1398 Bull. Chem. Soc. Jpn. Vol. 79, No. 9, 1398–1403 (2006)

Mixed $\mathrm{Re^{VII}}$–$\mathrm{Fe^{III}}$ and $\mathrm{Re^{VII}}$–$\mathrm{Cu^{II}}$ Complexes Prepared by the Use of the Complex Ligand $[\mathrm{Re(O)_3}(\mathrm{tpenH}\text{-}\kappa^3N,N'',N''')]^{2+}$ (tpen = N,N,N',N'-Tetrakis(2-pyridylmethyl)ethylenediamine)

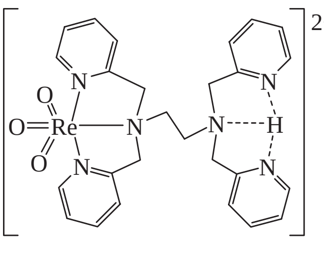
Toshihiro Tabeya, Masaaki Abe,[*,†] **and Yoichi Sasaki**[*,††]

Division of Chemistry, Graduate School of Science, Hokkaido University, Sapporo 060-0810

Received March 6, 2006; E-mail: ysasaki@sci.hokudai.ac.jp

Reactions of a $\mathrm{Re^{VII}}$ complex $[\mathrm{Re^{VII}(O)_3}(\mathrm{tpenH}\text{-}\kappa^3N,N'',N''')](\mathrm{ClO_4})_2$ ($[\mathbf{1}](\mathrm{ClO_4})_2$) (tpen = N,N,N',N'-tetrakis(2-pyridylmethyl)ethylenediamine) that has a free bis(2-pyridylmethyl)amino group with $\mathrm{Fe^{III}}$ and $\mathrm{Cu^{II}}$ (or $\mathrm{Cu^{I}}$) complexes in solution afforded three new mixed-metal complexes. From X-ray structural analyses, the counter anions ($\mathrm{EO_4}^-$) of the isolated complexes are a mixture of $\mathrm{ReO_4}^-$ and the original $\mathrm{ClO_4}^-$. The former was most likely produced by the decomposition of $[\mathbf{1}]^{2+}$ during reaction. The tetranuclear $\mathrm{Re^{VII}}$–$\mathrm{Fe^{III}}$ complex $[\{\mathrm{Re^{VII}(O)_3}(\mu\text{-tpen-}\kappa^3N,N'',N''':\kappa^3N',N'''',N''''')\}_2\mathrm{Fe^{III}}_2(\mu\text{-O})(\mu\text{-CH_3COO})_2]^{4+}$ ($[\mathbf{2}]^{4+}$) has an oxodi(acetato)-bridged diiron(III) unit with two $[\mathrm{Re^{VII}(O)_3}(\mathrm{tpen}\text{-}\kappa^3N,N'',N''')]^+$ groups coordinated to each iron(III) ion. Structures of the dinuclear $\mathrm{Re^{VII}}$–$\mathrm{Cu^{II}}$ complexes depend on the reactants. The reactions with $\mathrm{Cu^{II}(ClO_4)_2}$ in $\mathrm{CH_3OH/CH_3CN}$ and $\mathrm{Cu^{I}I(PPh_3)_2CH_3CN}$ in $\mathrm{CH_2Cl_2/CH_3CN}$ afforded $[\mathrm{Re^{VII}(O)_3}(\mu\text{-tpen-}\kappa^3N,N'',N''':\kappa^3N',N'''',N''''')\mathrm{Cu^{II}(CH_3CN)}]^{3+}$ ($[\mathbf{3}]^{3+}$) and $[\mathrm{Re^{VII}(O)_3}(\mu\text{-tpen-}\kappa^3N,N'',N''':\kappa^3N',N'''',N''''')\mathrm{Cu^{II}Cl}]^{2+}$ ($[\mathbf{4}]^{2+}$), respectively. The Cu centers have an axially elongated octahedral structure with a bis(2-pyridylmethyl)amino moiety and $\mathrm{CH_3CN}$ for $[\mathbf{3}]^{3+}$ or $\mathrm{Cl^-}$ of solvent origin for $[\mathbf{4}]^{2+}$ coordinated in the tetragonal plane. The axial sites are occupied by two weakly coordinated $\mathrm{EO_4}^-$ ligands in $[\mathbf{3}]^{3+}$ or $\mathrm{EO_4}^-$ and bridging $\mathrm{Cl^-}$ from a neighboring complex cation in $[\mathbf{4}]^{2+}$.

A hypodentate ligand is defined as a ligand that leaves part of its coordination sites uncoordinated.[1] Complexes that have a hypodentate ligand are important as building blocks for the construction of multifunctional metal complexes. We have recently prepared a number of compounds that have partially uncoordinated donor sites by using a potential tetradentate tris(2-pyridylmethyl)amine (tpa)[2–4] and a potential hexadentate ligand N,N,N',N'-tetrakis(2-pyridylmethyl)ethylenediamine (tpen).[5,6] Among them, the structurally most interesting complex is a $\mathrm{Re^{VII}}$ compound, $[\mathrm{Re(O)_3}(\mathrm{tpenH}\text{-}\kappa^3N,N'',N''')]^{2+}$ ($[\mathbf{1}]^{2+}$), that has a free bis(2-pyridylmethyl)amino moiety (Scheme 1).[6] The complex cation $[\mathbf{1}]^{2+}$ is regarded as a tridentate ligand, i.e., a derivative of bis(2-pyridylmethyl)amine (bpa) with a giant substituent at the central amino nitrogen. Using ligand $[\mathbf{1}]^{2+}$, we have already prepared a unique $\mathrm{Re^{VII}}$–$\mathrm{Re^{I}}$ dimer, $[\mathrm{Re(O)_3}(\mu\text{-tpen-}\kappa^3N,N'',N''':\kappa^3N',N'''',N''''')\mathrm{Re(CO)_3}]^{2+}$, which is a mixed-valence complex with the metal ions in extremely different oxidation states.[7] Since a variety of complexes with bpa and analogous tridentate ligands are known[8] for the first transition-metal ions, we have extended the coordination chemistry of $[\mathbf{1}]^{2+}$ to these transition-metal ions to find out if the complex cation $[\mathbf{1}]^{2+}$ behaves as a tridentate ligand just like bpa. However, slow decomposition of $[\mathbf{1}]^{2+}$ during the reaction prevented a thorough preparative study. Nevertheless, one dimeric $\mathrm{Fe^{III}}$ and two mononuclear $\mathrm{Cu^{II}}$ complexes with the $[\mathrm{Re(O)_3}(\mathrm{tpen}\text{-}\kappa^3N,N'',N''')]^+$ moiety were isolated. Even in these cases, the counter anions have been partially replaced by $\mathrm{ReO_4}^-$ which was produced by the decomposition of $[\mathbf{1}]^{2+}$. This paper reports the preparation, structures, and some properties of the three new complexes.



Scheme 1.

Experimental

Materials. The $\mathrm{Re^{VII}}$ tpen complex $[\mathrm{Re(O)_3}(\mathrm{tpenH}\text{-}\kappa^3N,N'',N''')](\mathrm{ClO_4})_2$ ($[\mathbf{1}](\mathrm{ClO_4})_2$) was prepared as reported previously.[6] The copper(I) complex $[\mathrm{CuI(CH_3CN)(PPh_3)_2}]$[9] and the iron(III) dimer $[\mathrm{Fe_2}(\mu\text{-O})(\mu\text{-CH_3COO})_2(\mathrm{mebpa})_2](\mathrm{ClO_4})_2$ (mebpa = N-methylbis(2-pyridylmethyl)amine) were prepared according to the published procedures.[10] The latter was used for obtaining reference data. All of the other reagents were obtained from commercial sources and used without further purification.

Caution: All the complexes reported in this paper were isolated as perchlorate salts. Percholorate salts are potentially explosive, and the complexes must be handled in small portions with extreme care.

[†] Present address: Department of Applied Chemistry, Graduate School of Engineering, Kyushu University, Nishi-ku, Fukuoka 819-0395

[††] Present address: Catalysis Research Center, Hokkaido University, Sapporo 001-0021

Published on the web September 5, 2006; doi:10.1246/bcsj.79.1398

Preparation of the Complexes. $[\{\mathrm{Re^{VII}(O)_3}(\mu\text{-tpen-}\kappa^3N,N'',N''':\kappa^3N',N'''',N''''')\}_2\mathrm{Fe^{III}_2}(\mu\text{-O})(\mu\text{-}\mathrm{CH_3COO})_2](\mathrm{ClO_4})_4\cdot4\mathrm{H_2O}$ ([2]$(\mathrm{ClO_4})_4\cdot4\mathrm{H_2O}$): To a methanol/acetonitrile (1:1 v/v) solution (10 $\mathrm{cm^3}$) of $[\mathrm{Re^{VII}(O)_3}(\text{tpenH-}\kappa^3N,N'',N''')](\mathrm{ClO_4})_2$ (100.9 mg, 1.18×10^{-4} mol) were added an aqueous solution (5 $\mathrm{cm^3}$) of $\mathrm{Fe(ClO_4)_3}\cdot n\mathrm{H_2O}$ (61.2 mg, 1.21×10^{-4} mol) and that (5 $\mathrm{cm^3}$) of sodium acetate trihydrate (49.0 mg, 3.56×10^{-4} mol). The mixture was stirred for 30 min, during which time a greenish brown solid precipitated. The solid was filtered, washed with diethyl ether, and dried in air. Yield, 46.1 mg (39.8% based on the Re complex). Anal. Calcd for $\mathrm{C_{56}H_{70}N_{12}O_{13}Cl_4Fe_2Re_2}$ ($[\{\mathrm{Re(O)_3}(\mu\text{-tpen-}\kappa^3N,N'',N''':\kappa^3N',N'''',N''''')\}]_2\mathrm{Fe_2}(\mu\text{-O})(\mu\text{-}\mathrm{CH_3COO})_2)(\mathrm{ClO_4})_4\cdot4\mathrm{H_2O}$): C, 33.08; H, 3.47; N, 8.27; Cl, 6.97%. Found: C, 32.94; H, 3.41; N, 8.27; Cl, 6.84%. FAB-MS (m/z): 1860 ($[\{\mathrm{ReO_3(tpen)}\}_2\mathrm{Fe_2(O)(CH_3COO)_2}](\mathrm{ClO_4})^{3+}$). IR (KBr disk)/$\mathrm{cm^{-1}}$: 727 ($\nu_{\mathrm{as}}$, FeOFe), 927 (Re=O), 1094 ($\mathrm{ClO_4}^-$), 1443 (ν_{sym}, COO), 1546 (ν_{as}, COO). ^{1}H NMR ($\mathrm{CD_3CN}$)/ppm: δ 15.4 (br, 6H, acetate $\mathrm{CH_3}$), 8.8, 8.2, and 7.5 (s, 16H, pyridyl protons at the Re site), 6.9 and 5.1 (br, 12H, pyridyl protons at the Fe sites). A dark green single crystal of [2]$(\mathrm{ClO_4})_{3.85}(\mathrm{ReO_4})_{0.15}\cdot1.5\mathrm{CH_3OH}$ used for X-ray structural analysis was obtained from the acetonitrile solution on by diffusion of methanol.

$[\mathrm{Re^{VII}(O)_3}(\mu\text{-tpen-}\kappa^3N,N'',N''':\kappa^3N',N'''',N''''')\mathrm{Cu^{II}(CH_3CN)}](\mathrm{ClO_4})_3\cdot2\mathrm{H_2O}$ ([3]$(\mathrm{ClO_4})_3\cdot2\mathrm{H_2O}$): An acetonitrile solution (10 $\mathrm{cm^3}$) of $[\mathrm{Re^{VII}O_3}(\text{tpenH-}\kappa^3N,N'',N''')](\mathrm{ClO_4})_2$ (63.4 mg, 7.49×10^{-5} mol) was added to a methanol solution (7 $\mathrm{cm^3}$) of $\mathrm{Cu^{II}(ClO_4)_2}\cdot6\mathrm{H_2O}$ (28.7 mg, 7.59×10^{-5} mol). The color of the solution rapidly changed from pale blue to deep blue. After stirring for 30 min at room temperature, the volume of the solution was reduced by using rotary evaporator to ca. 3 $\mathrm{cm^3}$. On addition of diethyl ether to the solution, a blue solid precipitated and was collected by filtration. The blue powder was then dissolved in methanol/acetonitrile (6:1, v/v). On slow evaporation of the solvent in air at room temperature, a white solid appeared that was removed by filtration. Further evaporation of the filtrate left blue solid that was filtered, washed with acetonitrile/diethyl ether (1:1, v/v) and dried in air. Yield, 21 mg (26% based on the Re complex). Anal. Calcd for $\mathrm{C_{28}H_{35}Cl_3N_7O_{17}CuRe}$ ($[\mathrm{Re(O)_3}(\mu\text{-tpen-}\kappa^3N,N'',N''':\kappa^3N',N'''',N''''')\mathrm{Cu(CH_3CN)}](\mathrm{ClO_4})_3\cdot2\mathrm{H_2O}$): C, 30.64; H, 3.21; N, 8.93; Cl, 9.69%. Found: C, 30.78; H, 3.19; N, 9.19; Cl, 9.2%. FAB-MS (m/z): 919 ($[\mathrm{Re(O)_3(tpen)Cu}](\mathrm{ClO_4})^{2+}$). IR (KBr disk)/$\mathrm{cm^{-1}}$: 927 (Re=O), 1094 ($\mathrm{ClO_4}^-$), 2293 ($N\mathrm{CCH_3}$). A blue single crystal used for X-ray structural analysis was obtained as a mixed perchlorate–perrhenate salt [3]$(\mathrm{ClO_4})_{1.39}(\mathrm{ReO_4})_{1.61}\cdot\mathrm{CH_3OH}\cdot1.25\mathrm{CH_3CN}$, by slow evaporation of the methanol/acetonitrile (4:1, v/v) solution of [3]$(\mathrm{ClO_4})_3\cdot2\mathrm{H_2O}$ at room temperature.

$[\mathrm{Re^{VII}(O)_3}(\mu\text{-tpen-}\kappa^3N,N'',N''':\kappa^3N',N'''',N''''')\mathrm{Cu^{II}Cl}](\mathrm{ReO_4})_{0.55}(\mathrm{ClO_4})_{1.45}\cdot0.5\mathrm{CH_3CN}$ ([4]$(\mathrm{ReO_4})_{0.55}(\mathrm{ClO_4})_{1.45}\cdot0.5\mathrm{CH_3CN}$): A dichloromethane solution (5 $\mathrm{cm^3}$) of $[\mathrm{Cu^I(CH_3CN)(PPh_3)_2}]$ (35.8 mg, 4.74×10^{-5} mol) was added to an acetonitrile solution (10 $\mathrm{cm^3}$) of $[\mathrm{Re^{VII}(O)_3(tpenH)}](\mathrm{ClO_4})_2$ (39.4 mg, 4.59×10^{-5} mol). The solution was stirred for 20 min at room temperature, during which time the color of the solution changed from yellow to deep orange. After stirring, the solution was evaporated at reduced pressure to ca. 7 $\mathrm{cm^3}$ and $\mathrm{NaClO_4}\cdot\mathrm{H_2O}$ (15 mg, 1.07×10^{-4} mol) was added. Green crystals deposited on diffusion of diethyl ether into the solution in a refrigerator for 1 day afforded green crystals which were collected by filtration and dried in air. Yield, 11.9 mg (24.4% based on the Re complex). Anal. Calcd for $\mathrm{C_{27}H_{29.5}Cl_{2.45}N_{6.5}O_{11}CuRe_{1.55}}$ ($[\mathrm{Re(O)_3}(\mu\text{-tpen-}\kappa^3N,N'',N''':\kappa^3N',N'''',N''''')\mathrm{CuCl}](\mathrm{ReO_4})_{0.55}(\mathrm{ClO_4})_{1.45}\cdot0.5\mathrm{CH_3CN}$): C, 30.59; H, 2.80; N, 8.59; Cl, 8.19%. Found: C, 30.64; H, 2.87; N, 8.87; Cl, 7.97%. FAB-MS (m/z): 757 ($[\mathrm{Re(O)_3(tpen)CuCl}]^+$), 1964 ($[\mathrm{Re(O)_3(tpen)CuCl}]_2(\mathrm{ClO_4})_2(\mathrm{ReO_4})^{2+}$). IR (KBr disk)/$\mathrm{cm^{-1}}$: 924 (Re=O), 1099 ($\mathrm{ClO_4}^-$).

Measurements. ^{1}H NMR spectra were recorded on a JEOL JMS-H110 spectrometer at 270 MHz, and were referenced to TMS (tetramethylsilane) at $\delta = 0$. Fourier transformed infrared (FT-IR) spectra were recorded on an FT/IR-600Plus spectrophotometer by using KBr pellets of the samples. UV–vis absorption spectra were obtained by using a Hitachi U-3000 spectrophotometer. Cyclic voltammetry was performed with a Hokuto HZ-3000 potentiostat at room temperature. The working and counter electrodes were a platinum disk and a platinum wire, respectively. The reference electrode was Ag/AgCl. The half-wave potential of $\mathrm{Fc/Fc^+}$ ($E_{1/2}(\mathrm{Fc^{0/+}})$) was 0.435 V. The sample solution (0.5×10^{-3} mol dm^{-3}) in 0.1 mol dm^{-3} $\mathrm{TBAPF_6}$ (tetra(n-butyl)ammonium hexafluorophosphate) acetonitrile was deoxygenated with a stream of argon.

X-ray Structural Determinations. Suitable crystals of [2]$(\mathrm{ClO_4})_{3.85}(\mathrm{ReO_4})_{0.15}\cdot1.5\mathrm{CH_3OH}$, [3]$(\mathrm{ClO_4})_{1.39}(\mathrm{ReO_4})_{1.61}\cdot\mathrm{CH_3OH}\cdot1.25\mathrm{CH_3CN}$, and [4]$(\mathrm{ClO_4})_{1.45}(\mathrm{ReO_4})_{0.55}\cdot0.5\mathrm{CH_3CN}$ were obtained as described in the experimental section. The selected crystals were mounted onto a thin glass fiber. X-ray diffraction data for [2]$(\mathrm{ClO_4})_{3.85}(\mathrm{ReO_4})_{0.15}\cdot1.5\mathrm{CH_3OH}$ and [3]$(\mathrm{ClO_4})_{1.39}(\mathrm{ReO_4})_{1.61}\cdot\mathrm{CH_3OH}\cdot1.25\mathrm{CH_3CN}$ were collected on a Rigaku AFC-8S diffractometer with a Mercury CCD area detector, and those of [4]$(\mathrm{ClO_4})_{1.45}(\mathrm{ReO_4})_{0.55}\cdot0.5\mathrm{CH_3CN}$ were collected on a Rigaku AFC-7R diffractometer, using graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Final cell parameters were obtained from a least-squares analysis of reflections with $I > 10\sigma(I)$. Space group determinations were made on the basis of systematic absences, a statistical analysis of intensity distribution, and the successful solution and refinement of the structures. Data were collected and processed using Crystal Clear.[11] An empirical absorption correction resulted in acceptable transmission factors. The data were corrected for Lorentz and polarization factors.

All calculations were carried out on a Silicon Graphics O2 computer system using teXsan.[12] The structures were solved by direct methods and expanded using Fourier and difference Fourier techniques. Details of crystal parameters and structure refinements are given in Table 1. Selected bond lengths and angles are shown in Tables 2 ([2]$(\mathrm{ClO_4})_{3.85}(\mathrm{ReO_4})_{0.15}\cdot1.5\mathrm{CH_3OH}$) and 3 ([3]$(\mathrm{ClO_4})_{1.39}(\mathrm{ReO_4})_{1.61}\cdot\mathrm{CH_3OH}\cdot1.25\mathrm{CH_3CN}$ and [4]$(\mathrm{ClO_4})_{1.45}(\mathrm{ReO_4})_{0.55}\cdot0.5\mathrm{CH_3CN}$).

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre: Deposition numbers 600213, 600211, and 600212 for [2]$(\mathrm{ClO_4})_{3.85}(\mathrm{ReO_4})_{0.15}\cdot1.5\mathrm{CH_3OH}$, [3]$(\mathrm{ClO_4})_{1.39}(\mathrm{ReO_4})_{1.61}\cdot\mathrm{CH_3OH}\cdot1.25\mathrm{CH_3CN}$, and [4]$(\mathrm{ClO_4})_{1.45}(\mathrm{ReO_4})_{0.55}\cdot0.5\mathrm{CH_3CN}$, respectively. Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

Results and Discussion

Preparation of the Complexes. The trioxorhenium(VII) complex of tpen, $[\mathrm{Re^{VII}(O)_3}(\text{tpenH-}\kappa^3N,N'',N''')]^{2+}$ ([1]$^{2+}$)[6] is remarkable in that the half of the tpen ligand is left uncoordinated. The free bis(2-pyridylmethyl)amino moiety should be able to act as a tridentate ligand to a different metal center. Initially, we prepared a dimer containing a $\mathrm{Re^I(CO)_3}$ center, $[\mathrm{Re^{VII}(O)_3}(\mu\text{-tpen-}\kappa^3N,N'',N''':\kappa^3N',N'''',N''''')\mathrm{Re^I(CO)_3}]^{2+}$,[7] in

Table 1. Crystallographic Data of [**2**]$(\mathrm{ClO_4})_{3.85}(\mathrm{ReO_4})_{0.15}\cdot1.5\mathrm{CH_3OH}$, [**3**]$(\mathrm{ClO_4})_{1.39}(\mathrm{ReO_4})_{1.61}\cdot\mathrm{CH_3OH}\cdot1.25\mathrm{CH_3CN}$, and [**4**]$(\mathrm{ClO_4})_{1.45}(\mathrm{ReO_4})_{0.55}\cdot0.5\mathrm{CH_3CN}$

	[**2**]$(\mathrm{ClO_4})_{3.85}(\mathrm{ReO_4})_{0.15}\cdot$ $1.5\mathrm{CH_3OH}$	[**3**]$(\mathrm{ClO_4})_{1.39}(\mathrm{ReO_4})_{1.61}\cdot$ $\mathrm{CH_3OH}\cdot1.25\mathrm{CH_3CN}$	[**4**]$(\mathrm{ClO_4})_{1.45}(\mathrm{ReO_4})_{0.55}\cdot$ $0.5\mathrm{CH_3CN}$
Formula	$\mathrm{C_{57.5}H_{68}Cl_{3.85}N_{12}O_{28.5}Fe_2Re_{2.15}}$	$\mathrm{C_{31.5}H_{38.75}Cl_{1.39}N_{8.25}O_{16}CuRe_{2.61}}$	$\mathrm{C_{27}H_{29.5}Cl_{2.45}N_{6.5}O_{11}CuRe_{1.55}}$
Formula weight	2031.77	1387.77	1060.09
Crystal size/mm	0.2 × 0.1 × 0.1	0.21 × 0.075 × 0.06	0.175 × 0.15 × 0.1
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	Cc	$P2_1/c$	$P\bar{1}$
a/Å	18.71(2)	9.033(5)	8.878(4)
b/Å	15.42(1)	26.22(5)	10.488(4)
c/Å	27.45(2)	18.16(1)	20.441(8)
$\alpha/^\circ$			77.60(1)
$\beta/^\circ$	99.29(3)	99.54(1)	83.20(1)
$\gamma/^\circ$			81.98(1)
V/Å^3	7819(1)	4242(1)	1833(1)
Z	4	4	2
$\rho_{\mathrm{calcd}}/\mathrm{g\,cm^{-3}}$	1.73	2.17	1.92
T/K	153	153	293
No. reflections measured	14234	19707	12141
No. of unique reflections	7945	8812	7944
$\mu/\mathrm{mm^{-1}}$	3.898	8.089	5.926
R_1, wR_2 a)	0.058, 0.183	0.051, 0.136	0.085, 0.243

a) $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = \{\Sigma[w(|F_o|^2 - |F_c|^2)^2]/\Sigma[w(|F_o|^2)^2]\}^{1/2}$, $w = \{\sigma^2(F_o^2) + [0.05(\max(F_o^2, 0) + 2F_c^2)/3]^2\}^{-1}$.

Table 2. Selected Bond Distances (Å) and Angles (°) for [**2**]$(\mathrm{ClO_4})_{3.85}(\mathrm{ReO_4})_{0.15}\cdot1.5\mathrm{CH_3OH}$

[**2**]$(\mathrm{ClO_4})_{3.85}(\mathrm{ReO_4})_{0.15}\cdot1.5\mathrm{CH_3OH}$			
Re1–O1	1.71(1)	Re2–O4	1.72(1)
Re1–O2	1.70(1)	Re2–O5	1.75(1)
Re1–O3	1.77(1)	Re2–O6	1.68(1)
Re1–N1	2.29(1)	Re2–N7	2.32(1)
Re1–N2	2.24(2)	Re2–N8	2.26(2)
Re1–N3	2.20(2)	Re2–N9	2.28(1)
Fe1–N4	2.34(1)	Fe2–N10	2.31(1)
Fe1–N5	2.17(2)	Fe2–N11	2.14(1)
Fe1–N6	2.13(2)	Fe2–N12	2.15(2)
Fe1–O7	1.79(1)	Fe2–O7	1.80(1)
Fe1–O8	2.03(1)	Fe2–O9	2.05(1)
Fe1–O10	1.96(1)	Fe2–O11	1.99(1)
Fe1···Fe2	3.08(2)	Re1···Re2	13.34(2)
N1–Re1–N2	73.8(6)	N7–Re2–N8	73.9(5)
N1–Re1–N3	74.1(6)	N7–Re2–N9	73.9(6)
O1–Re1–N1	158.4(6)	O4–Re2–N7	157.0(6)
O1–Re1–O2	106.4(7)	O4–Re2–O5	105.6(7)
O1–Re1–O3	105.2(7)	O4–Re2–O6	107.4(8)
N4–Fe1–N5	76.5(6)	N10–Fe2–N11	77.6(5)
N4–Fe1–N6	78.0(6)	N10–Fe2–N12	76.3(6)
N4–Fe1–O7	173.7(5)	N10–Fe2–O7	174.7(5)
O7–Fe1–O8	99.0(6)	O7–Fe2–O9	97.3(6)
O7–Fe1–O10	100.8(6)	O7–Fe2–O11	99.2(5)
Fe1–O7–Fe2	118.2(7)		

which the two Re ions are in extreme oxidation states, +VII and +I. We have also tried to synthesize heterometallic dinuclear complexes with metal ions such as $\mathrm{V^{IV}}$, $\mathrm{Mn^{III}}$, $\mathrm{Fe^{III}}$, $\mathrm{Co^{III}}$, $\mathrm{Ni^{II}}$, $\mathrm{Zn^{II}}$, $\mathrm{Cu^{II}}$, $\mathrm{Ru^{III}}$, and $\mathrm{Pt^{II}}$. It was difficult to obtain well-defined complexes possibly due to decomposition of the original $\mathrm{Re^{VII}}$ complex (vide infra). For two metal ions, $\mathrm{Fe^{III}}$ and $\mathrm{Cu^{II}}$, however, crystals of mixed-metal complexes were obtained. The reactions of [**1**]$^{2+}$ with $\mathrm{Fe(ClO_4)_3}$ in the presence of $\mathrm{CH_3COONa}$ provided a tetranuclear complex [**2**]$^{4+}$. Addition of $\mathrm{CH_3COONa}$ is useful since acetate ions form a well-defined stable dimeric structural unit with $\mathrm{Fe^{III}}$ that is suitable for the coordination of $[\mathrm{Re^{VII}(O)_3}(\text{tpen-}\kappa^3N,N'',N''')]^+$. From X-ray structural analysis, it was found that the dimeric unit, $\mathrm{Fe_2}(\mu\text{-O})(\mu\text{-CH_3COO})_2$,[13] is formed and the tridentate ligand $[\mathrm{Re^{VII}(O)_3}(\text{tpen-}\kappa^3N,N'',N''')]^+$ facially coordinates to each metal center. In the case of Cu, two types of dinuclear $\mathrm{Re^{VII}}$–$\mathrm{Cu^{II}}$ mixed-metal complexes, [**3**]$^{3+}$ and [**4**]$^{2+}$, were obtained depending on the starting copper complex. The $\mathrm{Cu^{II}}$ centers in both complexes have axially elongated octahedral structures (vide infra). With $\mathrm{Cu^{II}(ClO_4)_2\cdot6H_2O}$ as a starting material, [**3**]$^{3+}$ was isolated, in which $\mathrm{Cu^{II}}$ ion is coordinated by the three nitrogen atoms of the ligand $[\mathrm{Re^{VII}(O)_3}(\text{tpen-}\kappa^3N,N'',N''')]^+$, one acetonitrile, and two axial $\mathrm{EO_4}^-$ oxygen atoms, where $\mathrm{EO_4}^-$ is a disordered mixture of $\mathrm{ClO_4}^-$ and $\mathrm{ReO_4}^-$. When a $\mathrm{Cu^I}$ salt, $[\mathrm{Cu^I I(CH_3CN)(PPh_3)_2}]$, was used with the goal to obtain an emissive $\mathrm{Cu^I}$ complex,[14] the only product that was isolated was a $\mathrm{Cu^{II}}$ complex, [**4**]$^{2+}$, in which the copper center is coordinated by two bridging Cl^- ions (one in the tetragonal plane and the other in one of the axial site), and $\mathrm{EO_4}^-$, in addition to the three nitrogen atoms of $[\mathrm{Re^{VII}(O)_3}(\text{tpen-}\kappa^3N,N'',N''')]^+$. Interestingly, Cl^- and not I^- is found in the coordination sphere. The chlorine atom must have originated from the decomposition of the solvent $\mathrm{CH_2Cl_2}$. The 1:2 Cu complex has not been obtained in this study, although the bis(bpa) complex, $[\mathrm{Cu(bpa)_2}]^{2+}$ is known.[8i]

Table 3. Selected Bond Distances (Å) and Angles (°) for [**3**]$(ClO_4)_{1.39}(ReO_4)_{1.61}\cdot CH_3OH\cdot 1.25CH_3CN$ and [**4**]$(ClO_4)_{1.45}(ReO_4)_{0.55}\cdot 0.5CH_3CN$

	$[\mathbf{3}]^{2+}$	$[\mathbf{4}]^{2+}$
Re1–O1	1.73(1)	1.70(1)
Re1–O2	1.71(1)	1.72(1)
Re1–O3	1.72(1)	1.65(1)
Re1–N1	2.30(1)	2.28(1)
Re1–N2	2.24(1)	2.24(1)
Re1–N3	2.24(1)	2.20(1)
Cu1–O4	2.31(1)	2.50(1)
Cu1–O8	2.54(1)	
Cu1–N4	2.04(1)	2.07(1)
Cu1–N5	1.97(1)	1.96(1)
Cu1–N6	1.97(1)	1.98(1)
Cu1–N7	2.02(1)	
Cu1–Cl1		2.28(1)
Cu1–Cl1*		2.87(1)
N1–Re1–N2	74.2(3)	75.6(4)
N1–Re1–N3	74.7(3)	73.7(5)
O1–Re1–N1	156.9(3)	157.7(5)
O1–Re1–O2	106.2(3)	106.6(6)
O1–Re1–O3	107.0(3)	105.0(6)
N4–Cu1–N5	82.7(3)	83.0(5)
N4–Cu1–N6	83.7(3)	82.8(5)
N4–Cu1–N7	165.9(3)	
O4–Cu1–N7	91.1(3)	
N5–Cu1–N7	96.1(3)	
O4–Cu1–N7	91.1(3)	
O4–Cu1–O8	173.6(3)	
N4–Cu1–N7	168.6(3)	
N4–Cu1–Cl1		175.5(4)
N5–Cu1–Cl1		96.5(4)
O4–Cu1–Cl1		86.3(3)
Cl1–Cu1–Cl1*		86.8(1)

The counter anions of all the three complexes have a ReO_4^- that has partially replaced the ClO_4^- ions. The counter anions are statistically disordered between ClO_4^- and ReO_4^-. These facts clearly indicate the decomposition of $[\mathbf{1}]^{2+}$ during the reaction. This may explain the failure to prepare the mixed-metal complexes with other metal ions than Fe^{III} and Cu^{II}. It should be noted that the ratio of the two tetrahedral anions found in the crystals do not necessarily represent the whole samples. The ratio may be different for different batches of crystals or even from one crystal to another.

Structures. ORTEP drawings of the complex cations in [**2**]$(ClO_4)_{3.85}(ReO_4)_{0.15}\cdot 1.5CH_3OH$, [**3**]$(ClO_4)_{1.39}(ReO_4)_{1.61}\cdot CH_3OH\cdot 1.25CH_3CN$, and [**4**]$(ClO_4)_{1.45}(ReO_4)_{0.55}\cdot 0.5CH_3CN$ are shown in Figs. 1, 2, and 3, respectively. Selected bond distances and angles for [**2**]$(ClO_4)_{3.85}(ReO_4)_{0.15}\cdot 1.5CH_3OH$, and those for [**3**]$(ClO_4)_{1.39}(ReO_4)_{1.61}\cdot CH_3OH\cdot 1.25CH_3CN$, and [**4**]$(ClO_4)_{1.45}(ReO_4)_{0.55}\cdot 0.5CH_3CN$ are summarized in Tables 2 and 3, respectively.

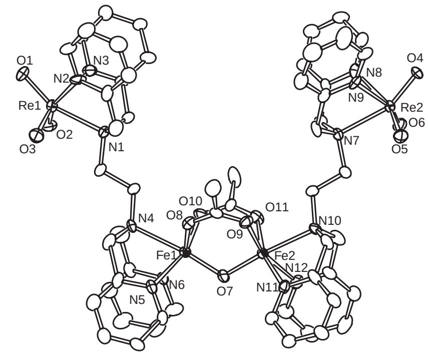


Fig. 1. ORTEP drawing of the complex cation in $[\{Re^{VII}(O)_3(\mu\text{-tpen-}\kappa^3N,N'',N''':\kappa^3N',N'''',N''''')\}_2Fe^{III}_2(\mu\text{-}O)(\mu\text{-}CH_3COO)_2](ClO_4)_{3.85}(ReO_4)_{0.15}\cdot 1.5CH_3OH$ with the atomic numbering scheme and 50% probability thermal ellipsoids.

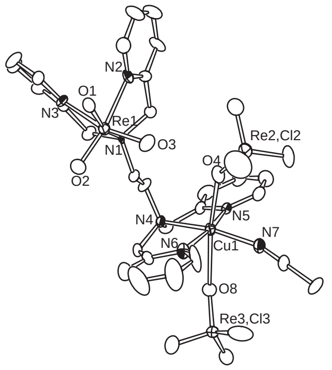


Fig. 2. ORTEP drawing of the complex cation in $[Re^{VII}(O)_3(\mu\text{-tpen-}\kappa^3N,N'',N''':\kappa^3N',N'''',N''''')Cu(CH_3CN)](ClO_4)_{1.39}(ReO_4)_{1.61}\cdot CH_3OH\cdot 1.25CH_3CN$ with the atomic numbering scheme and 50% probability thermal ellipsoids.

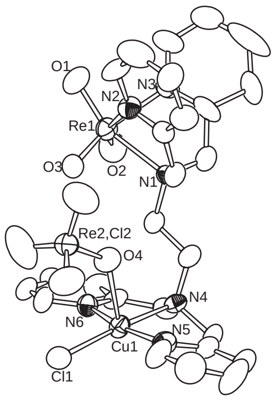


Fig. 3. ORTEP drawing of the complex cation in $[Re^{VII}(O)_3(\mu\text{-tpen-}\kappa^3N,N'',N''':\kappa^3N',N'''',N''''')CuCl](ClO_4)_{1.45}(ReO_4)_{0.55}\cdot 0.5CH_3CN$ with the atomic numbering scheme and 50% probability thermal ellipsoids.

The complex cation $[\mathbf{2}]^{4+}$ has a unique tetranuclear structure. The bis(2-pyridylmethyl)amino moiety of $[Re^{VII}(O)_3(\text{tpen-}\kappa^3N,N'',N''')]^+$ coordinates to each Fe^{III} center of the dimeric unit that is formed through one oxo and two acetato bridges. The overall structure is thus regarded as a di-μ-acetato-μ-oxodiiron(III) complexes having the bulky tridentate ligands $[Re^{VII}(O)_3(\text{tpen-}\kappa^3N,N'',N''')]^+$. The complex cation has a mirror plane consisting of the oxo and the carbon atoms of the acetate ion. Both amine nitrogen atoms coordinating to the Fe centers located trans positions to the bridging oxo ligand. Two $Re^{VII}(O)_3^{(+)}$ groups are oriented in the same direction away from the diiron moiety with their facial trioxo sites towards the outside of the molecule. One of the four counter anions is encapsulated inside the space formed by the two bis(2-pyridylmethyl)aminorhenium(VII) units and bridging acetate ions. The other three EO_4^- ions are located outside of the complex cation. The statistical distribution of Re and Cl in EO_4^- was determined by the ratio that gives minimum R values. It is interesting that the ratio of Cl and Re is different among the four counter anions EO_4^-. The encapsulated anion is pure ClO_4^-. Chlorine atoms of two of the other three EO_4^- anions are partially displaced by Re (the ratio of Cl:Re is determined to be 95:5 for one of them and 90:10 for the other). The bond distances and angles around the Re atom are similar to those of the parent complex, $[Re^{VII}(O)_3(\text{tpenH-}\kappa^3N,N'',N''')]^{2+}$ ($[\mathbf{1}]^{2+}$). Those around the Fe atoms are similar to those of other $Fe_2(\mu\text{-}O)(\mu\text{-}CH_3COO)_2$ complexes.[15]

The two Re–Cu complex cations $[\mathbf{3}]^{3+}$ and $[\mathbf{4}]^{2+}$ have dinuclear structures where the bis(2-pyridylmethyl)amino moiety of $[Re^{VII}(O)_3(\text{tpenH-}\kappa^3N,N'',N''')]^{2+}$ coordinates to a Cu^{II} center. In both complexes, geometrical structures of the copper centers are highly distorted octahedrons with significantly long axial bonds. The tetragonal plane is occupied by the three nitrogen atoms of the bis(2-pyridylmethyl)amino group. The Cu–N(amino) distance (2.04 Å for $[\mathbf{3}]^{3+}$ and 2.07 Å for $[\mathbf{4}]^{2+}$) is longer than the Cu–N(pyridyl) distances (1.97 and 1.97 for $[\mathbf{3}]^{3+}$ and 1.96 and 1.98 Å for $[\mathbf{4}]^{2+}$). The fourth site of the plane is coordinated by acetonitrile nitrogen (2.02 Å) for $[\mathbf{3}]^{3+}$ and Cl (2.28 Å) for $[\mathbf{4}]^{2+}$. The two axial sites (2.31 and 2.54 Å) of $[\mathbf{3}]^{3+}$ and one site (2.50 Å) of $[\mathbf{4}]^{2+}$ interact with the oxygen atoms of EO_4^-. The other axial site of $[\mathbf{4}]^{2+}$ weakly interacts with Cl^- (2.87 Å) of the neighboring molecule. The counter anions involved are statistically disordered between ClO_4^- and ReO_4^-. The ratio of the two elements in EO_4^- is again different among the crystallographically independent EO_4^-. The ratio for the two-coordinated EO_4^- ligands of $[\mathbf{3}]^{3+}$ was determined to be 9:91 and 30:70 (Cl:Re), while that for the free anion was purely ClO_4^-. In the case of $[\mathbf{4}]^{2+}$, the ratio for the coordinated EO_4^- was 50:50 and that for the free anion was 95:5. The Cu–N bond distances associated with bis(2-pyridylmethyl)amino group are within the range of Cu–N(amine) and Cu–N(pyridyl) distances of the Cu–bpa complexes.[8j,16–18] The bond distances and angles around the Re atom are again similar to those of the parent complex $[Re^{VII}(O)_3(\text{tpenH-}\kappa^3N,N'',N''')]^{2+}$ ($[\mathbf{1}]^{2+}$).

Spectroscopic Properties. The UV–visible absorption spectrum of $[\mathbf{2}]^{4+}$ in acetonitrile (Fig. 4) shows several visible bands (417 ($\varepsilon = 1200\,\mathrm{mol^{-1}\,dm^3\,cm^{-1}}$), 447 (1300), 501 (830), 538 (230), and 670 nm (180)) together with a UV band at 338 nm (7300). The spectrum in the visible region is characteristic of the complexes having a $\{Fe_2(\mu\text{-}O)(\mu\text{-}CH_3COO)_2\}$ moiety.[19] Since the spectrum of $[\mathbf{2}]^{4+}$ obeys Beer's law, complex $[\mathbf{2}]^{4+}$ keeps its structure in solution at least within the time scale of the measurement. The copper complexes are not sufficiently soluble in any solvent. The paramagnetic nature of $[\mathbf{2}]^{4+}$ precludes the detailed analysis of ^{1}H NMR spectrum, although some tentative assignments are made as in the Experimental Section.

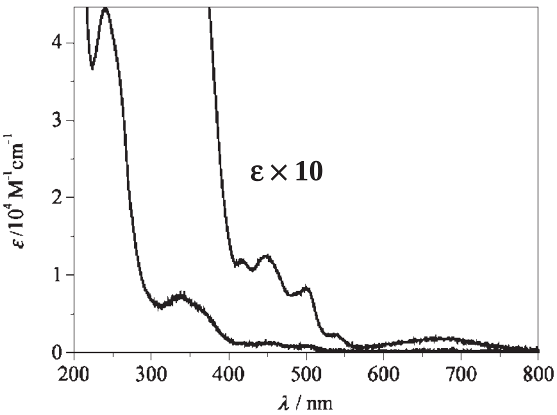


Fig. 4. Electronic absorption spectrum of $[\{Re^{VII}(O)_3(\mu\text{-tpen-}\kappa^3N,N'',N''':\kappa^3N',N'''',N''''')\}_2Fe^{III}_2(\mu\text{-}O)(\mu\text{-}CH_3COO)_2]^{3+}$ in acetonitrile.

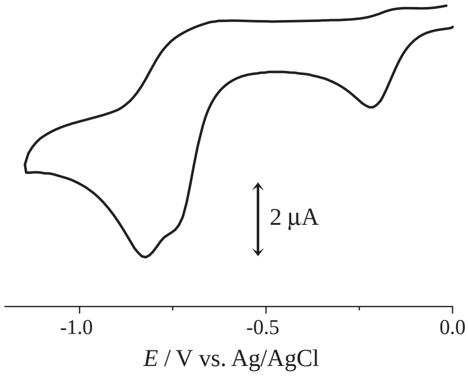


Fig. 5. Cyclic voltammograms (CV) of $[\{Re^{VII}(O)_3(\mu\text{-tpen-}\kappa^3N,N'',N''':\kappa^3N',N'''',N''''')\}_2Fe^{III}_2(\mu\text{-}O)(\mu\text{-}CH_3COO)_2](ClO_4)_4\cdot 4H_2O$ in $0.1\,\mathrm{mol\,dm^{-3}}$ $(n\text{-}C_4H_9)_4NPF_6$ acetonitrile (scan rate, $100\,\mathrm{mV\,s^{-1}}$).

^{1}H NMR spectrum of the Cu^{II} complex $[\mathbf{3}]^{3+}$ in acetonitrile showed some signals from $[Re^{VII}(O)_3(\text{tpen-}\kappa^3N,N'',N''')]^+$, in addition to broad signals from paramagnetic $[\mathbf{3}]^{3+}$, indicating that partial decomposition of $[\mathbf{3}]^{3+}$ proceeds in solution. Although the quantitative analysis of the UV–vis spectrum in acetonitrile is not feasible due to decomposition, a broad peak around 615 nm may be assigned to d–d transition of the Cu center.

Redox Properties of the $\mathbf{Re^{VII}}$**–**$\mathbf{Fe^{III}}$ **Complex.** Cyclic voltammogram (CV) of the complex $[\{Re^{VII}(O)_3(\mu\text{-tpen-}\kappa^3N,N'',N''':\kappa^3N',N'''',N''''')\}_2Fe^{III}_2(\mu\text{-}O)(\mu\text{-}CH_3COO)_2]^{4+}$ ($[\mathbf{2}]^{4+}$) were measured in acetonitrile (Fig. 5). Three irreversible reduction waves were observed at −0.22, −0.74, and −0.82 V vs Ag/AgCl. For comparison, the CV of the parent complex $[Re^{VII}(O)_3(\text{tpenH-}\kappa^3N,N'',N''')]^{2+}$ ($[\mathbf{1}]^{2+}$) was obtained in CH_3CN in the presence of equivalent amount of $(C_2H_5)_3N$ that was added to avoid possible proton-coupled reduction of the Re center by the proton source contaminated in solution. Irreversible reduction waves were observed at −0.70 and −0.84 V. For reference, the CV of $[Fe^{III}_2(\mu\text{-}O)(\mu\text{-}CH_3COO)_2(\text{mebpa})_2](ClO_4)_2$ was also measured in this study in acetonitrile and it showed one irreversible wave at −0.37 V corresponding to the one-electron reduction from $Fe^{III}Fe^{III}$ to $Fe^{II}Fe^{III}$. Thus, the CV peak at −0.22 V of $[\mathbf{2}]^{4+}$

is assigned to the reduction of the Fe center ($Fe^{III}Fe^{III}/Fe^{II}Fe^{III}$),[20] and those at −0.74 and −0.82 V are to the Re center. At this stage, it is not possible to discuss how many electrons are involved in the latter processes. The counterpart to the irreversible reduction wave of $[\mathbf{2}]^{4+}$ at −0.22 V was observed at −0.13 V on increasing the scan rate. In comparison, $[Fe^{III}_2(\mu\text{-O})(\mu\text{-CH}_3COO)_2(mebpa)_2]^{2+}$ showed the reoxidation wave at −0.25 V.

When triethylamine was added up to 3 equivalents to the solution containing $[\mathbf{2}]^{4+}$, a new irreversible reduction wave appeared at −0.57 V at the expense of the original wave at −0.22 V. Similarly, on the addition of triethylamine to the solution of $[Fe^{III}_2(\mu\text{-O})(\mu\text{-CH}_3COO)_2(mebpa)_2]^{2+}$, a new irreversible wave appeared at −0.62 V instead of that at −0.37 V. It is concluded that the reduction of $Fe^{III}Fe^{III}(\mu\text{-O})$ complexes ($[\mathbf{2}]^{4+}$ and $[Fe^{III}_2(\mu\text{-O})(\mu\text{-CH}_3COO)_2(mebpa)_2]^{2+}$) is proton-coupled with the water in CH_3CN to give $Fe^{II}Fe^{III}$-(μ-OH),[21] and the waves that appeared on addition of the base correspond to the proton-independent process, $Fe^{III}Fe^{III}(\mu\text{-O})/Fe^{II}Fe^{III}(\mu\text{-O})$.

Summary

Coordination of the tridentate ligand $[Re^{VII}(O)_3(tpen\text{-}\kappa^3 N,N'',N''')]^+$ with first row transition-metal ions competes with decomposition of the ligand during the reaction. An Fe^{III} complex was prepared under conditions favorable for the formation of the dimeric $\{Fe_2(\mu\text{-O})(\mu\text{-CH}_3COO)_2\}^{2+}$ unit. The complex cation $[\mathbf{2}]^{4+}$ is an Fe dimer with $[Re^{VII}(O)_3(tpen\text{-}\kappa^3 N,N'',N''')]^+$ moieties coordinated to each iron center. Two Cu^{II} complexes have axial-elongated octahedral Cu^{II} ions to which $[Re^{VII}(O)_3(tpen\text{-}\kappa^3 N,N'',N''')]^+$ coordinates meridionally in the tetragonal plane. The use of acetonitrile as a reaction solvent was not sufficient to avoid the decomposition of the original Re^{VII} complex ligand, since the decomposition product, ReO_4^-, is contained as a counter anion of the isolated products. Nevertheless, the present study shows that, if enough caution is paid, $[Re^{VII}(O)_3(tpen\text{-}\kappa^3 N,N'',N''')]^+$ acts as a ligand to produce various interesting heterometal composite compounds.

This work was supported by a Grant-in-Aid for Scientific Research on Priority Area (No. 16033201, "Reaction Control of Dynamic Complexes") to YS and a Scientific Research (C) (No. 16550048) to MA from Ministry of Education, Culture, Sports, Science and Technology, Japan.

References

1 E. C. Constable, *Prog. Inorg. Chem.* **1994**, *42*, 67.

2 H. Sugimoto, Y. Sasaki, *Chem. Lett.* **1997**, 541.

3 H. Sugimoto, Y. Sasaki, *Chem. Lett.* **1998**, 197.

4 L. Xu, Y. Sasaki, M. Abe, *Chem. Lett.* **1999**, 163.

5 M. Sokolov, K. Umakoshi, Y. Sasaki, *Inorg. Chem.* **2002**, *41*, 6237.

6 A. Mitani, M. Abe, K. Tsuge, Y. Sasaki, *Chem. Lett.* **2003**, *32*, 502.

7 T. Tabeya, M. Abe, A. Mitani, K. Tsuge, Y. Sasaki, *J. Nucl. Radiochem. Sci.* **2005**, *6*, 157.

8 For recent examples: a) S. Thewissen, M. D. M. Reijnders, J. M. M. Smits, B. De Bruin, *Organometallics* **2005**, *24*, 5964. b) B. Pitteri, M. Bortoluzzi, G. Marangoni, *Transition Met. Chem.* **2005**, *30*, 1008. c) R. K. Egdal, F. B. Larsen, A. D. Bond, C. J. McKenzie, *Inorg. Chim. Acta* **2005**, *358*, 376. d) C. J. Davies, G. A. Solan, J. Fawcett, *Polyhedron* **2004**, *23*, 3105. e) T. Yoshimura, K. Umakoshi, Y. Sasaki, *Chem. Lett.* **1999**, 267. f) T. Yoshimura, K. Umakoshi, Y. Sasaki, *Inorg. Chem.* **2003**, *42*, 7106. g) D. R. Van Staveren, E. Bothe, T. Weyhermuller, N. Metzler-Nolte, *Eur. J. Inorg. Chem.* **2002**, *6*, 1518. h) J. R. Hartman, R. W. Vachet, J. H. Callahan, *Inorg. Chim. Acta* **2000**, *297*, 79. i) T. Fujihara, A. Fuyuhiro, S. Kaizaki, *Inorg. Chim. Acta* **1998**, *278*, 15. j) M. Palaniandavar, R. J. Butcher, A. W. Addison, *Inorg. Chem.* **1996**, *35*, 467.

9 H. Araki, K. Tsuge, Y. Sasaki, S. Ishizaka, N. Kitamura, to be published.

10 K. B. Jensen, C. J. McKenzie, O. Simonsen, H. Toftlund, A. Hazell, *Inorg. Chim. Acta* **1997**, *257*, 163.

11 *Crystal Clear*, Rigaku Corporation, Tokyo, **1999**.

12 *teXsan, version 1.11*, Molecular Structure Corporation, The Woodlands, TX, **2000**.

13 a) M. V. Twigg, J. Burgess, *Comprehensive Coordination Chemistry II*, Elsevier, **2004**, Vol. 1, p. 494. b) D. M. Kurtz, Jr., *Chem. Rev.* **1990**, *90*, 606.

14 H. Araki, K. Tsuge, Y. Sasaki, S. Ishizaka, N. Kitamura, *Inorg. Chem.* **2005**, *44*, 9667.

15 a) S. M. Gorun, S. J. Lippard, *Inorg. Chem.* **1991**, *30*, 1625. b) H. Furutachi, M. Murayama, A. Shiohara, S. Yamazaki, S. Fujinami, A. Uehara, M. Suzuki, S. Ogo, Y. Watanabe, Y. Maeda, *Chem. Commun.* **2003**, 1900. c) R. J. O'Brien, J. F. Richardson, R. M. Buchanan, *Acta Crystallogr., Sect., C: Cryst. Struct. Commun.* **1991**, *47*, 2307. d) S. Nishino, H. Hoshino, S. Ohba, H. Matsushima, T. Tokii, Y. Nishida, *J. Chem. Soc., Dalton Trans.* **1999**, 1509. e) M. Ghiladi, K. B. Jensen, J. Jiang, C. J. McKenzie, S. Morup, I. Sotofte, J. Ulstrup, *J. Chem. Soc., Dalton Trans.* **1999**, 2675. f) S. Ito, T. Okuno, H. Matsushima, T. Tokii, Y. Nishida, *J. Chem. Soc., Dalton Trans.* **1996**, 4037.

16 T. Murakami, S. Hatakeyama, S. Igarashi, Y. Yukawa, *Inorg. Chim. Acta* **2000**, *310*, 96.

17 T. Buchen, A. Hazell, L. Jessen, C. J. McKenzie, L. P. Nielsen, J. Z. Pedersen, D. Schollmeyer, *J. Chem. Soc., Dalton Trans.* **1997**, 2697.

18 N. Niklas, F. W. Heinemann, F. Hampel, T. Clark, R. Alsfasser, *Inorg. Chem.* **2004**, *43*, 4663.

19 E. I. Solomon, T. C. Brunold, M. I. Davis, J. N. Kemsley, S.-K. Lee, N. Lehnert, F. Neese, A. J. Skulan, Y.-S. Yang, J. Zhou, *Chem. Rev.* **2000**, *100*, 235.

20 Redox studies of other $Fe_2(\mu\text{-O})(\mu\text{-CH}_3COO)_2$ complexes. a) W. H. Armstrong, A. Spool, G. C. Papaefthymiou, R. B. Frankel, S. J. Lippard, *J. Am. Chem. Soc.* **1984**, *106*, 3653. b) J. R. Hartman, R. L. Rardin, P. Chaudhuri, K. Pohl, K. Wieghardt, B. Nuber, J. Weiss, G. C. Papaefthymiou, R. B. Frankel, S. J. Lippard, *J. Am Chem. Soc.* **1987**, *109*, 7387. c) Y. Nishida, M. Nasu, *Inorg. Chim. Acta* **1990**, *169*, 143.

21 T. Inomata, M. Abe, T. Kondo, K. Umakoshi, K. Uosaki, Y. Sasaki, *Chem. Lett.* **1999**, 1097.