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Kinetics of the Outer-Sphere Oxidation of the Mixed Molybdenum(V)–Tungsten(V) Dinuclear Complex $[\mathrm{MoW(O)_2(\mu\text{-}O)_2(\mu\text{-}edta\text{-}}N,N')]^{2-}$ and of the Mixed-Bridged Complex $[\mathrm{W_2(O)_2(\mu\text{-}O)(\mu\text{-}S)(\mu\text{-}edta\text{-}}N,N')]^{2-}$ by $[\mathrm{Ir^{IV}Cl_6}]^{2-}$ in Aqueous Solution

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The kinetics of the outer-sphere oxidation of $[\mathrm{MoW(O)_2(\mu\text{-}O)_2(\mu\text{-}edta\text{-}}N,N')]^{2-}$ (abbreviated $\mathrm{MoWO_2}$) and of $[\mathrm{W_2(O)_2(\mu\text{-}O)(\mu\text{-}S)(\mu\text{-}edta\text{-}}N,N')]^{2-}$ (abbreviated $\mathrm{W_2OS}$) ($\mathrm{H_4edta}$ = ethylenediaminetetraacetic acid) with $[\mathrm{Ir^{IV}Cl_6}]^{2-}$ have been studied in aqueous perchlorate media at $I = 1.00$ M (M = mol dm^{-3}) and 18.0–40.0 °C. Pseudo-first-order rate constants (k_{obsd}) with the reductants in large excess over the oxidant are independent of $[\mathrm{H^+}]$ in the range 0.02–0.10 M for both reactions. The oxidation of the $\mathrm{W_2OS}$ complex conforms to the following rate law with significant retardation in the presence of $[\mathrm{Ir^{III}Cl_6}]^{3-}$: $-\mathrm{d}[\mathrm{Ir^{IV}}]/\mathrm{d}t = k_{\mathrm{obsd}}[\mathrm{Ir^{IV}}] = 2k_1k_2[\mathrm{W_2OS}][\mathrm{Ir^{IV}}]/(k_{-1}[\mathrm{Ir^{III}}] + k_2)$, where rate constants are defined as follows.

$$\text{“}\mathrm{W^{V}{}_2}\text{”} + \text{“}\mathrm{Ir^{IV}}\text{”} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{“}\mathrm{(W_2)^{V,VI}}\text{”} + \text{“}\mathrm{Ir^{III}}\text{”}$$

$$\text{“}\mathrm{(W_2)^{V,VI}}\text{”} \xrightarrow{k_2} (\text{“}\mathrm{W^{V}}\text{”}, \text{“}\mathrm{W^{VI}}\text{”})$$

$$\text{“}\mathrm{W^{V}}\text{”} + \text{“}\mathrm{Ir^{IV}}\text{”} \xrightarrow{\text{fast}} \text{“}\mathrm{W^{VI}}\text{”} + \text{“}\mathrm{Ir^{III}}\text{”}$$

Oxidation of the $\mathrm{MoWO_2}$ complex shows a simple second-order rate law, $-\mathrm{d}[\mathrm{Ir^{IV}}]/\mathrm{d}t = k_{\mathrm{obsd}}[\mathrm{Ir^{IV}}] = 2k_1[\mathrm{MoWO_2}][\mathrm{Ir^{IV}}]$, where k_1 is defined as above, but now $k_{-1} \ll k_2$, suggesting that the “$\mathrm{(MoW)^{V,VI}}$” intermediate is rapidly decomposed. Rapid-scanning spectroscopy shows no evidence for the accumulation of the “$\mathrm{(MoW)^{V,VI}}$” intermediate. k_1 at 25.0 °C, ΔH^*, and ΔS^* for the $\mathrm{W_2OS}$ and the $\mathrm{MoWO_2}$ oxidations are 8.3×10^2 M^{-1} s^{-1}, 40 kJ mol^{-1}, and -55 J K^{-1} mol^{-1} and 1.2×10^4 M^{-1} s^{-1}, 31.8 kJ mol^{-1}, and -60 J K^{-1} mol^{-1}, respectively. The k_{-1}/k_2 value at 25.0 °C for the $\mathrm{W_2OS}$ complex oxidation is 8.6×10^3 M^{-1}. The reactivity differences are ascribed to ΔH^* differences. The plot ln k_1 vs E_{pa} for the oxidations of $\mathrm{MoWO_2}$, $\mathrm{W_2OS}$, and related complexes ($[\mathrm{Mo_2(O)_2(\mu\text{-}O)_2(\mu\text{-}edta)}]^{2-}$ and $[\mathrm{W_2(O)_2(\mu\text{-}O)_2(\mu\text{-}edta)}]^{2-}$) is linear, suggesting that the reactions obey the Marcus theory for outer-sphere electron-transfer reactions. The effects of a mixed-metal structure and of substituting sulfide for oxide bridge are discussed. Oxidations by $[\mathrm{Fe^{III}(phen)_3}]^{3+}$ (phen = 1,10-phenanthroline) have been studied briefly.

Introduction

Molybdenum and tungsten in quinquevalent states tend to form dimeric complexes with a core $\mathrm{M_2(O)_2(\mu\text{-}X)(\mu\text{-}Y)}$, where M is Mo or W and X and Y are O or S (Figure 1).[3-5] Steric structures of analogous Mo and W complexes are very similar to each other, and various other properties are also comparable between the two elements. The most significant different property is perhaps their redox behavior. The redox potentials of the molybdenum(V) dimers are about 0.5 V more positive than those of the corresponding tungsten(V) dimers.[6]

The kinetics of the oxidation of $[\mathrm{Mo_2(O)_2(\mu\text{-}O)_2(\mu\text{-}edta)}]^{2-}$ (edta = ethylenediaminetetraacetate(4−)) and $[\mathrm{Mo_2(O)_2(\mu\text{-}O)_2(H_2O)_6}]^{2+}$ and their W analogues have been studied.[7-14] The tungsten complex is oxidized about 10^5 times faster than the analoguous molybdenum complex.[7,8,10,11] Moreover, the oxidations of the two edta complexes give apparently different rate laws.[7,10] That for the oxidation of $[\mathrm{Mo_2(O)_2(\mu\text{-}O)_2(\mu\text{-}edta)}]^{2-}$ (hereafter abbreviated $\mathrm{Mo_2O_2}$) by $[\mathrm{Ir^{IV}Cl_6}]^{2-}$ contains an $[\mathrm{Ir^{III}Cl_6}]^{3-}$ dependence, suggesting the involvement of a kinetically significant intermediate “$\mathrm{(Mo_2)^{V,VI}}$”,[7] whereas simple second-order rate law is obtained for the oxidation of $[\mathrm{W_2(O)_2(\mu\text{-}O)_2(\mu\text{-}edta)}]^{2-}$ (abbreviated $\mathrm{W_2O_2}$) by $[\mathrm{Ir^{IV}Cl_6}]^{2-}$.[10]

We recently reported a new mixed molybdenum(V)–tungsten(V) dimeric complex, $[\mathrm{MoW(O)_2(\mu\text{-}O)_2(edta)}]^{2-}$ (abbreviated $\mathrm{MoWO_2}$),[15] and a mixed-bridged complex, $[\mathrm{W_2(O)_2(\mu\text{-}O)(\mu\text{-}S)(edta)}]^{2-}$ (abbreviated $\mathrm{W_2OS}$).[6] The complexes with the $\mathrm{M_2(O)_2(\mu\text{-}X)(\mu\text{-}Y)}$ core have a direct metal-to-metal bond,[16,17] and the Mo–W bond is believed to exist in the $\mathrm{MoWO_2}$ complex.[15] The effect of the metal-to-metal bond on the kinetic behavior was ambiguous in the previous kinetic studies[7-14] and may be more clearly interpreted by the use of heterometal dinuclear complexes. The $\mathrm{MoWO_2}$ complex contains two metal ions with significantly different reactivity toward oxidation (in monomeric or homometal dimeric state), and it might be interesting to see if the two metal ions behave as one redox center or as two different metal ions. It might give us an opportunity to observe intermediate species such as “$\mathrm{Mo^{V}W^{VI}}$”. Also, the sulfide bridge might stabilize or destabilize the mixed-valence intermediate[18,19] and change the kinetic behavior from that of the bis(μ-oxo) analogue. In this paper therefore, we wish to report kinetic studies of the oxidation

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(3) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; Wiley: New York, 1988; pp 804-847.

(4) Stiefel, E. I. *Prog. Inorg. Chem.* **1977**, *22*, 1-223.

(5) Dori, Z. *Prog. Inorg. Chem.* **1981**, *28*, 239-307.

(6) Ikari, S.; Sasaki, Y.; Ito, T. *Inorg. Chem.* **1989**, *28*, 447-451.

(7) Wharton, R. K.; Ojo, J. F.; Sykes, A. G. *J. Chem. Soc., Dalton Trans.* **1975**, 1526-1530.

(8) Cayley, G. R.; Taylor, R. S.; Wharton, R. K.; Sykes, A. G. *Inorg. Chem.* **1977**, *16*, 1377-1381.

(9) (a) Sasaki, Y. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 1939-1944. (b) Kondo, S.; Sasaki, Y.; Saito, K. *Inorg. Chem.* **1981**, *20*, 429-433. (c) Sasaki, Y.; Ueno, B.; Saito, K. *J. Chem. Soc., Chem. Commun.* **1981**, 1135-1136. (d) Sasaki, Y.; Kawamura, R. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 3379-3386. (e) Kanesato, M.; Ebihara, M.; Sasaki, Y.; Saito, K. *J. Am. Chem. Soc.* **1983**, *105*, 5711-5713.

(10) Soares, A. B.; Taylor, R. C.; Sykes, A. G. *J. Chem. Soc., Dalton Trans.* **1980**, 1101-1104.

(11) Sharp, C.; Sykes, A. G. *Inorg. Chem.* **1988**, *27*, 501-503.

(12) Millan, C.; Diebler, H. *Inorg. Chem.* **1985**, *24*, 3729-3733.

(13) (a) McAllister, R.; Hicks, K. W.; Hurless, M. A.; Pittenger, S. T.; Gedridge, R. W. *Inorg. Chem.* **1982**, *21*, 4098-4100. (b) Chappelle, G. A.; MacStay, A.; Pittenger, S. T.; Ohashi, K.; Hicks, K. W. *Inorg. Chem.* **1984**, *23*, 2768-2771.

(14) Linn, D. E., Jr.; Ghosh, S. K.; Gould, E. S. *Inorg. Chem.* **1989**, *28*, 3225-3228.

(15) Ikari, S.; Sasaki, Y.; Nagasawa, A.; Kabuto, C.; Ito, T. *Inorg. Chem.* **1989**, *28*, 1248-1254.

(16) Brown, D. H.; Perkins, P. G.; Stewart, J. J. *J. Chem. Soc., Dalton Trans.* **1972**, 1105-1108. Brown, D. H.; Perkins, P. G. *Rev. Roum. Chim.* **1975**, *20*, 515-521.

(17) Jezowska-Trzebiatowska, B.; Glowiak, T.; Rudolf, M. F.; Sabat, M.; Sabat, J. *Russ. J. Inorg. Chem.* (*Engl. Transl.*) **1977**, *22*, 1590-1597.

(18) Oxidation of $[\mathrm{Mo_2(O)_2(\mu\text{-}S)_2(H_2O)_6}]^{2+}$ by $[\mathrm{Fe^{III}(phen)_3}]^{3+}$ gave a complicated rate law and did not clarify the effect of the sulfide bridges.[12]

(19) A mixed-bridged edta complex is known for molybdenum(V), but no kinetic study on its oxidation has been reported.[20]

(20) Ott, V. R.; Swieter, D. S.; Schultz, F. A. *Inorg. Chem.* **1977**, *16*, 2538-2545.

0020-1669/90/1329-1712$02.50/0

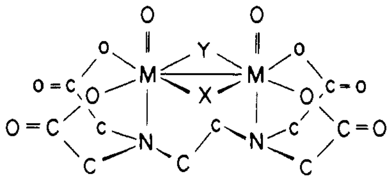

Figure 1. Schematic drawing of the structure of $[M_2(O)_2(\mu\text{-}X)(\mu\text{-}Y)(\mu\text{-edta})]^{2-}$ (M = Mo, W; X, Y = O, S).

Table I. Oxidation Potentials (V vs SSCE) for the Series of Complexes $[M_2(O)_2(\mu\text{-}X)(\mu\text{-}Y)(\mu\text{-edta})]^{2-}$ at I = 1.00 M and $[H^+]$ = 0.10 M[a]

M_2XY	E_{pa}/V (25 °C)	M_2XY	E_{pa}/V (25 °C)
Mo_2O_2	+0.89	W_2O_2	+0.35
$MoWO_2$	+0.47	W_2OS	+0.63

[a] Adjusted with $LiClO_4$ and $HClO_4$, respectively.

of the two new complexes by $[Ir^{IV}Cl_6]^{2-}$ (and briefly by $[Fe^{III}(phen)_3]^{3+}$ (phen = 1,10-phenanthroline)).

Experimental Section

Materials. $Na_2[MoW(O)_2(\mu\text{-}O)_2(\mu\text{-edta})]\cdot 4.5H_2O$[15] and $Na_2[W_2(O)_2(\mu\text{-}O)(\mu\text{-}S)(\mu\text{-edta})]$[6] were prepared as described previously. Commercial $Na_2[Ir^{IV}Cl_6]\cdot 6H_2O$ was recrystallized once from water. $Na_3[Ir^{III}Cl_6]\cdot H_2O$ was obtained by recrystallizing the commercially available reagent twice from water. The salt gave the reported absorption peak at 358 nm (ϵ = 74 M^{-1} cm^{-1}) (M = mol dm^{-3}).[21] $[Fe^{III}(phen)_3](ClO_4)_3\cdot H_2O$ was prepared as described in the literature.[22] A solution of $LiClO_4$ was prepared by the use of reagent that was recrystallized from water, and the solution was standardized by passing it through a cation-exchange column of Amberlite IR-120 and titrating it against standard NaOH solution.

Measurements. Visible absorption spectra were measured by using a Hitachi 340 spectrophotometer. Electrochemical measurements were carried out in aqueous solutions ([complex] = 0.001 M; I = 1.00 M; $[H^+]$ = 0.10 M ($LiClO_4$–$HClO_4$)) by using a Yanaco P-1100 polarographic analyzer with a glassy-carbon working electrode at 25 °C. Cyclic voltammograms were obtained at a scan rate of 20 mV/s. Potentials were recorded vs SSCE.

Kinetics. Kinetic and rapid-scanning spectrophotometric measurements were carried out by the use of a Union-Giken RA-401 stopped-flow spectrophotometer. Ionic strength and proton concentration were adjusted with $LiClO_4$ and $HClO_4$, respectively. All the kinetic runs were carried out under pseudo-first-order conditions with the $MoWO_2$ or the W_2OS complex in at least 20-fold excess over the oxidant, $[Ir^{IV}Cl_6]^{2-}$. The sodium salt of $[Ir^{III}Cl_6]^{3-}$ was added whenever necessary in at least 10-fold excess over $[Ir^{IV}Cl_6]^{2-}$. Decrease in the concentration of $[Ir^{IV}Cl_6]^{2-}$ was followed at 487 nm, where it has a strong absorption peak with ϵ = 4075 M^{-1} cm^{-1}.[23] The pseudo-first-order rate constant, k_{obsd}, were obtained by the use of a curve-fitting program run by a computer attached to the spectrophotometer. Slight deviations from the simulated first-order decay curve at the initial and the final part of the absorbance change were often observed for the W_2OS complex oxidation in particular. The first-order plots were otherwise reasonably linear for all the runs, and k_{obsd} values were estimated with reasonable accuracy.

Results

Oxidation Potentials. Oxidation potentials were obtained from the cyclic voltammograms measured at I = 1.00 M and $[H^+]$ = 0.10 M, which are identical with the conditions of the kinetic study. All the complexes gave irreversible oxidation wave. The oxidation potentials, E_{pa}, are summarized in Table I. These values are similar to those obtained at pH 7.5.[6,15] The pH independence of E_{pa} suggests that no protonation–deprotonation equilibrium is involved in the oxidation process. Reduction potentials of $[Mo_2(O)_2(\mu\text{-}X)(\mu\text{-}Y)(\mu\text{-edta})]^{2-}$ (X, Y = O, S) complexes depend significantly on the pH of the solution.[20,24]

Table II. Pseudo-First-Order Rate Constants (k_{obsd}) for the Oxidation of $[MoW(O)_2(\mu\text{-}O)_2(\mu\text{-edta})]^2$ by $[Ir^{IV}Cl_6]^{2-}$ at $[H^+]$ = 0.10 M ($HClO_4$) and I = 1.00 M ($LiClO_4$)[a]

temp/°C	$[[MoWO_4edta]^{2-}]$/ 10^{-4} M	k_{obsd}/s^{-1}
18.0	5.0	9.4
	7.5	14.3
	10.0	18.1
	12.5	23.1
25.0	5.0	12.4
	7.5	18.2
	8.1	19.2
	8.1	19.2[b]
	8.5	20.5[c]
	10.0	23.1
	10.0	24.8[d]
	12.5	30.1
	5.0	11.6[e]
	7.5	17.6[e]
	8.75	20.4[e]
	10.0	22.4[e]
	12.5	26.3[e]
33.0	5.0	17.8
	7.5	27.4
	8.5	31.4
	10.0	37.7
	12.5	44.1
40.0	5.0	24.4
	7.5	39.4
	8.5	44.1
	10.0	51.1
	12.5	60.8

[a] $[[Ir^{IV}Cl_6]^{2-}] = 2.10 \times 10^{-5}$ M. [b] $[H^+]$ = 0.02 M. [c] 5-fold excess of $[Ir^{III}Cl_6]^{3-}$ over $[Ir^{IV}Cl_6]^{2-}$ added. [d] 10-fold excess of $[Ir^{III}Cl_6]^{3-}$ over $[Ir^{IV}Cl_6]^{2-}$ added. [e] I = 0.50 M ($LiClO_4$).

Preliminary Observations on the Redox Reactions. On the mixing of a solution of each of the two dinuclear complexes, $[MoW(O)_2(\mu\text{-}O)_2(\mu\text{-edta})]^{2-}$ and $[W_2(O)_2(\mu\text{-}O)(\mu\text{-}S)(\mu\text{-edta})]^{2-}$, with that of $[Ir^{IV}Cl_6]^{2-}$, the strong brown color of the oxidant disappeared almost instantaneously due to rapid redox reaction. Stoichiometry of the redox reaction was studied with the solution containing oxidant in more than 2-fold excess over the reductant. The amount of the remaining $[Ir^{IV}Cl_6]^{2-}$ was estimated from the absorption intensity at 487 nm. For each reaction, 2 mol of the oxidant are consumed by 1 mol of the dinuclear complex. Thus, the total reactions are expressed as follows:

$$[MoWO_4(edta)]^{2-} + 2[Ir^{IV}Cl_6]^{2-} \rightarrow \text{“Mo}^{VI}\text{”} + \text{“W}^{VI}\text{”} + H_nedta^{(4-n)-} + 2[Ir^{III}Cl_6]^{3-} \quad (1)$$

$$[W_2O_3S(edta)]^{2-} + 2[Ir^{IV}Cl_6]^{2-} \rightarrow 2\text{“W}^{VI}\text{”} + H_nedta^{(4-n)-} + 2[Ir^{III}Cl_6]^{3-} \quad (2)$$

The edta ligand should be dissociated from the oxidized metal ions at $[H^+]$ = 0.1 M.[25] The “Mo^{VI}” and “W^{VI}” are in complicated monomer–dimer equilibria.[26,27]

Rapid-scanning spectroscopy (400–600 nm) was carried out to detect the possible intermediate “Mo^VM^{VI}” spectrophotometrically. A solution containing equal concentrations (5.2×10^{-4} M) of the $MoWO_2$ complex and $[Ir^{IV}Cl_6]^{2-}$ was used for that purpose. Within the time range from 30 ms to 3 s, no spectra other than those of reactants and products were observed. Therefore, it is concluded that the redox reaction occurs without the accumulation of the one-electron-oxidized intermediate.

Kinetics of the Oxidation of $[MoW(O)_2(\mu\text{-}O)_2(\mu\text{-edta})]^{2-}$ by $[Ir^{IV}Cl_6]^{2-}$. The oxidation was studied mostly at $[H^+]$ = 0.10 M ($HClO_4$) and I = 1.00 M ($LiClO_4$). First-order rate constants

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(21) Sykes, A. G.; Thorneley, R. N. F. *J. Chem. Soc. A* **1970**, 232–238.

(22) Schilt, A. A.; Taylor, R. C. *J. Inorg. Nucl. Chem.* **1959**, *9*, 211–221.

(23) Poulson, I. A.; Garner, C. S. *J. Am. Chem. Soc.* **1962**, *84*, 2032–2037.

(24) Ott, V. R.; Schultz, F. A. *J. Electroanal. Chem. Interfacial Electrochem.* **1975**, *59*, 47–60.

(25) Naarova, M.; Podlahova, J.; Podlaha, J. *Collect. Czech. Chem. Commun.* **1968**, *33*, 1991–2003.

(26) Hytko, K.-H.; Glemser, O. *Adv. Inorg. Radiochem.* **1976**, *19*, 239–315.

(27) (a) Ojo, J. F.; Taylor, R. S.; Sykes, A. G. *J. Chem. Soc., Dalton Trans.* **1975**, 500–505. (b) Himeno, S.; Hasegawa, S. *Inorg. Chim. Acta* **1984**, *83*, L5–L6. (c) Tytko, K.-H.; Baethe, G.; Cruywagen, J. J. *Inorg. Chem.* **1985**, *24*, 3132–3136. (d) Yokoi, K.; Matsubayashi, N.; Miyanaga, T.; Watanabe, I.; Murata, K.; Ikeda, S. *Chem. Lett.* **1987**, 1453–1456.

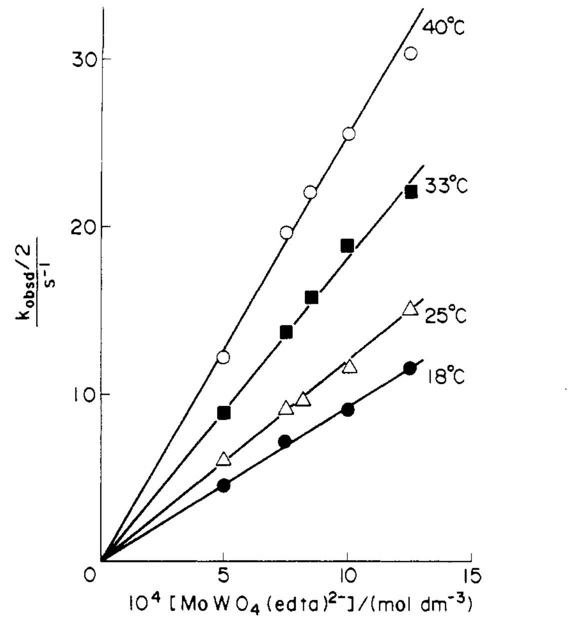


Figure 2. Dependence of k_{obsd} on [[MoWO$_4$edta]$^{2-}$] for the oxidation of [MoW(O)$_2$(μ-O)$_2$(μ-edta)]$^{2-}$ by [Ir^{IV}Cl$_6$]$^{2-}$ in aqueous solution (I = 1.00 M (LiClO$_4$), [H$^+$] = 0.10 M (HClO$_4$)) at various temperatures.

Table III. Second-order Rate Constants (k_1) for the Oxidation of [MoW(O)$_2$(μ-O)$_2$(μ-edta)]$^{2-}$ by [Ir^{IV}Cl$_6$]$^{2-}$ at [H$^+$] = 0.10 M (HClO$_4$) and I = 1.00 M (LiClO$_4$)

temp/°C	k_1/10^4 M^{-1} s^{-1}	temp/°C	k_1/10^4 M^{-1} s^{-1}
18.0	0.93 ± 0.03	33.0	1.82 ± 0.06
25.0	1.20 ± 0.04	40.0	2.56 ± 0.17

$\Delta H^* = 31.8 \pm 2.1$ kJ mol^{-1}
$\Delta S^* = -60 \pm 7$ J K^{-1} mol^{-1}

(k_{obsd}) are listed in Table II. Linear dependence of k_{obsd} on the excess concentration of the MoWO$_2$ complex is shown in Figure 2. A few runs at 25 °C confirmed the independence of k_{obsd} on [Ir^{III}] (up to 2 × 10^{-4} M) and on [H$^+$] (0.02 and 0.10 M). Thus, the system gives a simple second-order rate law with respect to the two reactants:

$$k_{obsd} = 2k_1[\mathrm{MoWO_2}] \tag{3}$$

Here the factor of 2 is given under the assumption that the first one-electron oxidation is followed by a rapid second one-electron-transfer process (vide infra). The second-order rate constants, k_1, at I = 1.00 M and corresponding activation parameters, ΔH^* and ΔS^*, are given in Table III. Ionic strength dependence of the reaction is small; k_1 values at I = 1.00 and 0.50 M are (1.20 ± 0.04) × 10^4 and (1.14 ± 0.08) × 10^4 M^{-1} s^{-1}, respectively, at 25.0 °C.

Oxidation of the MoWO$_2$ complex by [Fe^{III}(phen)$_3$]$^{3+}$ was found to be too fast to be followed by our stopped-flow apparatus, and the second-order rate constant should be much greater than 1 × 10^6 M^{-1} s^{-1}.

Table IV. Pseudo-First-Order Rate Constants (k_{obsd}) for the Oxidation of [W$_2$(O)$_2$(μ-O)(μ-S)(μ-edta)]$^{2-}$ by [Ir^{IV}Cl$_6$]$^{2-}$ at [H$^+$] = 0.10 M (HClO$_4$) and I = 1.00 M (LiClO$_4$) at 25 °C

[W$_2$OS]/ 10^{-4} M	[[Ir^{IV}Cl$_6$]$^{2-}$]/ 10^{-5} M	[[Ir^{III}Cl$_6$]$^{3-}$]/ 10^{-4} M	k_{obsd}/ s^{-1}
5.00	2.5	5.0	0.132
7.50	2.5	5.0	0.180
10.0	2.5	5.0	0.266
10.0	2.5	5.0	0.269[a]
10.0	1.25	2.5	0.270
12.5	2.5	5.0	0.356
12.5	1.25	2.5	0.388
15.0	2.5	5.0	0.428

[a] [H$^+$] = 0.02 M.

Table V. Dependence of [[Ir^{III}Cl$_6$]$^{3-}$] in Excess of [[Ir^{IV}Cl$_6$]$^{2-}$] on the Pseudo-First-Order Rate Constants (k_{obsd}) for the Oxidation of [W$_2$(O)$_2$(μ-O)(μ-S)(μ-edta)]$^{2-}$ by [Ir^{IV}Cl$_6$]$^{2-}$ at [H$^+$] = 0.10 M (HClO$_4$) and I = 1.00 M (LiClO$_4$)[a]

temp/ °C	[[Ir^{III}Cl$_6$]$^{3-}$]/ 10^{-4} M	k_{obsd}/ s^{-1}	temp/ °C	[[Ir^{III}Cl$_6$]$^{3-}$]/ 10^{-4} M	k_{obsd}/ s^{-1}
18.0	2.50	0.646	25.0	5.00	0.459
	3.75	0.509		6.25	0.393
	5.00	0.400	33.0	5.00	0.591
	6.25	0.344		6.25	0.475
	7.50	0.297		7.50	0.416
25.0	2.50	0.785		8.75	0.357
	3.75	0.600			

[a] [[W$_2$(O)$_2$(μ-O)(μ-S)(μ-edta)]$^{2-}$] = 1.5 × 10^{-3} M; [[Ir^{IV}Cl$_6$]$^{2-}$] = 2.5 × 10^{-5} M.

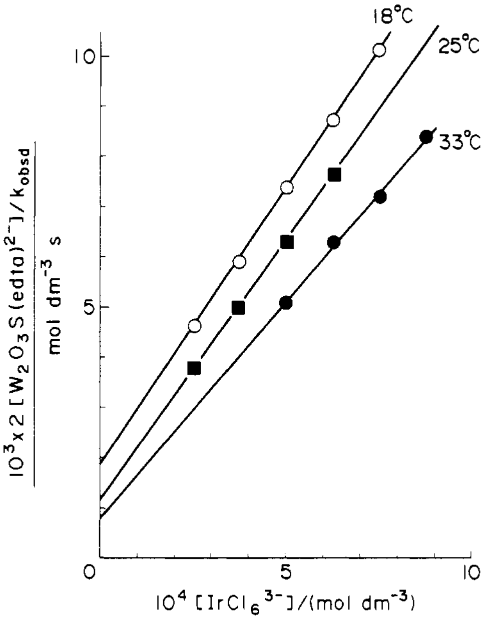


Figure 3. Dependence of k_{obsd} on [[Ir^{III}Cl$_6$]$^{3-}$] for the oxidation of [W$_2$(O)$_2$(μ-O)(μ-S)(edta)]$^{2-}$ (1.5 × 10^{-3} M) by [Ir^{IV}Cl$_6$]$^{2-}$ (2.5 × 10^{-5} M) in aqueous solution (I = 1.00 M (LiClO$_4$), [H$^+$] = 0.10 M (HClO$_4$)) at various temperatures.

Kinetics of the Oxidation of [W$_2$(O)$_2$(μ-O)(μ-S)(μ-edta)]$^{2-}$ by [Ir^{IV}Cl$_6$]$^{2-}$. The oxidation reaction was studied under the same conditions as those for the oxidation of the MoWO$_2$ complex. Unlike the MoWO$_2$ complex, the W$_2$OS complex shows a dependence on [Ir^{III}Cl$_6$$^{3-}$] in its oxidation by [Ir^{IV}Cl$_6$]$^{2-}$. In the absence of added [Ir^{III}Cl$_6$]$^{3-}$, the absorbance change did not fit to the first-order decay curve. The k_{obsd}'s were thus obtained in the presence of excess [Ir^{III}Cl$_6$]$^{3-}$ over [Ir^{IV}Cl$_6$]$^{2-}$. At a constant concentration of [Ir^{III}Cl$_6$]$^{3-}$ (5.0 × 10^{-4} M), k_{obsd} shows a linear dependence on the excess concentration of the W$_2$OS complex (Table IV). At a fixed concentration of the two redox reagents, dependence on the Ir^{III} complex concentration was studied at various temperatures (Table V). It was not possible to study the reaction above 40 °C, since the runs at 40 °C gave unreasonably large rate constants (this is likely to be due to the aquation of [Ir^{III}Cl$_6$]$^{3-}$).[21] Linear correlation between 1/k_{obsd} and [Ir^{III}] (Figure 3) conforms to the following rate law:

$$k_{obsd} = 2k_1k_2[\mathrm{W_2OS}]/(k_2 + k_{-1}[\mathrm{Ir^{III}}]) \tag{4}$$

The rate law is of the same form as that found for the oxidation of [Mo$_2$(O)$_2$(μ-O)$_2$(edta)]$^{2-}$ by [Ir^{IV}Cl$_6$]$^{2-}$.[7] The rate constants are defined as follows (MM' = W$_2$):

$$\text{“M}^{\mathrm{V}}\text{M}'^{\mathrm{V}}\text{”} + \text{“Ir}^{\mathrm{IV}}\text{”} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{“(MM')}^{\mathrm{V,VI}}\text{”} + \text{“Ir}^{\mathrm{III}}\text{”} \tag{5}$$

$$\text{“(MM')}^{\mathrm{V,VI}}\text{”} \xrightarrow{k_2} (\text{“M}^{\mathrm{V}}\text{”}, \text{“M}'^{\mathrm{VI}}\text{”}) \tag{6}$$

$$\text{“M}^{\mathrm{V}}\text{”} + \text{“Ir}^{\mathrm{IV}}\text{”} \xrightarrow{\text{fast}} \text{“M}^{\mathrm{VI}}\text{”} + \text{“Ir}^{\mathrm{III}}\text{”} \tag{7}$$

Table VI. Second-order Rate Constants (k_1) for the Oxidation of $[W_2(O)_2(\mu\text{-}O)(\mu\text{-}S)(\mu\text{-edta})]^{2-}$ by $[Ir^{IV}Cl_6]^{2-}$ at $[H^+] = 0.10$ M ($HClO_4$) and $I = 1.00$ M ($LiClO_4$)

temp/ °C	k_1/ 10^2 M^{-1} s^{-1}	temp/ °C	k_1/ 10^2 M^{-1} s^{-1}
18.0	5.35 ± 0.50	33.0	12.7 ± 5.0
25.0	8.26 ± 2.11		

$\Delta H^* = 40 \pm 3$ kJ mol^{-1}
$\Delta S^* = -55 \pm 10$ J K^{-1} mol^{-1}

Structural details on the species involved will be discussed in the next section. The fact of 2 in the rate law (4) is given, since the second one-electron transfer (eq 7) is assumed to be rapid.

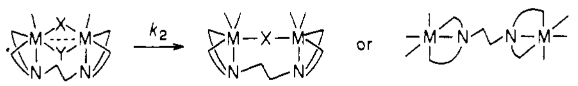
From the data given in Table III, k_1 and k_{-1}/k_2 at 25.0 °C were estimated to be 8.3×10^2 M^{-1} s^{-1} and 8.6×10^3 M^{-1}, respectively. The temperature dependence of k_1 and the corresponding activation parameters obtained are summarized in Table VI.

The tail end of the oxidation of the W_2OS complex by $[Fe^{III}(phen)_3]^{3+}$ could just be observed by our stopped-flow apparatus, and k_{obsd} at $[W_2OS] = 5.0 \times 10^{-4}$ M and $[Fe^{III}] = 1.25 \times 10^{-5}$ M may be of the order of 5×10^2 s^{-1}.

Discussion

Mechanism of the Reactions. Rapid-scanning spectrophotometric experiments for the oxidation of the $MoWO_2$ complex by $[Ir^{IV}Cl_6]^{2-}$ did not show any evidence for the existence of a detectable amount of the one-electron-oxidized intermediate. On the basis of the present observations as well as the previous results on the oxidation of the Mo_2O_2 and the W_2O_2 complexes,[7,10] it would be reasonable to discuss the reaction mechanism in terms of the general reaction scheme (5)–(7), where MM′ = Mo_2, MoW, or W_2.

MO studies on $[Mo_2(O)_2(\mu\text{-}X)_2(R\text{-cys})_2]^{2-}$ (X = O or S; cys = cysteinate dianion) indicated that d electrons from the two metal ions occupy pairwise a molecular orbital of practically metal–metal σ-bonding character.[16,17] From the similarity in steric structures and spectrophotometric properties, we have concluded that the two new complexes also have similar electronic structures with direct metal-to-metal bonds.[6,15] An electron is removed from the metal–metal σ-bonding orbital common to the four complexes during oxidation. This considerably weaken the metal-to-metal bond and may lead to the breakage of it. The process (eq 6) is schematically given as follows:



It is not necessary to assume decomposition to two uninuclear units. The edta ligand may be cleaved from the ions during or after the metal-to-metal bond rupture. The energy of the remaining electron becomes higher due to the cleavage of the metal-to-metal bond resulting in the rapid oxidation.

By application of the steady-state approximation to the concentration of the "$(MM')^{V,VI}$" intermediate, the following general rate law is obtained under the pseudo-first-order conditions with "$M^VM'^V$" in excess:

$$k_{obsd} = k_1k_2[\text{“}M^VM'^V\text{”}][Ir^{IV}]/(k_2 + k_{-1}[Ir^{III}]) \qquad (8)$$

For the reaction of the $MoWO_2$ complex, the observed simple second-order rate law is obtained by assuming that k_2 is sufficiently larger than $k_{-1}[Ir^{III}]$ in eq 8. The rate law is also consistent with the involvement of rapid oxidation of the one-electron-oxidized species, "$(MoW)^{V,VI}$" (eqs 5 and 9); namely, $k_3 \gg k_1$. It is not possible to kinetically exclude this alternative for the oxidation of the $MoWO_2$ complex, as stated previously for the oxidation of the W_2O_2 complex.[10]

$$\text{“}(MoW)^{V,VI}\text{”} + \text{“}Ir^{IV}\text{”} \xrightarrow{k_3} \text{“}Mo^{VI}\text{”} + \text{“}W^{VI}\text{”} + \text{“}Ir^{III}\text{”} \qquad (9)$$

In the case of the W_2OS complex, the full rate law is observed as in the case of the oxidation of the Mo_2O_2 complex. The process analogous to eq 9 would not be involved in the oxidation of the W_2OS complex, since the term $[\text{“}Ir^{IV}\text{”}]^2$ would be observed if eq 9 analogue were effective.

Table VII. Kinetic Parameters for the Outer-Sphere Oxidation of Complexes of the Type $[MM'(O)_2(\mu\text{-}X)(\mu\text{-}Y)(\mu\text{-edta})]^{2-}$ by $[Ir^{IV}Cl_6]^{2-}$ in Aqueous Media

MM′XY	k_1(25 °C)/ M^{-1} s^{-1}	ΔH^*/ kJ mol^{-1}	ΔS^*/ J K^{-1} mol^{-1}	$[Ir^{III}]$ dependence	ref
Mo_2O_2[a]	6.6	55.9 ± 1.3	−42 ± 4	yes	7
$MoWO_2$[a]	1.2×10^4	31.8 ± 2.1	−60 ± 7	not obsd	*c*
W_2O_2[b]	6.3×10^5	22.7 ± 0.8	−58 ± 3	not obsd	10
W_2OS[a]	8.3×10^2	40 ± 3	−55 ± 10	yes	*c*

[a] $I = 1.0$ M ($LiClO_4$). [b] $I = 0.5$ M ($LiClO_4$). [c] This work.

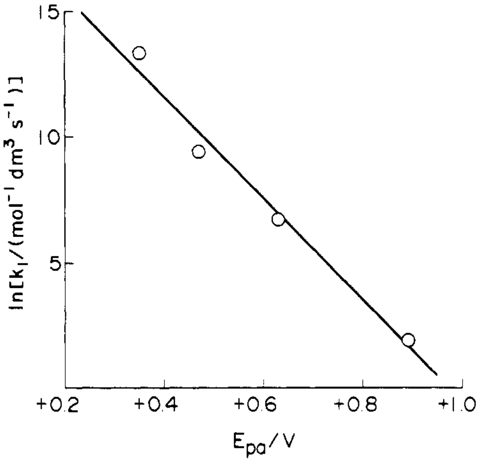


Figure 4. Relationship between ln k_1 (k_1, second-order rate constant at 25 °C for oxidation by $[Ir^{IV}Cl_6]^{2-}$) and E_{pa} (V vs SSCE) for the series of the complexes $[MM'(O)_2(\mu\text{-}X)(\mu\text{-}Y)(\mu\text{-etda})]^{2-}$ (MM′ = Mo_2, MoW, W_2, X = Y = O; MM′ = W_2, X = O, Y = S) at $I = 1.00$ M ($LiClO_4$) and $[H^+] = 0.10$ M ($HClO_4$).

The appearance of the $[Ir^{III}]$-dependent term in the rate law is a measure of the stability of the one-electron-oxidized intermediate against decomposition. The sulfide bridge appears to hold the two metals together in the intermediate more strongly than the oxide bridge does.

Correlation with the Redox Potentials. Table VII summarizes the kinetic data of the oxidation of a series of the four complexes including the two new ones by $[Ir^{IV}Cl_6]^{2-}$. It is concluded that the differences in the second-order rate constant, k_1, which span 5 orders of magnitude, are reflections of the different enthalpies of activation. ΔS^* values are similar for the four reactions, which may be a reflection of the very similar steric structures of the four complexes and thus the very similar transition states.

Figure 4 shows that ln k_1 values for the four complexes are linearly correlated with the oxidation potentials of these complexes. The slope is 0.52 for the corresponding plot of ln k_1 vs ln K (or $\Delta G°/RT$), where K is the equilibrium constant for the redox reaction estimated from the redox potentials and should be equal to k_1/k_{-1}. The series of the redox reactions thus obey the Marcus theory for outer-sphere electron-transfer reaction in the normal region.[28] It is reasonable to assume that the Marcus theory is applicable to the oxidation by $[Fe^{III}(phen)_3]^{3+}$ of these complexes too. The k_1 values for the oxidation of the $MoWO_2$ and the W_2OS complexes by $[Fe^{III}(phen)_3]^{3+}$ are estimated to be 3.5×10^6 and 2.4×10^5 M^{-1} s^{-1}, respectively, on the basis of the ratio $k_1(Fe^{III}(phen)_3{}^{3+})/k_1(Ir^{IV}Cl_6{}^{2-})$ for the Mo_2O_2 complex. The values are consistent with the observations.

The linear correlation enables us to further discuss the k_2 process. The correlation indicates that k_{-1} should decrease in the order $Mo_2O_2 > W_2OS > MoWO_2 > W_2O_2$. The k_{-1}/k_2 value for the W_2OS complex (8.6×10^3 M^{-1}) is five times greater than

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[28] (a) Marcus, R. A. *J. Chem. Phys.* **1965**, *43*, 679–701. (b) Marcus, R. A.; Sutin, N. *Inorg. Chem.* **1975**, *14*, 212–216.

that (1.7 × 10^3 M^{-1}) for the Mo_2O_2 complex. Thus, the k_2 for the W_2OS complex should be smaller by at least 1 order of magnitude than that for the Mo_2O_2 complex, suggesting the stabilization of the intermediate by the sulfide bridge.

Concluding Remarks. The redox behaviors of all the complexes including $MoWO_2$ should be understood in a similar way, as the free energy relationship holds. Two metal ions in the $MoWO_2$ complex behave practically as a single redox center, rather than as two different redox centers. The effect of the sulfide bridge is first to make the oxidation potential more positive and retard the first oxidation process and second to stabilize the intermediate to make the reverse process (k_{-1}) more effective.

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Heptacoordination of Manganese(II) by the Polyazacycloalkane [21]aneN$_7$. Crystal Structure of the [Mn([21]aneN$_7$)](ClO$_4$)$_2$ Solid Compound and Thermodynamics of Complexation in Water Solution

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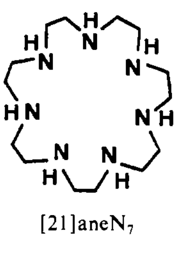
The thermodynamic parameters for the equilibrium of complexation between manganese(II) and 1,4,7,10,13,16,19-heptaazacycloheneicosane ([21]aneN$_7$) have been determined by potentiometry and microcalorimetry in 0.15 mol dm^{-3} NaClO$_4$ at 25 °C. The [21]aneN$_7$ ligand forms with manganese(II), in solution, a very stable complex (log K = 9.79 (1)) that preserves the metal ion from air oxidation, even in alkaline solution. The thermodynamic stability of this complex in solution is mainly entropic in nature ($\Delta H^\circ = -5.0$ (5) kcal mol^{-1}; $T\Delta S^\circ = 8.2$ kcal mol^{-1}). The absence of protonated complexes in solution suggests the heptacoordination of [21]aneN$_7$ to manganese(II). This is supported by the crystal structure of the complex [Mn([21]aneN$_7$)](ClO$_4$)$_2$. Crystals of this compound are orthorhombic, space group $P22_12_1$, with a = 9.751 (3) Å, b = 15.040 (4) Å, c = 32.781 (5) Å, V = 4807 (2) Å^3, Z = 8, d_{calc} = 1.53 g/cm^3, μ = 7.44 cm^{-1}, $F(000)$ = 2327.44, and M = 555.32. The structure has been solved by using the heavy-atom method and F_o and ΔF Fourier synthesis and was refined by least-squares methods to R = 0.085 (R_w = 0.069) for 1390 reflections having $I > 3\sigma(I)$. The asymmetric unit contains two independent [Mn([21]aneN$_7$)]$^{2+}$ complexed molecules in which manganese(II) is similarly heptacoordinated by [21]aneN$_7$, which disposes its nitrogen atoms at the vertices of an irregular polyhedron. The main difference between the two independent molecules is determined by the conformation of two chelate rings.

Introduction

The design of metal ion receptors has been mostly realized by means of synthetic macrocyclic molecules.[2] The achievement of selective interactions between the host macrocycles and the guest metal ions has produced a rapid advancement in the field of both biomimetic and abiotic model systems.[3,4] However, many metal ions have been so far disregarded by similar studies. Complexes of manganese(II) with synthetic macrocyclic ligands are almost unknown in spite of the importance of this metal ion in human living systems as a trace element.[4]

In the course of the present study, we have observed that the polyazacycloalkane 1,4,7,10,13,16,19-heptaazacycloheneicosane, hereafter abbreviated as [21]aneN$_7$, is a particularly suitable receptor for manganese(II), being able to wrap around this metal ion and achieve heptacoordination, forming a very stable complex that preserves the metal ion from air oxidation even in alkaline solution. The crystal structure of the compound [Mn([21]aneN$_7$)](ClO$_4$)$_2$ has been solved by single-crystal X-ray analysis. The heptacoordination of manganese(II) is achieved by means of the seven nitrogen donor atoms of the ligand. As far as we are aware, this is the first time that the heptacoordination of manganese(II), achieved by only one ligand, is described in terms of the crystal structure in the solid state and the thermodynamics of complexation equilibria in aqueous solution.



[21]aneN$_7$

Experimental Section

Materials. The complex [Mn([21]aneN$_7$)](ClO$_4$)$_2$ was synthesized by refluxing 20 mL of a water solution containing 0.1 mmol [21]aneN$_7$·7HCl[5] and 0.1 mmol of Mn(ClO$_4$)$_2$·7H$_2$O, followed by dropwise addition of a 0.2 mol dm^{-3} NaOH solution. When the pH of the reaction solution was about 9.5, solid NaClO$_4$·H$_2$O (8 g) was added in small portions. On cooling, a colorless microcrystalline powder of the complex separated. Elemental analysis and magnetic susceptibility agreed with that expected for the high-spin complex. Crystals of the complex suitable for X-ray analysis were obtained by slow evaporation of the mother solution at room temperature.

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(2) Izatt, R. M.; Christensen, J. J. *Synthesis of Macrocycles. The Design of Selective Complexing Agents*; Wiley: New York, 1987.

(3) Goedken, V. L. In *Coordination Chemistry of Macrocyclic Compounds*; Plenum Press: New York, 1979; Chapter 10.

(4) Hughes, M. N. *The Inorganic Chemistry of Biological Processes*; Wiley: New York, 1981.

(5) Micheloni, M.; Paoletti, P.; Bianchi, A. *Inorg. Chem.* **1985**, *24*, 3702.

0020-1669/90/1329-1716$02.50/0