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Substitution and Redox Properties of the Trimeric Incomplete Cuboidal Tungsten(IV) Aqua Ion $[W_3O_4(H_2O)_9]^{4+}$: Comparisons with $[Mo_3O_4(H_2O)_9]^{4+}$

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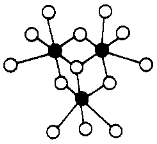
Rate constants (25 °C) for 1:1 substitution have been obtained from kinetic studies ($t_{1/2} > 1$ min) on the equilibration of $[W_3O_4(H_2O)_9]^{4+}$ with NCS^- in perchloric acid, $I = 2.0$ M ($LiClO_4$). Extensive (H_2O) acid dissociation of the W reactant (average $K_{aW} = 0.22$ M) is observed, which is similar to that of the Mo analogue, $[Mo_3O_4(H_2O)_9]^{4+}$. As far as can be ascertained, substitution proceeds solely by NCS^- replacement of H_2O on the conjugate-base form, with rate constant $k_T = 1.20$ M^{-1} s^{-1}. This is an order of magnitude slower than for the corresponding reaction on $[Mo_3O_4(H_2O)_9]^{4+}$ ($k_T \sim 13.5$ M^{-1} s^{-1} in perchlorate), indicating a less labile species. A similar effect has been observed in the case of the V state ions $[W_2O_4(H_2O)_6]^{2+}$ and $[Mo_2O_4(H_2O)_6]^{2+}$ (not in this case a conjugate-base pathway), where it has been reported that W substitutes 10 times slower. The kinetics of the oxidation of $[W_3O_4(H_2O)_9]^{4+}$ (reactant in excess) to W(V) with $[IrCl_6]^{2-}$ has been monitored by stopped-flow spectrophotometry. At 25 °C, the rate law $-d[IrCl_6^{2-}]/dt = 3k[W_3O_4^{4+}][IrCl_6^{2-}]$ applies, with an $[H^+]$ dependence identical with that observed in the substitution studies. The data yield a rate constant k_{Ir} for reaction of the conjugate-base form of 1.06×10^6 M^{-1} s^{-1}. This is 6 orders of magnitude larger than the substitution rate constant, and the reaction must therefore be outer-sphere. As in the case of the $[W_2O_4(H_2O)_6]^{2+}$ ion, $[W_3O_4(H_2O)_9]^{4+}$ is oxidized $\sim 10^6$ times faster than the Mo analogue, indicative of a much more strongly reducing species.

Introduction

The aqua (or aqua–oxo) ions of tungsten are more difficult to prepare than those of molybdenum,[1] and preparative routes are different from those already established for the latter. Thus, the $W^V{}_2$ dimer $[W_2O_4(H_2O)_6]^{2+}$ [2] and incomplete cuboidal trimeric $W^{IV}{}_3$ ions in the series $W_3O_xS_{4-x}{}^{4+}$ [3-7] have been prepared by procedures involving chlorotungstate, thiotungstate, or tungsten hexacarbonyl precursor complexes. The preparation and characterization of the aqua ion $[W_3O_4(H_2O)_9]^{4+}$, has recently been reported.[3]



An X-ray crystallographic study of the complex $(NH_4)_2\{N(C_2H_5)_4\}_3[W_3O_4(NCS)_9]\cdot nH_2O$ has confirmed the presence of the trimeric core $W_3O_4{}^{4+}$ [3] and is the basis for presuming that the aqua ion is $[W_3O_4(H_2O)_9]^{4+}$, which is structurally analogous to the already extensively studied $[Mo_3O_4(H_2O)_9]^{4+}$ ion.[8,9] It was of interest to us to investigate the effect of substituting W for Mo on the reactivity of the trimer. The substitution properties (reaction with NCS^-) and redox studies ($[IrCl_6]^{2-}$ as oxidant) here reported enable such a comparison to be made.

Experimental Section

All preparations of W products and kinetic studies on $[W_3O_4(H_2O)_9]^{4+}$ require O_2-free techniques. Standard procedures involving use of N_2 gas, rubber septa, Teflon tubing/needles, and nylon syringes as well as glovebag techniques were employed.

Reagents. Hexachlorotungsten(VI), WCl_6 (Aldrich Chemicals), and potassium iodide (BDH, AnalaR) were used to prepare potassium hexachlorotungstate(IV), $K_2[WCl_6]$ (see below). Sodium thiocyanate (AnalaR, BDH), perchloric acid (AnalaR, BDH), and *p*-toluenesulfonic acid, HPTS (Sigma Chemicals), were used as supplied. Sodium hexachloroiridate(IV), $Na_2[IrCl_6]\cdot 6H_2O$ (Johnson-Matthey), was used without further purification. Lithium perchlorate (Aldrich Chemicals) was recrystallized twice from water.

Preparation of $[W_3O_4(H_2O)_9]^{4+}$. The starting material, $K_2[WCl_6]$, was prepared by a method involving a dry reaction of potassium iodide and hexachlorotungsten(VI) in a sealed tube at 130 °C, as reported in the literature.[10] Solutions of $[W_3O_4(H_2O)_9]^{4+}$ in 2 M HPTS were obtained by a method similar to that described by Segawa and Sasaki.[3] This involved in our case heating $K_2[WCl_6]$ in 2 M HPTS at 90 °C for 2.5 h under a N_2 atmosphere, followed by cation-exchange chromatography (Dowex 50W-X8) after filtration. It was found that the original method, which involves the use of HCl instead of HPTS, yields mainly chloro species and a very low yield of the aqua ion. The modified procedure improves the yield of the aqua ion substantially. The aqua ion eluted in 4 M HPTS from a Dowex 50W-X8 column, after first washing with 1 and 2 M HPTS to remove any chloro species, was further purified on a Dowex 50W-X2 cation-exchange column. Stock solutions of $[W_3O_4(H_2O)_9]^{4+}$ were stored in 2 M HPTS under a N_2 atmosphere at 4 °C.

Solutions in 2 M $HClO_4$ used for kinetic studies were obtained by loading portions of stock solutions in HPTS onto a short Dowex 50W-X2 resin (1 cm × 3 cm) and eluting the aqua ion with 2.0 M $HClO_4$ after first washing with 0.5 M $HClO_4$ (75 mL). These solutions were used on the same day.

Stability. At 25 °C solutions of $[W_3O_4(H_2O)_9]^{4+}$ (1 mM) in perchloric acid (2 M) under N_2 showed signs of deterioration with 10–15% increase in absorbance at 455 nm over 20-h periods. After 2–3 days a brown precipitate formed that turned blue on exposure to air due to W-blue formation.[11]

Standardization of Reactants. Concentration of thiocyanate solutions were determined by titration against silver(I) (Convol, BDH) with iron(III) as indicator. Solutions of perchloric acid were titrated for $[H^+]$ against sodium hydroxide (Convol, BDH) with phenolphthalein as indicator. Solutions of $LiClO_4$ and the $[H^+]$ of stock $[W_3O_4(H_2O)_9]^{4+}$ solutions were determined by ion-exchanging onto Amberlite IR(H)120 resin followed by titration of the H^+ released. Concentrations of $[W_3O_4(H_2O)_9]^{4+}$ were determined spectrophotometrically at the 455-nm peak ($\epsilon = 375$ M^{-1} cm^{-1}/mol of trimer). All features of the spectrum agree with those already published.[3] Solutions of $[IrCl_6]^{2-}$ were determined at the 487-nm peak ($\epsilon = 4075$ M^{-1} cm^{-1}). When the solutions were stored in the dark at room temperature, $[IrCl_6]^{2-}$ in $HClO_4$ (0.1–2.0 M) was stable to aquation over 24 h. Teflon needles were used when $[IrCl_6]^{2-}$ solutions were handled.

Stoichiometry and Products of Redox Reaction. These were determined spectrophotometrically for studies with $[IrCl_6]^{2-}$ as oxidant. With $[IrCl_6]^{2-}$ in up to 10-fold excess a stoichiometry of 1 mol of $W(IV)_3$ to 6 mol of Ir(IV) was obtained by determining spectrophotometrically the amount of $[IrCl_6]^{2-}$ remaining. Reaction proceeds to a colorless solution with reactants in a $W(IV)_3$:Ir(IV) ratio of 1:6. From an experiment with $W(IV)_3$:Ir(IV) = 1:3, $W(V)_2$ was identified as the main product (peak

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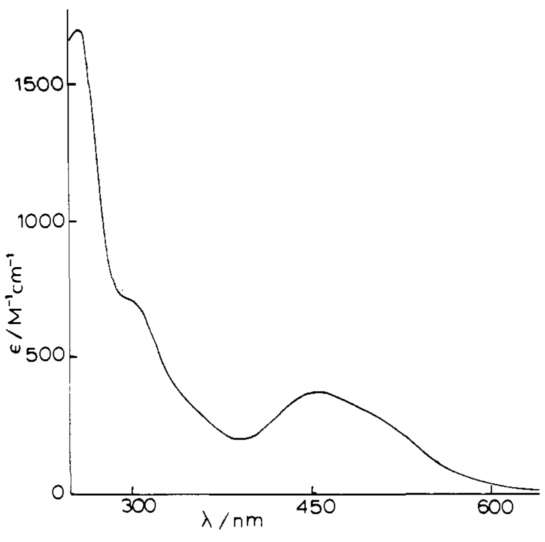

Figure 1. UV-vis spectrum of $[W_3O_4(H_2O)_9]^{4+}$ in 2 M $HClO_4$ (ϵ values per trimer).

Table I. First-Order Equilibration Rate Constants k_{eq}(25 °C) for the Reaction of $W_3O_4^{4+}$ (2.5–5.0) × 10^{-5} M with NCS^- (I = 2.00 M ($LiClO_4$))

$[H^+]$, M	$10^3[NCS^-]$, M	10^4k_{eq}, s^{-1}	$[H^+]$, M	$10^3[NCS^-]$, M	10^4k_{eq}, s^{-1}
0.25	0.75	3.80	1.50	1.00	0.91
	1.00	4.20		2.25	1.52
	1.75	5.73		3.50	2.09
	2.00	6.17	2.00	0.80	0.64
0.50	0.75	2.03		2.00	1.05
	2.00	3.42		3.00	1.51
	3.25	4.83		3.80	1.76
1.00	0.80	1.22		4.50	1.95
	2.00	1.98		0.08	0.73[a]
	3.5	2.96			

[a] $[W_3O_4^{4+}]$ = 0.36 × 10^{-3} M.

positions λ/nm ($\epsilon/M^{-1}\,cm^{-1}$ per dimer) at 430 (193) and 340 (278)).[2] With $W(IV)_3$:Ir(IV) = 1:4, there was instant loss of the Ir(IV) color followed by clouding of the solution (within a few minutes) as a result of W-blue W(V)/W(VI) mixed-valence products formed by the reaction of W^V_2 with W^{VI}.[11] For a run with $W(IV)_3$:Ir(IV) = 1:2, some W^{IV}_3 remained after completion of the reaction. Of the various possibilities, it is clearly preferable to carry out kinetic studies with W^{IV}_3 in large excess (>10-fold) of $[IrCl_6]^{2-}$, to constrain reaction to (1). The Ir(III)

$$2W^{IV}_3 + 6Ir^{IV} \rightarrow 3W^V_2 + 6Ir^{III} \qquad (1)$$

product present as $[IrCl_6]^{3-}$ has negligible absorbance ($\epsilon < 20\ M^{-1}\,cm^{-1}$) at 487 nm.[12]

Kinetics. For the reaction of NCS^- with $[W_3O_4(H_2O)_9]^{4+}$, large absorbance changes occur below 300 nm. Since PTS^- absorbs strongly in this region, it was preferable to work in ClO_4^- solutions. Although runs with NCS^- in excess gave significant changes from 300 to 320 nm, with $W_3O_4^{4+}$ in excess, absorbance changes were difficult to monitor. Reactant solutions in ClO_4^- were made up to I = 2.00 M with $LiClO_4$. The spectrum of $W_3O_4^{4+}$ over an extended range down to 250 nm is shown in Figure 1. Equilibration studies with NCS^- were followed on a Perkin-Elmer Lambda 9 instrument at 280 nm. Because of the long times (4–14 h) involved, and the instability of $[W_3O_4(H_2O)_9]^{4+}$ in perchloric acid solutions giving rise to uncertainty in absorbance A_∞ values, rate constants were evaluated by the Guggenheim method.[13]

Redox studies with $[IrCl_6]^{2-}$ were monitored at 487 nm (decay of $[IrCl_6]^{2-}$) by using a Dionex D-110 stopped-flow spectrophotometer and programs from OLIS (Jefferson, GA). The $W_3O_4^{4+}$ reactant was in large excess (>10-fold) of $[IrCl_6]^{2-}$, and both solutions were degassed prior to runs. The temperature was maintained at 25.0 ± 0.1 °C.

Treatment of Data. An unweighted linear least-squares program was used to obtain the gradients and intercepts of all linear plots. In the evaluation of k the origin was used as an additional data point.

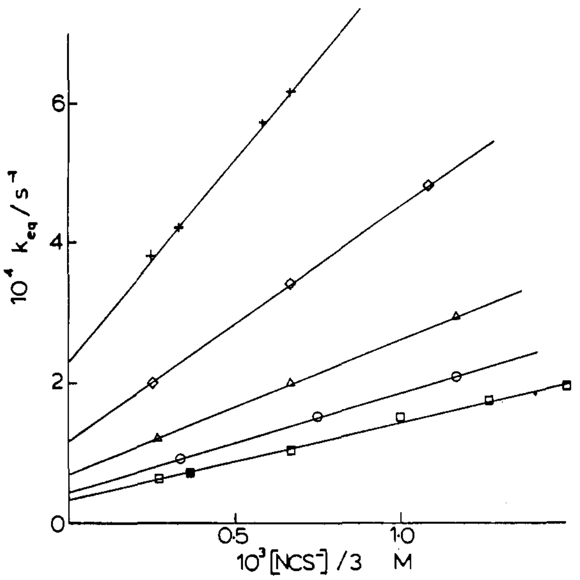

Figure 2. Dependence of first-order rate constants, k_{eq}(25 °C), for the equilibration of $[W_3O_4(H_2O)_9]_4^{4+}$ and NCS^- (reactant in large excess) on $[NCS^-]$ at $[H^+]$/M = 0.25 (+), 0.50 (◇), 1.00 (△), 1.50 (○), and 2.00 (□); I = 2.0 M ($LiClO_4$). One point with $W_3O_4^{4+}$ in excess is indicated by a solid symbol, the x-axis scale corresponding to $[W_3O_4^{4+}]$.

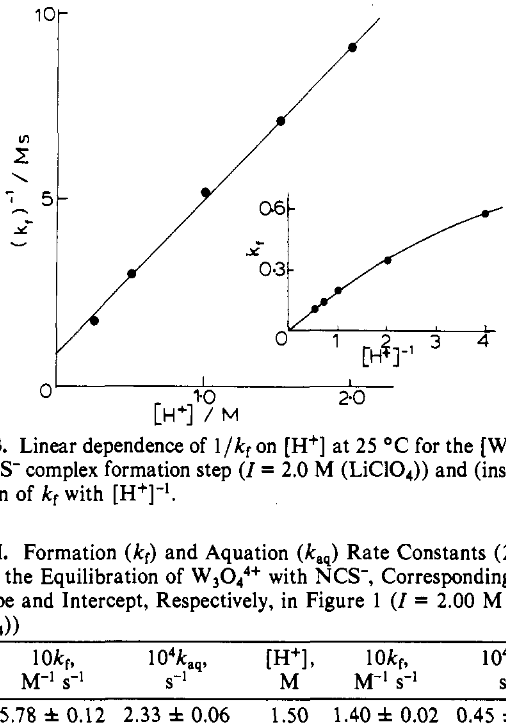

Figure 3. Linear dependence of $1/k_f$ on $[H^+]$ at 25 °C for the $[W_3O_4]^{4+}$ and NCS^- complex formation step (I = 2.0 M ($LiClO_4$)) and (inset) the variation of k_f with $[H^+]^{-1}$.

Table II. Formation (k_f) and Aquation (k_{aq}) Rate Constants (25 °C) for the Equilibration of $W_3O_4^{4+}$ with NCS^-, Corresponding to the Slope and Intercept, Respectively, in Figure 1 (I = 2.00 M ($LiClO_4$))

$[H^+]$, M	$10k_f$, $M^{-1}\,s^{-1}$	10^4k_{aq}, s^{-1}	$[H^+]$, M	$10k_f$, $M^{-1}\,s^{-1}$	10^4k_{aq}, s^{-1}
0.25	5.78 ± 0.12	2.33 ± 0.06	1.50	1.40 ± 0.02	0.45 ± 0.02
0.50	3.36 ± 0.02	1.19 ± 0.01	2.00	1.10 ± 0.04	0.35 ± 0.04
1.00	1.93 ± 0.02	0.70 ± 0.02			

Results

Substitution of NCS^- on $[W_3O_4(H_2O)_9]^{4+}$. With NCS^- in a large excess (>10-fold) of aqua $W_3O_4^{4+}$, first-order equilibration constants (k_{eq}) at 25 °C show a linear dependence on $[NCS^-]$. One run with $W_3O_4^{4+}$ in large excess (>10-fold expressed as monomer) identified the statistical factor of 3 as in previous studies.[8,14] Hence, k_{eq} values (Table I) can be expressed as in (2) (Figure 2).

$$k_{eq} = k_f[NCS^-]/3 + k_{aq} \qquad (2)$$

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Table III. First-Order Rate Constants k_{obs}(25 °C) for the Oxidation of $[W_3O_4(H_2O)_9]^{4+}$ (Reactant in >10-fold Excess) with $[IrCl_6]^{2-}$ in the Concentration Range (0.6–2.5) × 10^{-5} M (I = 2.00 M ($LiClO_4$))

$[H^+]$, M	$10^3 \times [W_3O_4{}^{4+}]$, M	k_{obs}, s^{-1}	$[H^+]$, M	$10^3 \times [W_3O_4{}^{4+}]$, M	k_{obs}, s^{-1}
0.31	0.05	85	1.0	0.11	62
	0.10	152		0.20	116
0.6	0.06	53		0.27	152
	0.10	89	1.5	0.09	39
	0.20	185		0.15	70
0.75	0.09	64		0.22	100
	0.15	115	2.0	0.08	20.0
	0.22	159		0.11	42
				0.20	69
				0.27	89

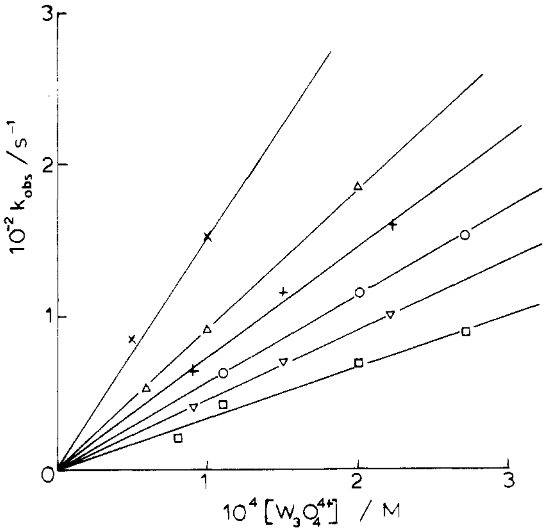


Figure 4. Dependence of first-order rate constants, k_{obs}(25 °C), for the $[IrCl_6{}^{2-}]$ oxidation of $[W_3O_4(H_2O)_9]^{4+}$ (reactant in excess) at $[H^+]$/M = 0.31 (×), 0.60 (△), 0.75 (+), 1.0 (○), 1.5 (▽), and 2.0 (□); I = 2.0 M ($LiClO_4$).

The dependence of k_f and k_{aq} on $[H^+]$ was investigated in the range $[H^+]$ = 0.25–2.00 M. Values of k_f and k_{aq} for the formation and aquation steps involving $W_3O_4{}^{4+}$ and $[W_3O_4(NCS)]^{3+}$, respectively, are shown in Table II.

The $[H^+]$ dependence can be described by the reaction scheme (3)–(5), where W_3OH^{3+} is the conjugate-base form of $W_3O_4{}^{4+}$

$$W_3{}^{4+} \rightleftharpoons W_3OH^{3+} + H^+ \quad K_{aW} \tag{3}$$

$$W_3OH^{3+} + NCS^- \underset{k_{-T}}{\overset{k_T}{\rightleftharpoons}} W_3OH(NCS)^{2+} \tag{4}$$

$$W_3(NCS)^{3+} \rightleftharpoons W_3OH(NCS)^{2+} + H^+ \quad K_{aWT} \tag{5}$$

here written as $W_3{}^{4+}$. Hence, the formation rate constant can be expressed as in (6). A plot of $k_f{}^{-1}$ against $[H^+]$ is linear (Figure 3). From a least-squares fit k_T = 1.20 ± 0.17 M^{-1} s^{-1} and K_{aW} = 0.20 ± 0.03 M. As in the case of $Mo_3O_4{}^{4+}$, reaction proceeds solely via the conjugate-base form.[8]

$$k_f = \frac{k_T K_{aW}}{[H^+] + K_{aW}} \tag{6}$$

Similarly, for the aquation step, expression 7 applies. A plot of $k_{aq}{}^{-1}$ against $[H^+]$ is linear with k_{-T} = (1.06 ± 0.48) × 10^{-3} s^{-1} and K_{aWT} = 0.07 ± 0.03 M.

$$k_{aq} = \frac{k_{-T} K_{aWT}}{[H^+] + K_{aWT}} \tag{7}$$

Oxidation of $[W_3O_4(H_2O)_9]^{4+}$ with $[IrCl_6]^{2-}$. Linear first-order kinetic plots were obtained with the aqua $W_3O_4{}^{4+}$ reactant in large excess, consistent with the rate law (8). First-order rate constants k_{obs} (Table III), give a linear dependence on $[W_3O_4{}^{4+}]$ (Figure 4), and the full rate law is therefore as in (9). Rate constants

$$-d[Ir(IV)]/dt = k_{obs}[IrCl_6{}^{2-}] \tag{8}$$

$$-d[Ir(IV)]/dt = 3k[W_3O_4{}^{4+}][IrCl_6{}^{2-}] \tag{9}$$

k show a predominantly inverse type of $[H^+]$ dependence for the range 0.31–2.0 M (Table IV, Figure 5). This dependence is assigned to the reaction of the conjugate-base form W_3OH^{3+} with $[IrCl_6]^{2-}$, as in (10) and (11). From this reaction scheme (12)

$$W_3{}^{4+} \rightleftharpoons W_3OH^{3+} + H^+ \quad K_{aW} \tag{10}$$

$$W_3OH^{3+} + [IrCl_6]^{2-} \xrightarrow{k_{Ir}} \text{products} \tag{11}$$

$$k = \frac{k_{Ir} K_{aW}}{[H^+] + K_{aW}} \tag{12}$$

is obtained. A linear plot of $k_{Ir}{}^{-1}$ against $[H^+]$ (Figure 5) gives k_{Ir} = (1.06 ± 0.28) × 10^6 M^{-1} s^{-1} and K_{aW} = 0.24 ± 0.08 M.

Table IV. Second-Order Rate Constants k(25 °C) for the $[IrCl_6]^{2-}$ Oxidation of $[W_3O_4(H_2O)_9]^{4+}$ (I = 2.00 M ($LiClO_4$))

$[H^+]$/M	0.31	0.6	0.75	1.0	1.5	2.0
$10^{-5}k/M^{-1}$ s^{-1}	51	31	24.4	18.9	15.3	11.2

Table V. Comparison of Substitution (NCS^- for H_2O) Formation Rate Constants (25 °C) for W and Mo Ions in the IV and V States (as Trimers and Dimers, Respectively)

reactant	reacn path	rate const, M^{-1} s^{-1}	ref
$[W_3O_4(H_2O)_9]^{4+}$	$[W_3OH]^{3+}$ + NCS^-	1.2[a]	this work
$[Mo_3O_4(H_2O)_9]^{4+}$	$[Mo_3OH]^{3+}$ + NCS^-	13.5[a]	14
$[W_2O_4(H_2O)_6]^{2+}$	$[H^+]$-indep path	2.52 × 10^3[b]	2
$[Mo_2O_4(H_2O)_6]^{2+}$	$[H^+]$-indep path	29 × 10^3[a]	16

[a] I = 2.00 M ($LiClO_4$). [b] I = 2.00 M (LiPTS).

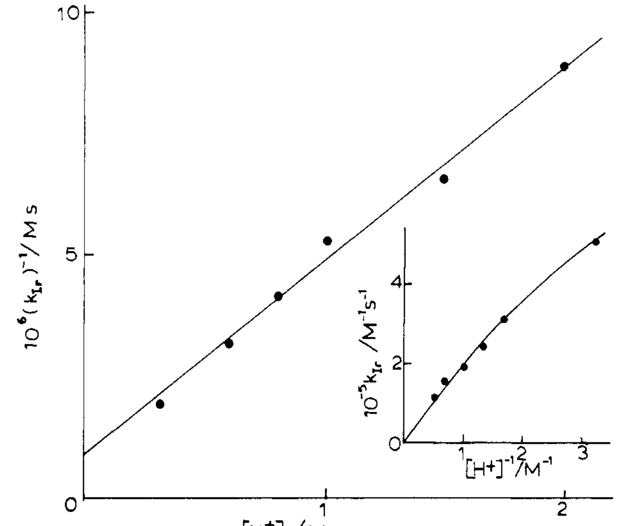


Figure 5. Linear dependence of $1/k_{Ir}$ on $[H^+]$ at 25 °C for the $[IrCl_6]^{2-}$ oxidation of $[W_3O_4(H_2O)_9]^{4+}$ (I = 2.0 M ($LiClO_4$)) and (inset) the variation of k_{Ir} with $[H^+]^{-1}$.

Discussion

No stable aquated monomeric or dimeric W(IV) ions have yet been isolated, and the incomplete cuboidal trimeric ion $[W_3O_4(H_2O)_9]^{4+}$ is the only stable form so far identified in acidic solutions. A similar situation holds for Mo(IV), where $[Mo_3O_4(H_2O)_9]^{4+}$ is now well established.[1] The studies in this paper are aimed at assessing the substitution and redox properties of $[W_3O_4(H_2O)_9]^{4+}$, with reference to the most relevant experimental approaches from previous studies on $[Mo_3O_4(H_2O)_9]^{4+}$.[8,9,14]

The rate constant (25 °C) for the 1:1 substitution of NCS^- for H_2O on the conjugate-base of $[W_3O_4(H_2O)_9]^{4+}$ (1.20 M^{-1} s^{-1}) is some 10 times smaller than the corresponding value for $[Mo_3O_4(H_2O)_9]^{4+}$ (13.5 M^{-1} s^{-1} in perchlorate).[15] Interestingly,

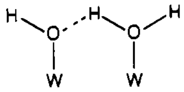
Table VI. Comparison of Rate Constants for $[IrCl_6]^{2-}$ Oxidation (25 °C) of W and Mo Ions in the IV and V States (as Trimers and Dimers, Respectively)

reactant	reacn path	rate const, $(M^{-1}\ s^{-1})$	mechanism	ref
$[W_3O_4(H_2O)_9]^{4+}$	conjugate-base[a]	1.06×10^6	outer-sphere	this work
$[Mo_3O_4(H_2O)_9]^{4+}$	conjugate-base[a]	4.5	inner-sphere (?)	8
$[W_2O_4(H_2O)_6]^{2+}$	$[H^+]$-indep[b]	6.6×10^4	outer-sphere	2
$[Mo_2O_4(H_2O)_6]^{2+}$	$[H^+]$-indep[c]	0.114	outer-sphere	29
$[W_2O_4(edta)]^{2-}$	$[H^+]$-indep[d]	6.3×10^5	outer-sphere	30
$[Mo_2O_4(edta)]^{2-}$	$[H^+]$-indep[c]	6.6	outer-sphere	31

[a] As in eq 11. [b] $I = 1.0$ M (LiPTS). [c] $I = 1.0$ M ($LiClO_4$). [d] $I = 0.50$ M ($LiClO_4$).

the ratio is identical with that obtained for the corresponding reactions of the V state ions $[W_2O_4(H_2O)_6]^{2+}$ and $[Mo_2O_4(H_2O)_6]^{2+}$ (in this case not a conjugate-base path) (Table V).[2,16] For the IV and V state ions tungsten is the less substitution-labile element therefore. In view of the virtually identical ionic radii for W and Mo ions, an explanation is not immediately apparent. Such effects are most likely related to the increased 5d participation due in the W case to the relativistic expansion effect,[17] which results in stronger $W-OH_2$ bonds. It should be noted that rate constants for H_2O substitution on the d^0 ions $[WO_4]^{2-}$ (0.44 s^{-1}) and $[MoO_4]^{2-}$ (0.33 s^{-1}) are very similar.[18] An associative process has been proposed for these two reactions.

From the present studies the acid dissociation (H_2O) constant K_{aW} is 0.20 M (NCS^-) and 0.24 M ($[IrCl_6]^{2-}$), giving an average value of 0.22 M at 25 °C, $I = 2.00$ M ($LiClO_4$). This value is similar to that for $[Mo_3O_4(H_2O)_9]^{4+}$ (average $K_{aM} = 0.42$M),[8] bearing in mind the quite large errors (±15%). A comparison of X-ray crystal structure determinations of $W_3O_xS_{4-x}$[3-7] and $Mo_3O_xS_{4-x}^{4+}$[19-23] indicates essentially identical metal to ligand (bridging and terminal) bond distances. At this time we see no reason for different pK_{aW} and pK_{aM} values except in terms of stronger $W-OH_2$ bonds in the tungsten case, leading to more extensive acid dissociation, which is an effect in the direction opposite to that observed. It is possible that the high acid dissociation constants stem from proton bridging as illustrated



and previously detected.[24,25] In the case of $W_3O_4^{4+}$, as with $Mo_3O_4^{4+}$, it can be inferred (from X-ray structures) that there are H_2O's on adjacent metal atoms with metal–OH_2 bonds parallel to each other. The W–W (2.53 Å)[3] and Mo–Mo (2.52 Å)[19c] separations are to all intents identical, and appropriate for such bonding. For the NCS^- (4.8 $M^{-1}\ s^{-1}$) and $HC_2O_4^-$ (3.3 $M^{-1}\ s^{-1}$) substitutions on the $[Mo_3O_4(H_2O)_9]^{4+}$ conjugate base,[8] rate constants are sufficiently alike to suggest an I_d dissociative-interchange mechanism for substitution. This mechanism is widely recognized as being appropriate to conjugate-base forms,[26-28] and a similar mechanism is likely to apply therefore in the case of the $[W_3O_4(H_2O)_9]^{4+}$ reaction with NCS^-. The $[W_3O_4(H_2O)_6]^{4+}$ study has also demonstrated that, as in the Mo case, a statistical factor must be taken into account when considering rate constants with first the trimer and then NCS^- in excess.

The rate constant (25 °C) for $[IrCl_6]^{2-}$ oxidation of the conjugate base of $[W_3O_4(H_2O)_9]^{4+}$ ($1.06 \times 10^6\ M^{-1}\ s^{-1}$) is $\sim 10^6$ times greater than that observed for H_2O substitution by NCS^- on $[W_3O_4(H_2O)_9]^{4+}$ (Tables V and VI). The reaction must therefore proceed via an outer-sphere redox process. This is in contrast with the same reaction of $Mo_3O_4^{4+}$, where an inner-sphere redox process is a likely assignment.[29] Rate constants for the reaction of the corresponding edta complexes[30,31] are also included in Table VI.

Product analysis of the $[IrCl_6]^{2-}$ reaction by UV–vis spectrophotometry has indicated some oxidation through to W(VI). With $W_3O_4^{4+}$ in excess, a stoichiometry consistent with (1) is assumed to apply, with W^V_2 the dominant product. However, contributions from an alternative route involving formation of monomeric W^V, (13), and competition between dimerization and oxidation to W(VI), cannot be ruled out.

$$W^{IV}_3 + 3Ir^{IV} \rightarrow W^{V}_2 + W^{V} + 3Ir^{III} \qquad (13)$$

The form of the $[H^+]$ dependence observed for the $[IrCl_6]^{2-}$ oxidation of $W_3O_4^{4+}$ is of interest. Since, the rate of oxidation exceeds that for substitution by almost 6 orders of magnitude, an inner-sphere mechanism can be ruled out. Hence, an initial acid dissociation of the aqua W^{IV}_3 followed by outer-sphere electron transfer is proposed. Since the product W(V) is more extensively hydrolyzed (number of oxo ligands per W), an increase in hydrolysis prior to electron transfer is believed to favor the W(IV) → W(V) redox change. Previous examples of this type of behavior have been reported in the outer-sphere $[IrCl_6]^{2-}$ oxidation of V(III), where VOH^{2+} is the sole reactant.[12]

Conclusions

While similar structure types (and dimensions) are obtained for Mo and W in the IV and V states, consistent with their identical radii, substitution reactions for the aqua ions are 10 times slower for W as compared to Mo. Much more dramatic is the contrast in redox properties with W some 10^5–10^6 times the stronger reductant, which is the prime reason that different preparative routes are required. It is also the reason that Mo and W are not interchangeable in enzymic systems. Although no reduction potentials have yet been determined for either W^{IV}_3 or Mo^{IV}_3 aqua ions,[32] the ease of oxidation by $[IrCl_6]^{2-}$ is consistent with $W_3O_4^{4+}$ being a much more strongly reducing species (more negative $E°$) than the latter.

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(15) Calculated from previous data for $[H^+] = 0.75$–2.0 M, $I = 2.0$ ($LiClO_4$), by using an acid dissociation value $K_{aM} = 0.42$ M for $[Mo_3O_4(H_2O)_9]^{4+}$ as determined (25 °C) for studies in which $I = 2.00$ M (LiPTS).[8]

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