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# Electron Transfer. 124. Oxidations of Trinuclear Tungsten Cations[1]

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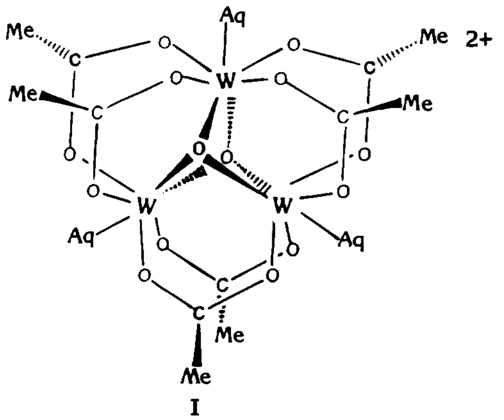
Aqueous solutions of the trinuclear dioxo-capped acetato-bridged complex $[W_3(\mu_3\text{-}O)_2(\mu\text{-}OAc)_6(H_2O)_3]^{2+}$, “-$(W^{IV})_3$” (**I**), and the related monoxo-capped cation $[W_3(\mu_3\text{-}O)(\mu\text{-}OAc)_6(H_2O)_3]^{2+}$, “$(W^{III})_2W^{IV}$” (**II**), are resistant to the action of all but very strong oxidants. Oxidations with Ce(IV), Cr(VI), $MnO_4^-$ and $HIO_4$ yield preponderantly W(VI). Although these conversions require several steps, the initial act of electron transfer to the oxidant is rate-determining in each case. Rate laws for oxidation of $(W^{IV})_3$ with $MnO_4^-$ and $HCrO_4^-$ at low pH values contain $[H^+]$- and $[H^+]^2$-proportional terms associated with partial conversion of these oxidants to more reactive mono- and diprotonated forms. In addition, the $(W^{IV})_3{-}HCrO_4^-$ system features a 1:1 Ox•Red complex ($Q_{assn}$ = 51 ± 8 $M^{-1}$ at 21 °C). The $(W^{IV})_3$−I(VII) reaction is accelerated by lowering $[H^+]$, possibly reflecting deprotonation of a W(IV)-bound aqua ligand of the reductant. In the $(W^{IV})_3$−Ce(IV) reaction, the supply of active oxidant is partially depleted by conversion of monomeric Ce(IV) to an unreactive dimer and also by transformation of the monomer to a negligibly reactive protonated species. The $2e^-$ oxidant, $HIO_4$, reacts with $(W^{IV})_3$ substantially more slowly than either the $1e^-$ acceptor, Ce(IV), or the oxidants Mn(VII) and Cr(VI), which can utilize combinations of paths, suggesting that the overall conversion is best initiated by a single-electron transfer. Such reactions must be predominantly outer-sphere since they proceed many orders of magnitude more rapidly that ligand substitution at the W(IV) center. Only the $(W^{III})_2W^{IV}{-}IrCl_6^{2-}$ reaction exhibits a simple bimolecular rate expression. The observed rate constant, 3 $M^{-1}\ s^{-1}$, when considered in the framework of the Marcus model, corresponds to an electron self-exchange rate for the couple $W_{334/344}$ between $10^{-6.0}$ and $10^{-4.3}$ $M^{-1}\ s^{-1}$, thus falling well below reported values for several 4d- and 5d-based systems but approaching the values typifying 3d-based couples. It is suggested that interconversions between members of redox series of trinuclear acetato-bridged complexes of the type at hand entail changes in the bond connectivities about the transition metal centers, a feature increasing the Franck−Condon barrier to electron transfer.

Interest in the solution chemistry of tungsten has widened perceptibly in recent years.[2] As with its congeners, chromium and molybdenum, all oxidation states between 2+ and 6+ are represented, and further experimental scope arises from the ease with which the lower oxidation states form binuclear and polynuclear complexes, including some “mixed-valence” species. Tungsten is the only 5d block element observed to exhibit enzymatic activity. Several formate dehydrogenases,[3] carboxylic acid reductases,[4] and an aldehyde ferredoxin oxidoreductase[5] have been shown to be tungsten enzymes.

Investigations of the redox chemistry of tungsten are generally complicated by the very strongly reducing character of its lower oxidation states[6] and by the demonstrated ability of some low-valent species to bond to molecular $N_2$.[7] However, the trinuclear acetato-bridged tungsten(IV) cation, **I**, first characterized by Bino and co-workers[8] is unusually stable in air, and the closely related complex **II**,[9] which may be designated a $(W^{III})_2W^{IV}$ derivative, is similarly unreactive. Prompted in part by the ease with which complexes **I** and **II** may be handled,[10] we have examined their reactions with several inorganic oxidants. Reactions are much slower than the corresponding reductions by carboxylate-free $Mo_3$ cations.[11] Moreover, cation **II**, which features the lower net tungsten oxidation state, is generally oxidized more sluggishly than the $(W^{IV})_3$ complex.



**I**

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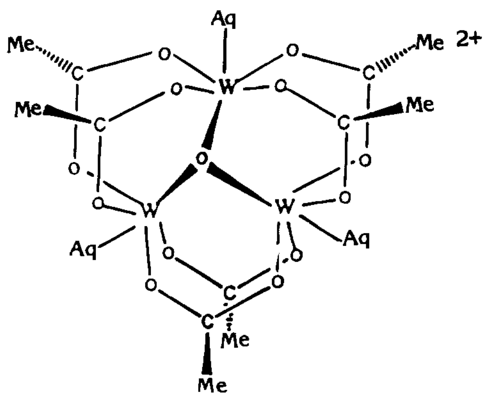

II

## Experimental Section

**Materials.** Potassium permanganate (Aldrich), sodium dichromate (Aldrich), sodium periodate (Alfa), sodium hexachloroiridate(IV) ($Na_2IrCl_6{\cdot}6H_2O$; Alfa), and cerium(IV) perchlorate (0.50 M in 6 M $HClO_4$; G. F. Smith) were used as received. The $(W^{IV})_3$ complex (I) was prepared by heating $W(CO)_6$ with a mixture of acetic acid and acetic anhydride, and the $(W^{III})_2W^{IV}$ derivative, by treating sodium tungstate hydrate with granulated zinc and acetic anhydride, using the procedures of Powell and Richens.[10] Both complexes were purified by cation exchange chromatography on Dowex 50W-X2-200 resin and eluted with 1.0 M $HClO_4$ as described.[10]

**Stoichiometric Studies.** Stoichiometries of the more rapid oxidation of the $(W^{IV})_3$ complex with that reductant in excess were measured at 445 nm by adding deficient quantities of the oxidant to a known excess of $(W^{IV})_3$, waiting until reaction had ceased, and then measuring the decreases in absorbance. These changes were compared to those resulting from addition of an excess of the oxidant. The slower oxidations of the $(W^{III})_2W^{IV}$ complex, **II**, were often complicated by development of turbidity late in the reactions. Determinations with the latter reductant were satisfactory only for Cr(VI) oxidations, which were examined at 352 nm. Results are summarized in Table 1.

**Kinetic Measurements.** Rate constants for oxidation of the $(W^{IV})_3$ complexes were determined from absorbance changes at 445 nm, whereas oxidations of the $(W^{III})_2W^{IV}$ cation were examined at 668 nm. Except for the relatively rapid $(W^{IV})_3$–Ce(IV) reaction, which was studied using a Durrum–Gibson stopped-flow spectrophotomer, reactions were followed on a Beckman 5260 recording spectrophotometer. Ionic strength was maintained at 1.0 M by addition of $HClO_4/NaClO_4$. Experiments were generally carried out under pseudo-first-order conditions. No more than 10% of the added (excess) oxidant was consumed during a complete run. Pseudo-first-order rate constants obtained from replicate experiments agreed to within 6%.

**Additional Observations.** The $(W^{IV})_3$ cation (I) did not react at a measurable rate with $VO_2^+$, $S_2O_8^{2-}$, or $HIO_3$ (each at aconcentration as great as 0.05 M) in 0.15 M $HClO_4$. Reaction with $Br_2$ was perceptible but inconveniently slow, whereas reaction with $BrO_3^-$ was slow and appeared to be autocatalytic. Reactions with bromite ($BrO_2^-$) and chlorite ($ClO_2^-$) featured absorbance increases due to formation of the elemental halogen; these reactions reflected decomposition in the acid medium rather than action of the tungsten reagent. Reactions of $(W^{III})_2W^{IV}$ (II) were, in general, still more sluggish. Among the various oxidants examined, reaction was detectable only with $HCrO_4^-$ and $IrCl_6^{2-}$.

## Results and Discussion

In marked contrast to a host of complexes of low-valent molybdenum and tungsten, which undergo oxidation with particular ease[6,11] and must therefore be manipulated under anaerobic conditions, cations I and II are singularly resistant to all but the strongest oxidants, and solutions of these trinuclear species may be handled in air without difficulty. Such reactions which occur, although generally slow, frequently appear to be stoichiometrically straightforward.

Stoichiometries of the reactions of $(W^{IV})_3$ and $(W^{III})_2W^{IV}$ (Table 1) indicate that conversion is preponderantly to W(VI) in each case.

$$(W^{IV})_3 + 6Ce^{IV} \rightarrow 3W^{VI} + 6Ce^{III} \qquad (1)$$

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

$$5(W^{IV})_3 + 6Mn^{VII} \rightarrow 15W^{VI} + 6Mn^{II} \qquad (3)$$

$$3(W^{III})_2W^{IV} + 8Cr^{VI} \rightarrow 9W^{VI} + 8Cr^{III} \qquad (4)$$

The exponential decay curves showed no distortions or irregularities attributable to the formation or destruction of intermediate species on a time scale comparable to that of the net conversion. Hence, the initial act of electron transfer to the oxidant must be rate determining in each case.

Representative kinetic data pertaining to oxidations by periodate and Ce(IV) are assembled in Table 2. Both reactions are first order in reductant, and both are seen to be more rapid at higher pH values. The Ce(IV) data are complicated by the recognized[12] partial dimerization of this oxidant under our reaction conditions. Concentrations of mononuclear Ce(IV) in this table have been calculated by using the (slightly acid-dependent) dimerization constants tabulated by Baes and Mesmer.[12c] Rate laws for these systems, as well as those for reactions with the remaining oxidants, are listed in Table 3. Also included are kinetic parameters resulting from least-squares refinements of the observed rate constants in terms of these expressions. Specific rates calculated from these parameters are compared with observed values in Table 2.

The $[H^+]$- and $[H^+]^2$-proportional components observed for the oxidations of $(W^{IV})_3$ with $MnO_4^-$ and $HCrO_4^-$ are analogous to terms reported for an array of earlier reactions involving these reagents[13] and are undoubtedly associated with partial conversion of the oxidants to their more reactive monoprotonated and diprotonated forms. Since these dependencies do not exhibit kinetic saturation effects within the range examined, our data do not allow us to evaluate acidity constants. An approach toward kinetic saturation with respect to $[Cr^{VI}]$ points to partial formation of a $(W^{IV})_3$-$HCrO_4^-$ complex. The estimated association quotient ($Q_{assn} = 51 \pm 8$ $M^{-1}$) is not unreasonable for an outer-sphere adduct formed from a dipositive and uninegative species.[14]

The $(W^{IV})_3$–I(VII) reaction is found to proceed more rapidly at lower acidities. Within the range studied, I(VII) is converted largely to the weak acid $H_5IO_6$ (apparent $pK_A$ 1.64).[15,16] The acidity constant (0.92) obtained from treatment of our data does not correspond to this value and may instead reflect deprotonation of a W(IV)-bound aqua ligand of the reductant. The latter process may occur also in the oxidations by Mn(VII) and Cr(VI), but its effects would be obscured by the sharper $[H^+]$-dependencies associated with protonation of the oxidants.

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(12) See, for example: (a) Heidt, L. J.; Smith, M. E. *J. Am. Chem. Soc.* **1948**, *70*, 2476. (b) King, E. L.; Pandow, M. L. *J. Am. Chem. Soc.* **1952**, *74*, 1966. (c) Baes, C. F., Jr.; Mesmer, R. F. *The Hydrolysis of Cations*; Wiley-Interscience: New York, 1976; pp 138–146.

(13) See, for example: (a) Espenson, J. H. *Acc. Chem. Res.* **1970**, *3*, 347. (b) Morrow, J. I.; Perlman, S. *Inorg. Chem.* **1973**, *12*, 2453. (c) Moore, F. M.; Hicks, K. W. *Inorg. Chem.* **1975**, *14*, 413. (d) Howlett, K. E.; Sulfab, Y. *Inorg. Chim. Acta*, **1976**, *17*, 129. (e) Hicks, K. W. *J. Inorg. Nucl. Chem.* **1976**, *38*, 1381.

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**Table 1.** Stoichiometries of the Oxidations of Trinuclear Tungsten Cations[a]

| reductant | oxidant | waiting period, min | [red], M × $10^5$ | [ox], M × $10^5$ | $10^5\Delta$[red], M | $10^5\Delta$[ox], M | $\Delta$[ox]/$\Delta$[red] |
|---|---|---|---|---|---|---|---|
| $(W^{IV})_3$ | Ce(IV) | 4.0 | 15.0 | 15.0 | 2.4 | | 6.2 |
| | | | 15.0 | 30.0 | 4.8 | | 6.2 |
| | | | 15.0 | 45 | 7.2 | | 6.2 |
| | | | 15.0 | 60 | 10.2 | | 5.9 |
| | | | 15.0 | 75 | 13.0 | | 5.8 |
| | $MnO_4^-$ | 10 | 15.0 | 5.0 | 3.8 | | 1.32 |
| | | | 15.0 | 10.0 | 7.2 | | 1.39 |
| | $HCrO_4^-$ | 30 | 15.0 | 10.0 | 4.9 | | 2.04 |
| | | 20[b] | 5.0 | 30.0 | | 10.0 | 2.00 |
| $(W^{III})_2W^{IV}$ | $HCrO_4^-$ | 200[b] | 5.0 | 25.0 | | 11.8 | 2.36 |
| | | 240[b] | 5.0 | 25.0 | | 13.4 | 2.68 |
| | | 130[b] | 8.0 | 30.0 | | 19.9 | 2.48 |

[a] Reactions in 1.0 M $HClO_4$ at 25 °C; $\lambda$ = 445 nm unless otherwise indicated. [b] $\lambda$ = 352 nm.

**Table 2.** Kinetic Data for Oxidations of Trinuclear Tungsten(IV) (Complex **I**)[a]

| A. oxidations with periodate[b] | | | B. oxidations with Ce(IV)[c] | | | |
|---|---|---|---|---|---|---|
| [I(VII)], M × $10^2$ | [$H^+$], M | $10^3k$, $s^{-1}$ [d] | [$Ce^{IV}$]$_{tot}$, M × $10^3$ | [$Ce^{IV}$]$_{monomer}$, M × $10^3$ [e] | [$H^+$], M | $k$, $s^{-1}$ [d] |
| 1.00 | 0.140 | 1.22 (1.15) | 2.00 | 1.79 | 1.00 | 6.7 (6.9) |
| 2.00 | 0.130 | 2.4 (2.4) | 4.0 | 3.36 | 1.00 | 12.9 (12.9) |
| 4.0 | 0.110 | 5.2 (5.2) | 6.0 | 4.7 | 1.00 | 18.4 (18.0) |
| 7.0 | 0.080 | 9.9 (10.5) | 9.0 | 6.4 | 1.00 | 25 (24) |
| 8.5 | 0.065 | 13.3 (13.8) | 12.5 | 8.5 | 1.00 | 30 (33) |
| 10.0 | 0.050 | 18.2 (17.6) | 2.00 | 1.78 | 0.80 | 8.0 (7.7) |
| 4.0 | 0.21 | 3.7 (3.6) | 2.00 | 1.75 | 0.60 | 9.1 (8.8) |
| 4.0 | 0.36 | 2.6 (2.5) | 2.00 | 1.72 | 0.40 | 11.0 (10.2) |
| 4.0 | 0.56 | 1.85 (1.75) | 2.00 | 1.69 | 0.20 | 12.3 (12.3) |
| 4.0 | 0.76 | 1.25 (1.36) | 2.00 | 1.66 | 0.10 | 13.0 (13.6) |

[a] Reactions at 21 °C; $\mu$ = 1.00 M ($NaClO_4$–$HClO_4$; $\lambda$ = 445 nm. [b] [$(W^{IV})_3$] = 6.0 × $10^{-3}$ M. [c] [$(W^{IV})_3$] = 3.0 × $10^{-3}$ M. [d] Parenthetical values were calculated using rate laws and parameters in Table 3. [e] Concentrations of monomeric Ce(IV) were calculated from the data of Baes and Mesmer.[12c]

**Table 3.** Rate Laws and Kinetic Parameters for Oxidations of Trinuclear Tungsten Cations[a]

| oxidant (Ox) | rate law | eq no. | parameters[b] |
|---|---|---|---|
| | A. Oxidations of the $(W^{IV})_3$ Cation (**I**)[c] | | |
| $MnO_4^-$ | [Red][Ox]($k_0 + k_1$[$H^+$]) | 5 | $k_0 = 58 \pm 1$ $M^{-1}$ $s^{-1}$; $k_1 = 35 \pm 2$ $M^{-2}$ $s^{-1}$ |
| Cr(VI) | $\frac{Q[\mathrm{Red}][\mathrm{Ox}]}{1 + Q[\mathrm{Ox}]}(k_1[\mathrm{H}^+] + k_2[\mathrm{H}^+]^2)$ | 6 | $k_1 = 0.17 \pm 0.03$ $M^{-1}$ $s^{-1}$; $k_2 = 0.071 \pm 0.012$ $M^{-2}$ $s^{-1}$;<br>$Q = 51 \pm 8$ $M^{-1}$ |
| $HIO_4$ | $\frac{[\mathrm{Red}][\mathrm{Ox}]k_A K_{HA}}{K_{HA} + [\mathrm{H}^+]}$ | 7 | $k_A = 0.25 \pm 0.01$ $M^{-/1}$ $s^{-1}$; $K_{HA} = 0.12 \pm 0.01$ |
| Ce(IV)[d] | $\frac{[\mathrm{Red}][\mathrm{Ox}]_M k_A K_{HA}}{K_{HA} + [\mathrm{H}^+]}$ | 8 | $k_A = (9.4 \pm 0.4) \times 10^3$ $M^{-1}$ $s^{-1}$; $K_{HA} = 0.69 \pm 0.06$ |
| | B. Oxidations of the $(W^{III})_2W^{IV}$ Cation (**II**)[e] | | |
| $IrCl_6^{2-}$ | $k$[Ox][Red] | 9 | $k = 3.5 \pm 0.5$ $M^{-1}$ $s^{-1}$ |
| Cr(VI) | [Red][Ox]($k_0 + k_1$[$H^+$]) | 5 | $k_0 = 0.042 \pm 0.008$ $M^{-1}$ $s^{-1}$; $k_1 = 0.37 \pm 0.02$ $M^{-2}$ $s^{-1}$ |

[a] $\mu$ = 1.0 M ($NaClO_4$–$HClO_4$). [b] $Q$ indicates a Cr(VI)–$(W^{IV})_3$ association quotient; $K_{HA}$ is a deprotonation quotient. [c] Reactions at 21 °C; [$(W^{Iv})_3$] = (3.0–6.0) × $10^{-6}$; $\lambda$ = 445 nm. [d] [Ox]$_M$ designates the concentation of mononuclear Ce(IV), calculated from the data of Baes.[12c] [e] Reactions at 25 °C; [$(W^{III})_2W^{IV}$] = 1.2 × $10^{-4}$ M; $\lambda$ = 668 nm.

The $(W^{IV})_3$-Ce(IV) reaction is complicated by partition of the oxidant into mono- and dinuclear cations. Rate law 8 implies that the activated complex for this conversion involves only the monomer, the concentrations of which may be estimated from earlier data.[12c] The pool of effective oxidizing species is further depleted by partial conversion to a protonated form, which appears to be negligibly reactive. The p$K_A$ value (0.16) pertaining to this equilibrium lies close to that listed by Sherrill (0.22)[17] but falls somewhat below that reported by Offner and Skoog (0.72).[18]

Rate laws 5–8 for the oxidations of $(W^{IV})_3$, which mainly reflect differences in speciation among the several oxidants, are relatively uninformative concerning mechanistic features associated with the W(IV) center. We note, however, that the 2e$^-$ oxidant I(VII) reacts significantly more slowly (under comparable conditions) either than the le$^-$ acceptor Ce(IV) or than Mn(VII) or Cr(VI), which can utilize combinations of one- and two-electron paths, suggesting that the overall reaction is best initiated by a single-electron transfer. Powell and Richens[10] have found that replacement of ligated water on $(W^{IV})_3$ and on

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[17] Sherrill, M. S.; King, C. B.; Spooner, R. C. *J. Am. Chem. Soc.* **1943**, *65*, 170. Note that this p$K$ refers to the interconversion of the species $Ce(OH)^{3+}$ and $Ce(OH)_2^{2+}$. The more acidic tetrapositive ion $Ce(OH)^{4+}$(aq) assumes importance only at acidities much greater than those considered here.

[18] Offner, H. G.; Skoog, D. A. *Anal. Chem.* **1966**, *38*, 1520.

its $(\mathrm{Mo^{IV}})_3$ analog proceeds many orders of magnitude more slowly than the redox reactions at hand. If one assumes that substitution of the oxidant at W(IV) is a necessary step for an inner-sphere redox process, we may conclude that the reactions in this study are initiated predominantly by outer-sphere $1e^-$ transfer.

Among the oxidations of $(\mathrm{W^{III}})_2\mathrm{W^{IV}}$ (**II**), that by $\mathrm{IrCl_6}^{2-}$ is the only member of the present series exhibiting a simple bimolecular rate expression. Since the substitution-inert character of both redox partners ensures an outer-sphere route, the observed rate constant ($k_{\mathrm{W,Ir}} = 3\ \mathrm{M^{-1}\ s^{-1}}$) may be used, along with the self-exchange rate constant for $\mathrm{IrCl_6}^{2-/3-}$ ($k_{\mathrm{Ir}(4,3)} = 10^{5.4}\ \mathrm{M^{-1}\ s^{-1}}$)[19] and eq 10 (which arises from the treatment of

$$\log k_{\mathrm{W,Ir}} = 0.50(\log k_{\mathrm{Ir}(4,3)} + \log k_{\mathrm{W}} + \log k_{\mathrm{W,Ir}}) \quad (10)$$

Marcus),[20,21] to estimate a range of electron self-exchange rates ($k_{\mathrm{W}}$ values) for the couple $\mathrm{W}_{334/344}$. Since $\mathrm{IrCl_6}^{2-}$ ($E° = 0.87$ V)[22] oxidizes $(\mathrm{W^{III}})_2\mathrm{W^{IV}}$ nearly completely but reaction with $\mathrm{Fe^{3+}(aq)}$ ($E° = 0.77$ V) is imperceptible, the formal potential of this reductant may be taken to lie between these $E°$ limits, yielding a log $k_{\mathrm{W,Ir}}$ value between zero and 1.7, corresponding to a self-exchange rate, $k_{\mathrm{W}}$, between $10^{-6.0}$ and $10^{-4.3}\ \mathrm{M^{-1}\ s^{-1}}$. A rate in this range falls well below reported values for several 4d- and 5d-based systems (Table 4) but, somewhat unexpectedly, approaches the values typifying a number of 3d-based couples, for which electron transfer may be associated with proportionately greater distortions of metal−ligand bonds, as well as changes in coordination number and multiplicities.

**Table 4.** Electron Self-Exchange Rates for Transition Metal Complexes[a]

| 4d and 5d systems | | 3d systems | |
|---|---|---|---|
| couple | log *k* | couple | log *k* |
| $\mathrm{Ru(NH_3)_6}^{3+/2+}$ | 3.6 | $\mathrm{Cr(H_2O)_6}^{3+/2+}$ | −4.7 |
| $\mathrm{Ru(bipy)_3}^{3+/2+}$ | 8.6 | $\mathrm{Mn(H_2O)_6}^{3+/2+}$ | −3.5 |
| $\mathrm{Mo(CN)_8}^{3-/4-}$ | 4.5 | $\mathrm{Cu^{2+/+}(aq)}$ | −5.0 |
| $\mathrm{Ag^{III,II}(S_4Ph_4Por)}$ | 5.6[b] | $\mathrm{Co(en)_3}^{3+/2+}$ | −4.7 |
| $\mathrm{IrCl_6}^{2-/3-}$ | 5.3 | $[\mathrm{VO(OH)}]^{2+/+}$ | −2[c] |
| $\mathrm{Os(phen)_3}^{3+/2+}$ | 8.5 | | |

[a] log *k* values pertain to 25 °C ($\mu = 1.0$ M) and are from ref 21 unless otherwise indicated. [b] Complexes of sulfonated tetraphenylporphyrin (Langley, R.; Hambright, P.; Williams, R. F. X. *Inorg. Chim. Acta.* **1985**, *104*, L25). [c] Macartney, D. H. *Inorg. Chem.* **1986**, *25*, 2222.

Note, in this connection, that although the structures of the $(\mathrm{W^{IV}})_3$ and $(\mathrm{W^{III}})_2\mathrm{W^{IV}}$ (cations **I** and **II**) are closely related, they differ in the number of bridging oxo groups, hence in the coordination number of tungsten, suggesting that interconversions between members of redox series of this type in aqueous media may entail changes in the bond connectivities about the metal centers. Since such a series presumably includes a $\mathrm{W^{III}(W^{IV})_2}$ species, a (hitherto uncharacterized) $1e^-$ oxidation product of complex **II**, it is reasonable to suspect that changes of this nature may accompany its oxidation as well, substantially increasing the Franck−Condon barrier to self-exchange. Such an effect does not intrude with the remaining 4d and 5d redox couples listed in this table.

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(21) See, for example: Creutz, C.; Sutin, N. In *Inorganic Reactions and Methods*; Zuckerman, J. J., Ed.; VCH Publishers: Deerfield Beach, FL, 1986; Vol. 15, pp 13−51.

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