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# Solution Chemistry of the Tungsten(V) Aqua Dimer $W_2O_4^{2+}$: Kinetics of Oxidation with $[IrCl_6]^{2-}$ and Other Oxidants and Conditions for Tungsten Blue Formation

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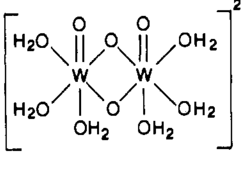
Redox properties of the recently prepared bis($\mu$-oxo) $W^V$ aqua dimer, $[W_2O_4(H_2O)_6]^{2+}$, are considered. The kinetics of the oxidation of $W_2O_4^{2+}$ (reactant in excess) to $W^{VI}$ with $[IrCl_6]^{2-}$ have been investigated in *p*-toluenesulfonic acid (HPTS), $I = 1.0$ M (LiPTS). At 25 °C, the rate law $-d[IrCl_6^{2-}]/dt = 2k[W_2O_4^{2+}][IrCl_6^{2-}]$ applies, with no dependence on $[H^+] = 0.5$–$1.0$ M, and $k = 6.6 \times 10^4$ $M^{-1}$ $s^{-1}$. The latter is 26 times greater than the rate constant for $NCS^-$ substitution on $W_2O_4^{2+}$. It is also $6 \times 10^5$ times faster than the corresponding $Mo_2O_4^{2+}$ reaction (0.114 $M^{-1}$ $s^{-1}$), indicating a kinetically much more strongly reducing species. In the case of edta complexes $[W_2O_4(edta)]^{2-}$ and $[Mo_2O_4(edta)]^{2-}$, it has previously been shown that the W complex is oxidized $\sim 10^5$ times faster. The $[PtCl_6]^{2-}$ and $BrO_3^-$ oxidations of $W_2O_4^{2+}$ are also much more rapid than the corresponding reactions of $Mo_2O_4^{2+}$. With $[IrCl_6]^{2-}$ the reaction proceeds as $W^V_2 \rightarrow W^{V,VI} \rightarrow W^{VI}$ (molecularity of latter not established), and with $[PtCl_6]^{2-}$ and $BrO_3^-$ solutions also become colorless. In all cases with $W_2O_4^{2+}$ in excess, the blue color of $W^V/W^{VI}$ mixed-valence species develops subsequently over a few minutes. The $W^{V,VI}$ intermediate in the $[IrCl_6]^{2-}$ reaction is not the precursor of this tungsten blue, which is generated by excess $W^V_2$ reacting with $W^{VI}$. No blue coloration is observed in corresponding studies with $Mo_2O_4^{2+}$.

## Introduction

The preparation and characterization of the bis($\mu$-oxo) $W^V$ aqua ion has been reported recently from this laboratory.[1]



An X-ray crystal structure of $Ba[W_2O_4(edta)]\cdot 3.5H_2O$,[2] linked with the observation of rapid conversion of $W_2O_4^{2+}$ to $[W_2O_4(edta)]^{2-}$,[1,3] as well as Dowex ion-exchange chromatographic behavior (2+ charge), forms the basis of this characterization. The ion is therefore analogous to that of $Mo^V$, $[Mo_2O_4(H_2O)_6]^{2+}$,[4] which has been extensively studied,[4-8] although the preparative route is different from that normally employed for $Mo^V$. A study of the 1:1 substitution equilibration with $NCS^-$ has indicated that $W_2O_4^{2+}$ (2520 $M^{-1}$ $s^{-1}$ at 25 °C) is some 10 times less labile than $Mo_2O_4^{2+}$.[1] We now address the question of redox properties of $W_2O_4^{2+}$. Redox studies on $Mo_2O_4^{2+}$ have been reported previously.[4-7]

## Experimental Section

**Reagents.** Solutions of the yellow tungsten(V) aqua ion $[W_2O_4(H_2O)_6]^{2+}$, peak positions $\lambda$/nm (absorption coefficient, $\epsilon/M^{-1}$ $cm^{-1}$) 430 (193) and 340 (278) per dimer, were prepared by the procedure already described.[1] This involves aquation of $(NH_4)_2[WOCl_5]$ in 0.10 M *p*-toluenesulfonic acid (Sigma Chemicals) and subsequent purification on a Dowex 50W-X2 (Sigma Chemicals) cation-exchange column under rigorous $O_2$-free conditions. The oxidant sodium hexachloroiridate(IV), $Na_2[IrCl_6]\cdot 6H_2O$ (Johnson-Matthey), was used without further purification, peak at 487 nm ($\epsilon$ 4075 $M^{-1}$ $cm^{-1}$).[4] Solutions of $[IrCl_6]^{2-}$ in HPTS (0.2–1.0 M) were stable to aquation over several hours when stored out of light. Lithium *p*-toluenesulfonate was prepared by neutralization of the acid with lithium carbonate (Koch-Light) followed by recrystallization. Ammonium hexachloroplatinate(IV), $(NH_4)_2[PtCl_6]$ (Johnson Matthey), peak at 454 nm ($\epsilon$ 48 $M^{-1}$ $cm^{-1}$), and sodium bromate (BDH, GPR) were used without further purification.

**Table I.** Pseudo-First-Order Rate Constants ($k_{obsd}$) for the Oxidation of $W_2O_4^{2+}$ with $[IrCl_6]^{2-}$ ($[H^+] = 1.0$ M (Except As Indicated); $I = 1.0$ M (LiPTS))

| $10^4[IrCl_6^{2-}]$, M | $10^3[W_2O_4^{2+}]$, M | $k_{obsd}$, $s^{-1}$ |
|---|---|---|
| 0.3 | 0.30 | 46.1 |
| 0.4 | 0.40 | 50.3 |
| 0.4 | 0.40 | 51.2[a] |
| 0.4 | 0.40 | 51.9[b] |
| 0.5 | 0.50 | 65.2 |
| 0.6 | 0.64 | 84.7 |
| 0.6 | 0.75 | 105 |
| 0.6 | 0.90 | 117 |

[a] $[H^+] = 0.75$ M. [b] $[H^+] = 0.50$ M.

**Stoichiometry and Products.** These were determined spectrophotometrically for the $[IrCl_6]^{2-}$ oxidation. Relevant peak positions and absorption coefficients are as above, with the product $[IrCl_6]^{3-}$ contributing little to the absorbance.[4] From studies at 487 nm with $[IrCl_6]^{2-}$ in excess (up to 3-fold in moles), the reaction conforms to (1). The molecularity

$$W^V_2 + 2Ir^{IV} \rightarrow 2W^{VI} + 2Ir^{III} \tag{1}$$

of the $W^{VI}$ product is uncertain, and for the acidic conditions employed, a description $W^{VI}_x$ applies. At the concentrations used $W^{VI}$ is colorless.

In the case of less extensively studied 2-equiv oxidant $[PtCl_6]^{2-}$, (2) is assumed to apply, the product being square-planar $[PtCl_4]^{2-}$.[9] With

$$W^V_2 + Pt^{IV} \rightarrow 2W^{VI} + Pt^{II} \tag{2}$$

the multiequivalent oxidant bromate an overall change $BrO_3^- \rightarrow Br^-$ is possible.[10,11] On addition of increasing amounts of $W_2O_4^{2+}$ to $BrO_3^-$ a yellow → colorless change is observed until the ratio of ~5 equiv of W(V) to 1 mol of $BrO_3^-$ is reached, when final solutions become blue. The last stage(s) of the $BrO_3^- \rightarrow Br^-$ conversion are in competition therefore with the $W^V_2 \rightarrow$ W-blue conversion.

**Kinetic Studies.** Runs with $[IrCl_6]^{2-}$ were monitored by using a Dionex D-110 stopped-flow spectrophotometer, with both solutions air-free. The $W_2O_4^{2+}$ reactant was in large $\geq$10-fold molar excess of $[IrCl_6]^{2-}$, and the ionic strength was adjusted to 1.0 M (LiPTS). Kinetic plots of absorbance ($A$) changes at 487 nm, ln $(A_t - A_\infty)$ against time $t$, were linear to 3–4 half-lives and were treated on-line as previously described in papers from this laboratory. The formation of tungsten blue products in a second stage was monitored by conventional time range spectrophotometry ($t_{1/2} > 30$ s). Certain experiments were excluded because

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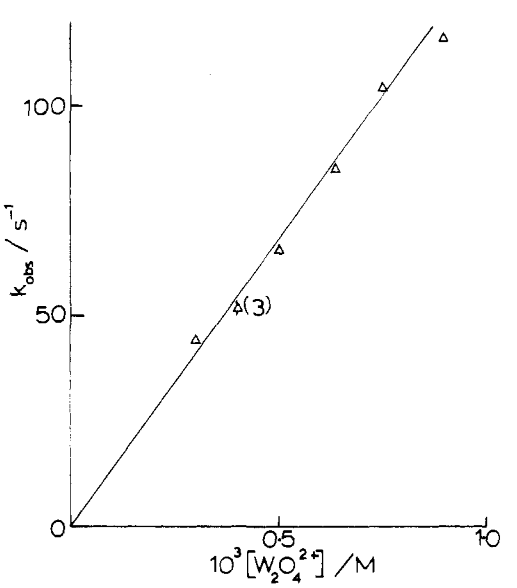

**Figure 1.** Variation of first-order rate constants, $k_{obsd}$, (25 °C), for the reaction of $[IrCl_6]^{2-}$ with the $W^V$ aqua dimer $[W_2O_4(H_2O)_6]^{2+}$; $I = 1.00$ M (LiPTS).

of the need to avoid tungsten blue precipitates in the stopped-flow apparatus.

Studies with 2-equiv $[PtCl_6]^{2-}$ and multiequivalent (up to 6) $BrO_3^-$ as oxidants were less extensive but sufficient to enable comparisons with $Mo_2O_4^{2+}$.[3] Similar (yellow) colors of the reactants in the case of the $[PtCl_6]^{2-}$ reaction, with overlapping absorbance bands, gave too small absorbance changes for stopped-flow studies.

## Results

**Oxidation with $[IrCl_6]^{2-}$.** Linear first-order plots were obtained with the $W_2O_4^{2+}$ reactant in large excess, in accordance with (3).

$$-d[Ir^{IV}]/dt = k_{obsd}[IrCl_6^{2-}] \qquad (3)$$

First-order rate constants $k_{obsd}$ (Table I) gave a linear dependence on $[W_2O_4^{2+}]$ (Figure 1) consistent with the full rate law (4). Rate

$$-d[Ir^{IV}]/dt = 2k[W_2O_4^{2+}][IrCl_6^{2-}] \qquad (4)$$

constants were independent of $[H^+]$ in the range 0.5–1.0 M. The slope of the line in Figure 1 (unweighted least squares) gives $k = (6.6 \pm 0.04) \times 10^4$ $M^{-1}$ $s^{-1}$. The tungsten blue color developed after completion of reactions (see below).

**Oxidation with $[PtCl_6]^{2-}$ and $BrO_3^-$.** In experiments with $[PtCl_6]^{2-}$ (0.25 mM) as oxidant for $W_2O_4^{2+}$ (0.25 mM) at $I =$ 0.20 M (HPTS), reaction was complete on mixing ($t_{1/2} < 1$ min). With $BrO_3^-$ (2.5 mM) as oxidant for $W_2O_4^{2+}$ (0.25 mM), $I =$ 0.20 M (HPTS), a first-order rate constant 4.37 $s^{-1}$ was obtained at 25 °C by the stopped-flow method (λ 430 nm). Precipitation was a problem when higher concentrations of $W^{VI}$ were generated. A rate constant 0.015 $s^{-1}$ was determined for the reaction of $Mo_2O_4^{2+}$ with $BrO_3^-$ (identical conditions, λ 295 nm) by the conventional method (this work). Assuming the same stoichiometry applies, the reaction of $W_2O_4^{2+}$ is 280 times faster.

**Formation of Tungsten Blue.** A pronounced blue color is obtained on oxidation of $W_2O_4^{2+}$ with less than the stoichiometric amount of oxidant for conversion to $W^{VI}$. Absorbance changes are as illustrated in Figure 2. The blue color is attributed to mixed-valence forms, very likely of the isopolytungstate kind.[13] In corresponding studies with $Mo_2O_4^{2+}$, no similar tendency to obtain the molybdenum blue state is observed (see however ref 14). The tungsten blue color is not observed with $[IrCl_6]^{2-}$ and $[PtCl_6]^{2-}$, in amounts equal to or in excess of the stoichiometric ratios for conversion to $W^{VI}$. The secondary nature of the blue formation (strong absorbance 600–1300 nm) was confirmed as follows. On mixture of equimolar (0.25 mM) amounts of $[IrCl_6]^{2-}$ with $W_2O_4^{2+}$ at $[H^+] = 0.30$ M, $I = 0.50$ M (LiPTS), rapid consumption of $[IrCl_6]^{2-}$ leaving half of the $W_2O_4^{2+}$ unreacted was followed by conventional time range formation of the blue color (Figure 3). In a separate experiment $W^{VI}$ (0.5 mM) was generated by mixing $[IrCl_6^{2-}]$ and $W_2O_4^{2+}$ in a 2:1 ratio to give a colorless solution. Using this solution, a kinetic run with $W^{VI}$ (0.25 mM) and $W_2O_4^{2+}$ (0.125 mM) gave an absorbance time plot identical to the one the above (Figure 3). Absorbance changes do not correspond to a single kinetic stage, and precipitation was observed after 3 min. From similar runs at $[H^+] = 0.17$ and 0.50 M, rates are slower at the higher $[H^+]$ and precipitation is incident at an early stage. When the mixture is allowed to stand, the precipitate settles. For three runs at low $[H^+]$, $I = 0.20$ M (HPTS), with $[W^{VI}] = 0.10$, 0.05, and 0.05 mM and $[W_2O_4^{2+}]$ = 0.95, 0.98, and 0.48 mM, respectively, initial slopes were, as far as we could tell, in a ratio of approximately 4:2:1, consistent with a rate law involving both reactants (Figure 4). The final absorbance in the third of the three runs was approximately twice that in the other two. Because of the uncertainty in precise final absorbance values, Guggenheim kinetic plots were carried out;[15]

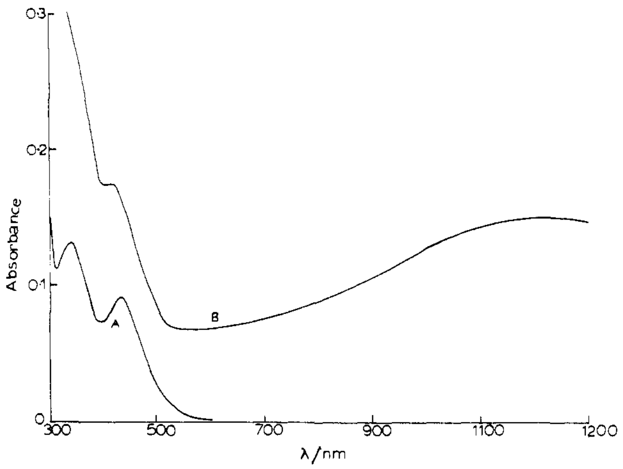

**Figure 2.** Comparison of the UV–vis–near-IR spectra of the yellow $W^V$ aqua dimer $[W_2O_4(H_2O)_6]^{2+}$ (0.48 mM) (A) and the tungsten blue product (B) formed 30 min after mixing $[W_2O_4(H_2O)_6]^{2+}$ (0.48 mM) with $W^{VI}$ (0.05 mM); $I = 0.20$ M (HPTS).

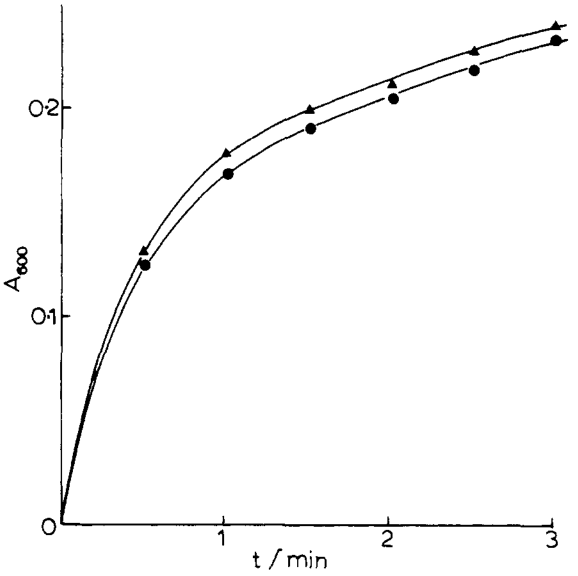

**Figure 3.** Experiment demonstrating that the tungsten blue color is produced at the same rate for kinetic runs with $W_2O_4^{2+}$ (0.125 mM) and $W^{VI}$ (0.25 mM expressed as monomer) (▲) and with $W_2O_4^{2+}$ (0.25 mM) and $[IrCl_6]^{2-}$ (0.25 mM) (●); $[H^+] = 0.30$ M; $I = 0.50$ M (LiPTS).

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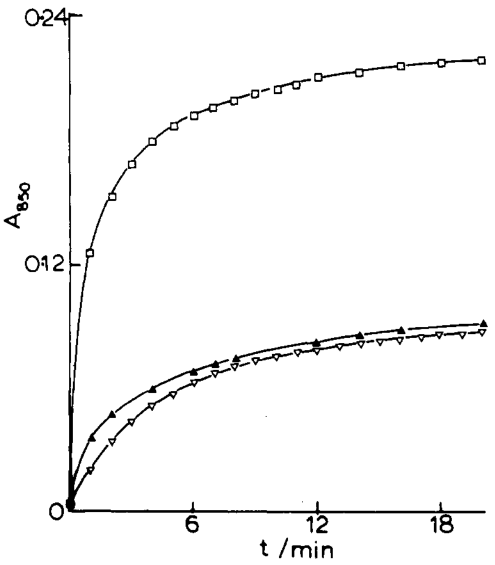

**Figure 4.** Comparative experiments (25 °C) in which tungsten blue formation is monitored at 850 nm with $W_2O_4^{2+}$ (0.95 mM) and $W^{VI}$ (0.10 mM expressed as monomer) (□), with $W_2O_4^{2+}$ (0.98 mM) and $W^{VI}$ (0.05 mM) (▲), and with $W_2O_4^{2+}$ (0.48 mM) and $W^{VI}$ (0.05 mM) (▽); $I$ = 0.20 M (HPTS).

these confirmed that there are at least two kinetic stages for blue formation.

## Discussion

The rate law for the oxidation of $W_2O_4^{2+}$ with $[IrCl_6]^{2-}$ is consistent with a reaction sequence (5)–(6). The dimer $W^{V,VI}$

$$W^V_2 + Ir^{IV} \xrightarrow{k} W^{V,VI} + Ir^{III} \qquad (5)$$

$$W^{V,VI} + Ir^{IV} \xrightarrow{\text{fast}} 2W^{VI} + Ir^{III} \qquad (6)$$

may cleave to give monomeric forms before oxidation in (6). In the case of the corresponding $Mo_2O_4^{2+}$ reaction, $I$ = 1.00 M ($LiClO_4$), an oxidant-independent rate law term $k_0$ was observed: $-d[IrCl_6^{2-}]/2dt = k_0[Mo_2O_4^{2+}] + k_{Ir}[Mo_2O_4^{2+}][IrCl_6^{2-}]$. Reactions at 25 °C required >30 min, with $k_0 = 2.95 \times 10^{-6}$ $s^{-1}$ at $[H^+]$ = 1.0 M. This step was assigned to a rate-determining $Mo_2O_4^{2+}$ bridge cleavage process. The $[IrCl_6]^{2-}$ oxidation of $W_2O_4^{2+}$ is much faster, and no evidence for a similar oxidant-independent process was obtained. This is consistent with earlier observations that, on addition of 10 M HCl, $W_2O_4^{2+}$ is converted to $[WOCl_5]^{2-}$ at a significantly slower rate than $Mo_2O_4^{2+}$ is converted to $[MoOCl_5]^{2-}$,[1] and on this evidence the $W_2O_4^{2+}$ core is more stable to cleavage.

The rate constant $k_{Ir}$ for oxidation of $Mo_2O_4^{2+}$ exhibits a dependence $k_2 + k_3[H^+]^{-1}$, whereas no $[H^+]$ dependence was detected for the $W_2O_4^{2+}$ reduction of $[IrCl_6]^{2-}$ ($[H^+]$ = 0.50–1.00 M). By comparison of rate constants for the $[IrCl_6]^{2-}$ and $[Fe(phen)_3]^{3+}$ oxidations of $Mo_2O_4^{2+}$ and $[Mo_2O_4(edta)]^{2-}$, it has been concluded that the $[IrCl_6]^{2-}$ oxidation of $Mo_2O_4^{2+}$ is outer sphere.[4] Contributions from $k_3$ were explained by the more favorable reaction that might result from $Mo^V$ increasing its extent of hydrolysis prior to oxidation to $Mo^{VI}$. Since an $[H^+]^{-1}$ dependence is not detected in the $W_2O_4^{2+}$ reaction, this explanation may require modification. Acid dissociation constants for $W_2O_4^{2+}$ and $Mo_2O_4^{2+}$ have not been determined, but would be expected to be of similar magnitude. One possible interpretation in the case of $Mo_2O_4^{2+}$ is that $k_0$ corresponds to monomer formation while $k_3$ is for a step in which one μ-oxo bridge of $Mo_2O_4^{2+}$ has cleaved. Such an interpretation is not however consistent with other observations.[16]

The rate constant for the $[IrCl_6]^{2-}$ oxidation of $W_2O_4^{2+}$ ($6.6 \times 10^4$ $M^{-1}$ $s^{-1}$) is ~26 times greater than that observed for $H_2O$ substitution by $NCS^-$ on $W_2O_4^{2+}$ at 25 °C,[1] and the reaction is therefore most likely an outer-sphere redox process. It is some $6 \times 10^5$ times greater than $k_2$ (0.114 $M^{-1}$ $s^{-1}$) for the reaction of $[IrCl_6]^{2-}$ with $Mo_2O_4^{2+}$ [4] (Table II), a trend that is observed also for the $[IrCl_6]^{2-}$ oxidation of the edta complexes $[W_2O_4(edta)]^{2-}$ and $[Mo_2O_4(edta)]^{2-}$ (~$10^5$).[17] This trend is consistent with $W_2O_4^{2+}$ being a much more powerful reductant than $Mo_2O_4^{2+}$. With $[PtCl_6]^{2-}$ and $BrO_3^-$, $W_2O_4^{2+}$ likewise behaves as a much stronger reductant. In the former case no rate constants were determined, but the $[PtCl_6]^{2-}$ oxidation of $Mo_2O_4^{2+}$ is extremely slow,[4] whereas the reaction with $W_2O_4^{2+}$ is fast. With $BrO_3^-$ as oxidant the rate constant is 280 times faster for $W_2O_4^{2+}$. The rate constant with $W_2O_4^{2+}$ ($1.7 \times 10^3$ $M^{-1}$ $s^{-1}$) is similar to that for $NCS^-$ substitution into $[W_2O_4(H_2O)_6]^{2+}$ ($2.5 \times 10^3$ $M^{-1}$ $s^{-1}$), and this reaction may therefore be substitution controlled. An inner-sphere reaction is a necessary requirement if the reaction proceeds by O atom transfer.

**Table II.** Summary of Rate Constants for $[IrCl_6]^{2-}$ Oxidation of $[M_2O_4(H_2O)_6]^{2+}$ and $[M_2O_4(edta)]^{2-}$ (M = Mo, W)

| reactant | $k$(25 °C), $M^{-1}$ $s^{-1}$ | ref | reactant | $k$(25 °C), $M^{-1}$ $s^{-1}$ | ref |
|---|---|---|---|---|---|
| $W_2O_4^{2+}$ [a] | $6.6 \times 10^4$ | this work | $[W_2O_4(edta)]^{2-}$ [c] | $6.3 \times 10^5$ | 3 |
| $Mo_2O_4^{2+}$ [b] | 0.114 | 4 | $[Mo_2O_4(edta)]^{2-}$ [b] | 6.6 | 17 |

[a] $I$ = 1.0 M (LiPTS). [b] $I$ = 1.0 M ($LiClO_4$). [c] $I$ = 0.50 M ($LiClO_4$).

The observation that blue solutions are formed on reacting $W_2O_4^{2+}$ with $W^{VI}$ has a counterpart in Mo chemistry,[18] although in corresponding experiments (under the conditions employed in this study) no molybdenum blue mixed-valence species are formed. Formation of tungsten blue is characterized by an increase in absorbance in the 600–1300-nm range corresponding to the formation of mixed-valence $W^V/W^{VI}$ product(s). No molecular formula is established yet for this product. The structure of a blue tetrameric $W^V_2W^{VI}_2$ anion $[W_4O_8Cl_8(H_2O)_4]^{2-}$,[12] obtained from 12 M HCl, has been determined. However, a product of higher nuclearity might seem more likely for the conditions used here.[14] It has been demonstrated that the blue color does not correspond to the formation of binuclear $W^{V,VI}$ in (5). Formation of the tungsten blue color occurs more rapidly at low $[H^+]$, under which condition precipitation is less marked.

Normal air-free storage procedures (under $N_2$) were used for $W_2O_4^{2+}$ stock solutions. Storage is not easy however because any ingress of $O_2$ results in the formation of a tungsten blue precipitate.[1] Overnight (typical) stock solutions of $W_2O_4^{2+}$ (5 mM) in 2.0 M $H^+$ generally gave traces of a blue solid deposit (predominantly on the sides of vessels), and recolumning (loading at $[H^+]$ = 0.3 M) was necessary.

As in the case of the $Mo^V$ dimer $Mo_2O_4^{2+}$, it is not easy to quantify meaningfully reduction potentials for the $W_2O_4^{2+}$ ion. There are for example uncertainties regarding the degree of hydrolysis and structure of the VI state products. As yet no accurate measurements have been reported. Previously however, from studies on the Keggin heteropolyanions incorporating W and Mo, it has been concluded that the $W^{VI}/W^V$ couple is >0.4 V more strongly reducing (the reduction potential is more negative) than the $Mo^{VI}/Mo^V$ couple.[19] Latimer has also listed potentials for the $WO_3(s)/W_2O_5$ (0.03 V) and $MoO_3(aq)/MoO_2^+$ (0.40 V) couples.[20] Differences of this magnitude are consistent with experimental observations reported in this paper.

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**Registry No.** $[W_2O_4(H_2O)_6]^{2+}$, 111919-72-3; $[IrCl_6]^{2-}$, 16918-91-5; $[PtCl_6]^{2-}$, 16871-54-8; $BrO_3$, 15541-45-4.

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