

The intense broad absorption maximum exhibited by the intermediate near 530 nm suggests that it might be a Cr(IV) species,[24] but its decomposition is seen here to be unimolecular, whereas Cr(IV), as generated in the absence of molybdenum, has been found to decay (via disproportionation) bimolecularly.[25] We suspect instead that we are seeing a complex in which a Cr(IV) center is bound to a partially oxidized molybdenum cluster, e.g., $Mo^{IV}Mo^{V}Mo^{V}$ or (more probably) $Mo^{IV}Mo^{IV}Mo^{VI}$. The observed disappearance of this intermediate may then be attributed either to internal electron transfer within this complex or to its dissociation into redox-active fragments, the subsequent reactions of which are too quick to be reflected in the kinetic picture.

In sum, the present study, which is preliminary in nature, emphasizes the high degree of redox versatility of $(Mo^{IV})_3$(aq). Earlier work[4a–c] has demonstrated the ease with which this trimer is reduced to Mo(III) species, and we find that it reacts readily with both two- and one-electron oxidants. Moreover, our ex-

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periments with Fe(III) point to the importance (although not the essentiality[5b,c]) of ligand bridging. At the same time, our results underscore the extent to which Mo(IV) is stabilized in solution by trimerization. Each oxidation yields three Mo(VI)'s a net change of six units, yet in all cases, rates are governed by the initial 1e$^-$ and 2e$^-$ transaction. Ensuing redox acts and steps involving the breakup of partially oxidized Mo clusters proceed much more rapidly.

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Electronic Structure and Bonding in Trinuclear Molybdenum and Tungsten Cluster Compounds of M_3X_{13} Type

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This paper is concerned with some newly observed electronic properties of trinuclear cluster compounds belonging to the M_3X_{13} structural type and particularly with the way in which the preferred number of electrons in the compounds of this type is influenced by the identity of the ligand intimately associated with the metal cluster. The ground-state electronic structures of a number of trinuclear molybdenum and tungsten cluster compounds have been studied by employing SCF–Xα–SW molecular orbital calculations. The calculations have been performed for the molybdenum and tungsten systems with six, eight, and nine metal d electrons. The results have been shown to give consistent and satisfactory explanations for the electron populations and related properties of these compounds. The M–M bonding in these cluster compounds has been examined in detail by employing the results of the present calculations and compared with a long-established bonding scheme of less rigorous origin. Comparative studies have also been carried out on the followed trimolybdenum systems: $Mo_3(\mu_3\text{-}X)(\mu\text{-}Y)_3$ (X = O, Y = O, X = O, Y = Cl, X = S, Y = S). It has been found that the preferred oxidation levels in these systems are directly related to the significant differences in their electronic structures caused by different interactions between the metal atoms and the intimate ligand atoms.

Introduction

Discrete triangular M–M bonded cluster compounds of molybdenum and tungsten have received much attention in recent years in the study of bonds betwen transition-metal atoms.[1] Among several structurally distinct types of the compounds,[2-5] a particularly common and important structural type, often designated as M_3X_{13}, has been of continuing interest to us.[6-11] This structural type is characterized by a central M_3X_4 core about which there may be a considerable variety and arrangement of peripheral ligands. Within the M_3X_4 core, one of the four intimate ligands, X, is a triply bridging, or capping, atom above the plane of the equilateral triangle of the metal atoms and the three others are edge-bridging atoms below it. The capping and edge-bridging intimate ligands need not be the same, but in all cases the M_3X_4 unit retains C_{3v} symmetry. For the compound as a whole this symmetry may be lowered by the outer nine ligands. Electronically, the compounds within this type are usually further classified according to the number of electrons in the metal cluster that are primarily involved in metal–metal bonding.

There has been a continuing effort to formulate electronic descriptions of bonding in equilateral-triangular metal systems of various structural types.[12-14] The electronic structure of the molybdenum and tungsten compounds of the M_3X_{13} type has, thus far, been investigated only by use of the empirical Cotton–Haas MO method[12] and the Fenske–Hall method.[14] A simple but widely accepted formulation of the M–M bonding in the Mo and W systems is the one based on treatment of the Mo_3O_{13} unit by the Cotton–Haas method.[12] According to this scheme, the M_3X_{13} compounds should be stable when there are six metal d electrons available to enter the low-energy 1a$_1$ and 1e metal cluster obitals, which correspond to three M–M σ-bonding orbitals. The compounds with seven or eight metal electrons might also be stable, since the additional electrons would occupy the next higher (2a$_1$) orbital, which is approximately M–M nonbonding. All higher MOs that are mainly localized in the M_3 cluster, namely, the 2e, 3e, and 1a$_2$ orbitals, are M–M antibonding. Thus, the bonding scheme has given a satisfactory explanation for the existence of both six-electron systems, such as $[Mo_3O_4(C_2O_4)_3(H_2O)_3]^{2-}$,[6] and eight-electron systems, such as $[Mo_3OCl_3(O_2CCH_3)_3(H_2O)_3]^{2+}$.[7]

Recent work in our laboratory has revealed several important but previously unrecognized characteristics of this type of cluster compound. It has been found that while the systems with three μ-O or μ-S atoms appear to favor a six-electron population, the compounds with three μ-Cl atoms in place of the oxygen or sulfur atoms usually have eight metal d electrons[10] and, remarkably, they can even have nine electrons.[11] It has also been found that in spite of a close structural similarity between homologous molybdenum and tungsten species, their redox behavior can be very different.[10] These new discoveries apparently cannot be interpreted through the existing electronic descriptions of the structural type. Therefore, more detailed and more rigorous theoretical exploration of the electronic structures of this structural type was considered necessary. We have carried out molecular orbital calculations on a number of molybdenum and tungsten compounds of the M_3X_{13} type, employing the density functional SCF–Xα–SW method. We report here the results of calculations on some newly

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