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Reactivity of di- and tri-nuclear complexes of heavy mid-transition elements: A case of oxo-carboxylato-bridged complexes

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Abstract: Kinetics of the ligand substitution and oxidation reactions, pulse radiolysis, cyclic voltammetry, and function as excited-state quenchers, are discussed for the two types of complexes with the core structures, $M_3(\mu_3\text{-}O)(\mu\text{-}RCOO)_6$ (R = CH_3, C_6H_5; M_3 = Ru_3, Rh_3, $RhRu_2$) and $Ru_2(\mu\text{-}O)(\mu\text{-}CH_3COO)_2$. Some important conclusions are (i) strong trans labilization by the oxide bridge, (ii) stabilization of the mixed-valence states on forming metal-dπ-oxo-pπ molecular orbitals to give multi-step multi-electron redox behavior, and (iii) protonation at the oxide-bridge to show proton-coupled one-step two-electron transfer. Trans-labilization by the metal-metal bond is also demonstrated for some Pt-Pt, Re-Re, and Mo-Mo bonded complexes.

Introduction

Oxide, hydroxide and carboxylate bridged di- and polynuclear complexes are common to many transition elements and are found in active centers of some metalloenzymes (1). Understanding of their reactivity is therefore of fundamental importance from chemical and biochemical points of view. It is also related to some catalytic reactions involving these complexes. Heavy mid-transition elements such as Ru, Os, and Re give various di- and trinuclear complexes with different substitution inert oxidation states and thus they are useful for systematic studies of substitution and redox properties. We wish to discuss here the effect of the bridging groups, specifically bridging oxide, and also that of metal-metal bond on the ligand substitution and redox properties. We focus attention to the two types of complexes whose structures are depicted in Figure 1. These are the complexes with a trinuclear unit, $M_3(\mu_3\text{-}O)(\mu\text{-}RCOO)_6$ (R = CH_3, C_6H_5; M_3 = Ru_3, Rh_3, $RhRu_2$) and a dinuclear unit, $Ru_2(\mu\text{-}O)(\mu\text{-}CH_3COO)_2$. Some relevant information on the metal-metal bonded complexes of other metal ions such as Mo, Re and Pt will be also discussed.

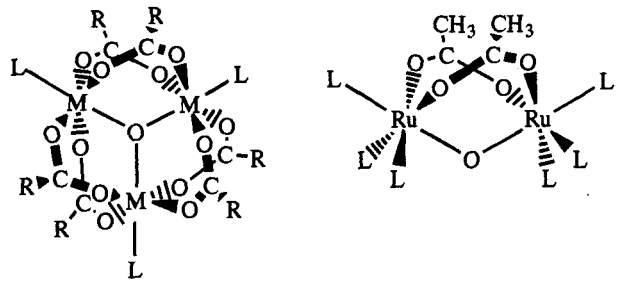

Figure 1. Structures of di- and trinuclear complexes discussed in this paper.

Ligand Substitution Properties

Trans effect of the oxide bridge.

Although the existence of a strong trans effect on ligand substitution reactions has well been established for the terminal oxide ions as exemplified by those of oxovanadium(IV) complexes (2), there has been only a few reports on the trans effect of bridging oxide or hydroxide ions. Table I shows the first-order rate constants for the pyridine (py) exchange reactions in the presence of excess py-d_5 for some oxo-bridged and oxo-centered di- and tri-nuclear ruthenium complexes with $Ru_2(\mu\text{-}O)(\mu\text{-}CH_3COO)_2$ and $Ru_3(\mu\text{-}O)(\mu\text{-}RCOO)_6$ cores (3-5). Trans effect of the oxide bridge has been clearly observed for the dinuclear complex, $[Ru_2(\mu\text{-}O)(\mu\text{-}CH_3COO)_2(py)_6]^{2+}$, in which the positions trans to the oxide-bridge are at least 10 times more labile than the cis positions (3). The first-order rate constants with [py-d_5] = 0.125 mol dm^{-3} is 2.2 x 10^{-4} s^{-1} at 50 °C. Evidence for the trans labilization of the central oxide of the triangular triruthenium complexes has been provided by the comparison of the substitution rate of methanol for the terminal aqua ligands (Table II) with the water exchange rates of the hexaaqua complexes (6,7). The rate constants listed in Table II are several orders of magnitude larger than those of water-exchange reactions of mononuclear complexes, $[Ru(H_2O)_6]^{3+}$ and $[Rh(H_2O)_6]^{3+}$. Activation parameters suggest more dissociative character for the substitution reactions of the trinuclear complexes.

Trans effect of metal-metal bond.

A metal-metal bond may cause significant trans-labilization as exemplified by the tetranuclear Pt(II) complex, $Pt_4(\mu\text{-}CH_3COO)_8$ (8). The in-plane acetate ligands, which occupy the trans positions to the Pt-Pt bonds, exchange rapidly with free acetates (4.4 M^{-1}s^{-1} at 25 °C) in acetonitrile, while those in out-of-plane positions are inert without exchanging for more than 2 weeks. Trans effect of a metal-metal bond is also seen in the axial ligand substitution reactions of some tetracarboxylato-dimetal complexes. A rapid CF_3COO^- exchange of $Mo_2(CF_3COO)_4$ with bulk CF_3COO^- has been explained by facile CF_3COO^- coordination at the axial sites followed by intramolecular rearrangement (9). A dirhenium(III) complex, $[Re_2(CH_3COO)_2Cl_4(py)_2]$ where py ligands occupy two axial positions, undergoes rapid pyridine exchange reaction without substitution for the basal Cl^- ligands (10). Diplatinum(III) complexes with a single Pt-Pt bond also have labile axial positions (11).

Table I. First-order rate constants for the pyridine exchange with excess pyridine-d_5 in acetonitrile.

complex [a]	k/s^{-1}(60 °C)	$\Delta H^{\neq}$/kJ mol^{-1}	$\Delta S^{\neq}$/(J K^{-1}mol^{-1})	ref.
$[Ru_2(\mu\text{-}O)(\mu\text{-}CH_3COO)_2(py)_6]^{2+}$	2.2 x 10^{-4} [b]	----------	----------	3a
$[Ru_2(\mu\text{-}O)(\mu\text{-}CH_3COO)_2(bpy)_2(py)_2]^{2+}$	5.5 x 10^{-5} [b]	----------	----------	3a
$[Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(py)_3]^{+}$	5.0 x 10^{-5}	123 ± 6	+41 ± 19	4
$[Ru_3(\mu_3\text{-}O)(\mu\text{-}C_6H_5COO)_6(py)_3]^{+}$	4.9 x 10^{-6}	----------	----------	5
$[Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(py)_3]$	2.1 x 10^{-3}	122 ± 14	+69 ± 44	4
$[Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(CO)(py)_2]^{+}$	6.3 x 10^{-5}	126 ± 9	+52 ± 27	4

[a] py = pyridine, bpy =2,2'-bipyridine. [b] at 50 °C, pyridine trans to the oxide bridge.

Table II. First-order rate constants for solvent substitution reactions of $[M_3(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(H_2O)_3]^{+}$

M_3	metal center	incoming ligand	leaving ligand	k/s^{-1}(25.2°C)	$\Delta H^{\neq}$/kJ mol^{-1}	$\Delta S^{\neq}$/(J K^{-1}mol^{-1})	ref.
Ru_3	Ru	CD_3OD	H_2O	7.7 x 10^{-4}	103 ± 6	+41 ± 12	6
$RhRu_2$	Ru	CD_3OD	H_2O	9.9 x 10^{-5}	109 ± 4	+44 ± 9	6,14
$RhRu_2$	Rh	CD_3OD	H_2O	7.9 x 10^{-5}	103 ± 3	+22 ± 6	6
Rh_3	Rh	CD_3OD	H_2O	1.3 x 10^{-3}	102 ± 9	+42 ± 32	6
Ru_3	Ru	isonicotinamide	H_2O	5.5 x 10^{-3} M^{-1} [a]	117 ± 11	+85 ± 36	7

[a] at 40 °C

Redox Properties.

Two important properties of an oxide bridge associated with the redox behavior are (i) π-donor properties to construct dπ-pπ molecular orbitals to stabilize mixed valence oxidation states (12), and (ii) function as a Lewis base which becomes more significant as the metal oxidation states decrease.

Reversible multi-electron multi-step redox system.

One of the most important aspects of the transition-metal cluster complexes is their multi-electron redox behavior. Yet, the cluster complexes showing reversible multi-electron redox behavior are rare because the complexes are usually not stable over wide range of oxidation states. The $Ru_3(\mu_3\text{-}O)(\mu\text{-}RCOO)_6$ complexes provide an unique opportunity to construct multi-electron multi-step redox systems, as Ru(II), (III) and (IV) states are all kinetically inert. Furthermore, the central oxide ion participates in constructing π-molecular orbital system based on dπ-pπ interaction (13-15). With the π-molecular orbital system, the three metal ions interact strongly and each oxidation state from (2II,III) to (III,2IV) is stabilized to observe four reversible successive one-electron steps in its cyclic voltammograms. Thus the complex, $[Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(py)_3]^+$ displays reversible four one-electron redox behavior (13). More extensive redox behavior based on the triruthenium unit may be constructed either by connecting the units by using bridging ligands such as pyrazine (pz) and 4,4'-bipyridine (16,17) or introducing a redox active ligand such as N-methyl-4,4'-bipyridinium cation into the trinuclear unit (18). An example of the former approach is the 'trimer' of the triruthenium unit, $\{[Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(py)_2]_2[Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(CO)(\mu\text{-}pz)_2\}^{2+}$ which is a 10-step 13-electron reversible redox system (16) We have adopted the latter approach, and found that the complex $[Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(mbpy^+)_3]^{4+}$ ($mbpy^+$ = *N*-methyl-4,4'-bipyridinium ion) behaves as a 8-step 10-electron reversible redox system (Fig. 2) (18). Analogous complexes with different metal ion assemblies $[RhRu_2(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(mbpy^+)_3]^{4+}$ and $[Rh_3(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(mbpy^+)_3]^{4+}$ are 6-step 6-electron and 2-step 5-electron reversible redox systems, respectively (18). Of particular interest is the splitting pattern of the ligand-based redox waves, $mbpy^+$/mbpy. While it splits into two (1:2 current ratio) for the Ru_3, no splitting was observed for the Rh_3 complex. It has been suggested that the ligand-ligand interaction through the π-system is not effective for the Rh_3 complex where the π-orbitals are fully occupied. In the case of the Ru_3 complex, the anti-bonding π-orbital is empty.

Although the metal-oxidation states are delocalized over the dπ-pπ system of the Ru_3O moiety for the py and $mbpy^+$ complexes, there are structural and spectroscopic evidences that the monocarbonyl triruthenium(II,2III) complex $[Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(CO)(py)_2]$ has localized electronic state, in which

Table III. Redox potentials of some oxo-bridged di and trinuclear complexes.

complexes [a]	V vs Ag/Ag^+				ref.
	(2II,III)/(II,2III)	(II,2III)/(III)	(III)/(2III,IV))	(2III,IV)/(III,2IV)	
$[Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(py)_3]^+$	-1.59	-0.32	+0.74	+1.67	14
$[Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(CO)(py)_2]$	-1.23	+0.27	+0.91		19
$[RhRu_2(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(py)_3]^+$		-0.77	+0.79	+1.68	14
$[Rh_3(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(py)_3]^+$			+0.99		14
	(II)/(II,III)	(II,III)/(III)	(III)/(III,IV)	(III,IV)/(IV)	
$[Ru_2(\mu\text{-}O)(\mu\text{-}CH_3COO)_2(py)_6]^{2+}$	(-1.64)	-0.81	+0.60	+1.71	3a
$[Ru_2(\mu\text{-}O)(\mu\text{-}CH_3COO)_2(bpy)_2(py)_2]^{2+}$	(-1.47)	-0.77	+0.57	+1.52	3a
$[Ru_2(\mu\text{-}O)(\mu\text{-}CH_3COO)_2(bpy)_2(Him)_2]^{2+}$	(-0.94)	(-0.76)	+0.39		29
$[Ru_2(\mu\text{-}O)(\mu\text{-}CH_3COO)_2(bpy)_2(Meim)_2]^{2+}$	(-1.54)	-0.93	+0.40		29

[a] Him = imidazole, Meim = 1-methylimidazole.

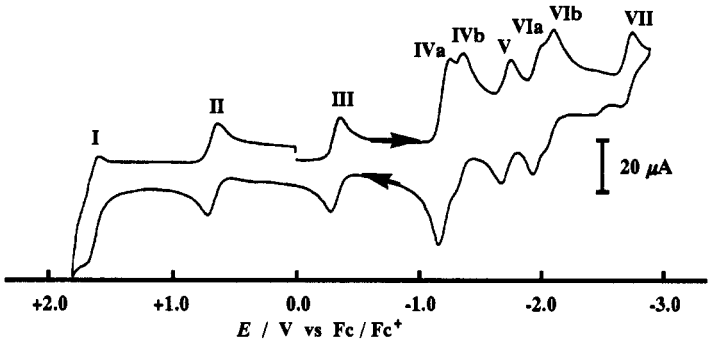

Figure 2. Cyclic voltammogram of $[Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(mbpy^+)_3]^{4+}$ in acetonitrile (waves I, II, III, V and VII are cluster-core based and those IV and VI are ligand-based).

divalent state is localized on carbonyl-coordinated Ru due to strong π-back-bonding of the CO ligand. In-situ FT-IR spectoelectrochemical study at different oxidation states revealed that one-electron oxidation takes place at the Ru-CO on the basis of the shift of the ν(CO) values (19).

Proton-coupled one-step multi-electron redox reactions.

Bridging oxide acts as a protonation site, and can promote proton-coupled multi-electron redox reaction. Figure 3 shows the cyclic voltammograms of $[Ru_2(\mu\text{-}O)(\mu\text{-}CH_3COO)_2(bpy)_2(Meim)_2]^{2+}$ (bpy = 2,2'-bipyridine) in acetonitrile in the presence of proton donors (20). It should be noted that the reduction waves corresponding to the (III,III)/(III,II) and (III,II)/(II,II) processes shift remarkably to the positive direction in the presence of a strong proton donor, *p*-toluenesulfonic acid. The shift is caused by the protonation at the oxide bridge of the (III,II) and (II,II) states. In the presence of a weak proton donor such as imidazole (pK_a = 14.4), the two reduction waves are collapsed to give an apparent one-step two-electron transfer wave. This is explained by considering that imidazole can transfer its proton to the oxide bridge of the (II,II) state but not to that of the (III,II) state. This is significant in view of the reaction mechanism of some enzymes containing similar structural units. Dinuclear complexes with linear oxide bridge, such as $[Cl_3(py)_2Os(\mu\text{-}O)OsCl_2(CH_3COO)(py)_2]$ (21) and $[Re_2(\mu\text{-}O)(bpy)_4Cl_2]^{2+}$ (22) and a di-μ-oxo complex such as $[Re_2(\mu\text{-}O)_2(Metpa)_2]^{4+}$ (Metpa = bis(6-methyl-2-pyridylmethyl)(2-pyridylmethyl)amine) (23) do not show similar behavior on addition of proton donors in acetonitrile solution. It seems that the μ-oxo-di-μ-carboxylato moiety is favorable for the proton-assisted reversible redox reactions, since in the other cases the single oxide-bridge must bent on protonation and the di-μ-oxo complex must rearrange its strong metal-metal interaction.

The diruthenium $mbpy^+$ complex, $[Ru_2(\mu\text{-}O)(\mu\text{-}CH_3COO)_2(bpy)_2(mbpy^+)_3]^{4+}$, has been studied as a multi-electron-transfer system (vide supra). The complex behaves as a 7-electron redox system in acetonitrile although the reversibility is poor (24). Reversibility is improved on addition of *p*-toluenesulfonic acid, however, with significant shift of the metal-centered reduction waves to positive potentials. The ligand-based redox waves remain practically unshifted. Thus, while the $mbpy^+$/mbpy process occurs at the Ru_2(III,II) state with splitting in the absence of any proton source, it does at the Ru_2(II,II) state without splitting in the presence of the acid.

Kinetics of the oxidation with $[Fe(phen)_3]^{3+}$.

In order to compare the chemical redox reactions with electrochemical one, we have carried out the kinetic study of the oxidation of $[Ru_2(\mu\text{-}O)(\mu\text{-}CH_3COO)_2(py)_6]^{2+}$ and $[Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(py)_3]^+$ by $[Fe(phen)_3]^{3+}$ in acetonitirle (25). Second-order rate constants at 25 °C are 2.33×10^5 and 2.05×10^6 $M^{-1}s^{-1}$, respectively, at I = 0.001 M. It should be noted that the relevant redox potentials (+0.60 and

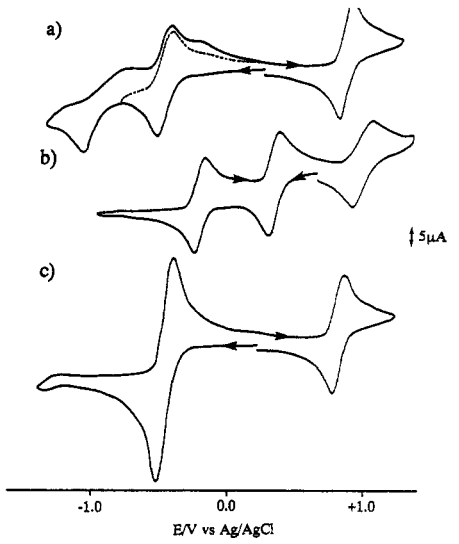

Figure 3. Cyclic voltammograms of $[Ru_2(\mu\text{-}O)(\mu\text{-}CH_3COO)_2(bpy)_4(Meim)_2]^{2+}$ in acetonitrile: (a) no acid, (b) 1 eq of p-toluenesulfonic acid added, (c) 1 eq of imidazole added.

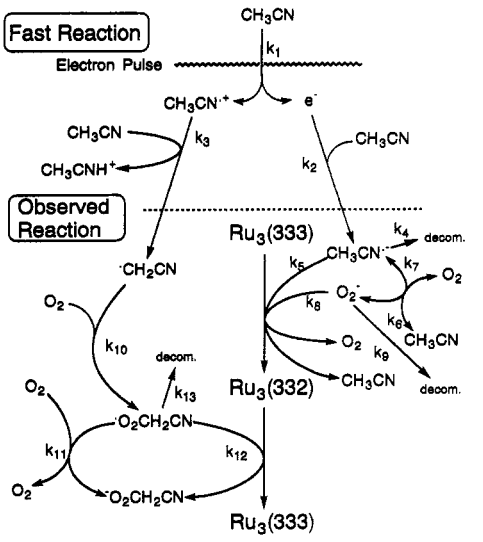

Figure 4. Pulse-radiolysis reaction scheme of $[Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(py)_3]^+$ in CH_3CN (reproduced with permission from Ref. 26. Copyright ©1993 American Chemical Society).

+0.74 V vs Ag/Ag^+ for the dimer and the trimer, respectively) indicate that the oxidation of the trimer is thermodynamically less favorable. This is in opposite direction to the observed rate constants. It may be that the bigger size and smaller charge of the trimer would make solvent rearrangement easier to result in the faster rate.

Pulse-radiolysis.

Pulse-radiolysis experiment enables us to study the immediate reduction product on electron-irradiation and its successive reactions. Figure 4 summarizes the reaction pathway for the triruthenium complex, $[Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(py)_3]^+$, in acetonitrile (26). In the absence of dissolved dioxygen, reaction with $CH_3CN^{\bullet-}$ gave one-electron reduced species Ru3(II,2III) (k_5 = 6.1 x 10^{10} $M^{-1}s^{-1}$). UV-visible absorption spectrum of the reduced species as determined by differential optical density at wavelengths from 340 to 700 nm is identical to that of the isolated Ru3(II,2III) complex in acetonitrile. In the presence of dissolved O_2, initial products of electron pulse irradiation, $CH_3CN^{\bullet-}$ and $^{\bullet}CH_2CN$, react rapidly with O_2 to give O_2^- and $^{\bullet}O_2CH_2CN$, respectively. The triruthenium complex Ru3(III) then reacts with O_2^- to give Ru3(II,2III) (k_8 = 3.5 x 10^9 $M^{-1}s^{-1}$) which is reoxidized by $^{\bullet}O_2CH_2CN$ to the original Ru3(III) complex (k_{12} = 2.7 x 10^9 $M^{-1}s^{-1}$). The reactions of the diruthenium(III) complex, $[Ru_2(\mu\text{-}O)(\mu\text{-}CH_3COO)_2(py)_6]^{2+}$, in acetonitrile are also explained by a similar scheme to that for the triruthenium complex (Figure 4) with corresponding rate constants, k_5' = 8.0 x 10^{10} $M^{-1}s^{-1}$, k_8' = 1.1 x 10^{10} $M^{-1}s^{-1}$, and k_{12}' = 7.5 x 10^9 $M^{-1}s^{-1}$ (27). These rate constants are somewhat larger than the corresponding ones for the triruthenium complex. This is in the reverse direction of the one-electron reduction potential which is more negative for the dimer (-0.81 and -0.32 V vs Ag/Ag^+). It should be noted that the spectrum of the Ru_2(II,III) species determined by the pulse-radiolysis experiment is different from that obtained by the spectroelectrochemical method. There must be some rearrangement reaction after the electrochemical reduction.

Photoquenching Reactions.

Luminescence quenching of $[Ru(bpy)_3]^{2+}$ was studied using the di- and trinuclear complexes as quenchers with the hope to observe electron-transfer quenching reactions (28). The results are, however, interpreted

by an energy-transfer mechanism. The luminescence life-time in the presence of the quencher ((2.5 - 15) x 10^{-4} M) gave a linear Stern-Volmer plot from which the second-order quenching rate constants (k_q) were evaluated. The k_q (x 10^9 $M^{-1}s^{-1}$) values at 22 °C in acetonitrile for the quenchers, $[Ru_2(\mu\text{-}O)(\mu\text{-}CH_3COO)_2(py)_6]^{2+}$, $[Ru_2(\mu\text{-}O)(\mu\text{-}CH_3COO)_2(py)_4(imidazole)_2)]^{2+}$, $[Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(py)_3]^{+}$, $[RhRu_2(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(py)_3]^{+}$, and $[Rh_3(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(py)_3]^{+}$ were 2.34, 1.44, 3.95, 1.82, and <0.01, respectively. There is no clear correlation between k_q and redox potentials. Rather, the complex having stronger absorption in the region of the luminescence peak of $[Ru(bpy)_3]^{2+}$, tends to show larger k_q values. It is thus concluded that the quenching mechanism is of a Forster type energy transfer.

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REFERENCES

1. For example, (a) L. Que, Jr. and A. E. True, *Prog. Inorg. Chem.* **38**, 97 (1990), (b) R. G. Wilkins, *Chem. Soc. Rev.* 171 (1992), (c) V. L. Pecoraro, *Manganese Redox Enzymes,* Verlag-Chemie, New York (1992), (d) K. W. Kramarz and J. R. Norton, *Prog. Inorg. Chem.* **42**, 1 (1994).
2. K. Saito and Y. Sasaki, *Adv. Inorg. Bioinorg. Mechanisms* **1**, 176 (1982).
3. (a) Y. Sasaki, M. Suzuki, A. Nagasawa, A. Tokiwa, M. Ebihara, T. Yamaguchi, C. Kabuto, T. Ochi, and T. Ito, *Inorg. Chem.* **30**, 4903 (1991), (b) Y. Sasaki, M. Suzuki, A. Tokiwa, M. Ebihara, T. Yamaguchi, C. Kabuto, and T. Ito, *J. Am. Chem. Soc.* **110**, 6251 (1988).
4. M. Abe, Y. Sasaki, A. Nagasawa, and T. Ito, *Bull. Chem. Soc. Jpn.* **65**, 1411 (1992).
5. M. Abe, Y. Sasaki, T. Yamaguchi, and T. Ito, *Bull. Chem. Soc. Jpn.* **65**, 1585 (1992).
6. Y. Sasaki, A. Nagasawa, A. Tokiwa-Yamamoto, and T. Ito, *Inorg. Chim. Acta* **212**, 175 (1993).
7. G. Powell, D. T. Richens, and A. K. Powell, *Inorg. Chim. Acta* **213**, 147 (1993).
8. T. Yamaguchi, Y. Sasaki, A. Nagasawa, T. Ito, N. Koga, and K. Morokuma, *Inorg. Chem.* **28**, 4311 (1989).
9. K. Teramoto, Y. Sasaki, K. Migita, M. Iwaizumi, and K. Saito, *Bull. Chem. Soc. Jpn.* **52**, 446 (1979).
10. M. Ichimura, Y. Sasaki, and T. Ito, unpublished.
11. K. Umakoshi and Y. Sasaki, *Adv. Inorg. Chem.* **40**, 187 (1993).
12. Y. Sasaki, *J. Mol. Liquid* in press.
13. B. J. Baumann, D. J. Salmon, S. T. Wilson, T. J. Meyer, and W. E. Hatfield, *Inorg. Chem.* **17**, 3342 (1978).
14. Y. Sasaki, A. Tokiwa, and T. Ito, *J. Am. Chem. Soc.* **109**, 6341 (1987).
15. K. Takahashi, K. Umakoshi, A. Kikuchi, Y. Sasaki, M. Tominaga, and I. Taniguchi, *Z. Natsuforsch.* **50b**, 551 (1995).
16. (a) B. J. Baumann, D. J. Salmon, S. T. Wilson, P. L. Hood, and T. J. Meyer, *J. Am. Chem. Soc.* **101**, 2916 (1979), (b) B. J. Baumann, S. T. Wilson, D. J. Salmon, and T. J. Meyer, *Inorg. Chem.* **18**, 2472 (1979).
17. Y. Sasaki, M. Hashimoto, M. Hishikawa, M. Abe, and T. Ito, unpublished.
18. M. Abe, Y. Sasaki, Y. Yamada, K. Tsukahara, S. Yano, and T. Ito, *Inorg. Chem.* in press.
19. S. Ye, H. Akutagawa, K. Uosaki, and Y. Sasaki, *Inorg. Chem.* in press.
20. A. Kikuchi, T. Fukumoto, K. Umakoshi, Y. Sasaki, and A. Ichimura, *J. Chem. Soc., Chem. Commun.*, in press.
21. Y. Imbe, K. Umakoshi, C. Matsunami, and Y. Sasaki, *Inorg. Chem.* **34**, 813 (1995).
22. T. Takahira, K. Umakoshi, and Y. Sasaki, *Chem. Lett.* 2315 (1994).
23. H. Sugimoto, K. Umakoshi, M. Suzuki, and Y. Sasaki, unpublished.
24. T. Fukumoto, K. Umakoshi, Y. Yamada, K. Tsukahara, S. Yano, and Y. Sasaki, unpublished.
25. J. F. Ojo, Y. Hasegawa, Y. Sasaki, and M. Abe, unpublished.
26. T. Imamura, T. Sumiyoshi, K. Takahashi, and Y. Sasaki, *J. Phys. Chem.* **97**, 7786 (1993).
27. T. Imamura, A. Kishimoto, T. Sumiyoshi, K. Takahashi, T. Fukumoto, and Y. Sasaki, *Bull. Chem. Soc. Jpn.* in press.
28. K. Matsuoka, N. Ohta, and Y. Sasaki, unpublished.
29. T. Fukumoto, A. Kikuchi, K. Umakoshi, and Y. Sasaki, unpublished.