Bull. Chem. Soc. Jpn., **77**, 1139–1146 (2004) 1139

A Pair of Seven-Coordinate Oxorhenium Complexes: $[Re^{IV}O(tpen)]^{2+}$ and $[Re^{V}O(tpen)]^{3+}$ (tpen = *N*,*N*,*N*′,*N*′-Tetrakis(2-pyridylmethyl)ethylenediamine)

**Hai-Ying Jin, Shinji Ikari,[1] Kimiko Kobayashi,[2] Keisuke Umakoshi,[3] Hideki Sugimoto,[4]
Ayako Mitani, Masaaki Abe, Yoichi Sasaki,* and Tasuku Ito*,[1]**

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

[1]Department of Chemistry, Graduate School of Science, Tohoku University, Sendai 980-8578

[2]The Institute of Physical and Chemical Research, Wako-shi, Saitama 351-0100

[3]Department of Applied Chemistry, Faculty of Engineering, Nagasaki University, Bunkyo-machi, Nagasaki 852-8521

[4]Department of Chemistry, Graduate School of Science, Osaka City University, Sumiyoshi-ku, Osaka 558-8585

Received September 8, 2003; E-mail: ysasaki@sci.hokudai.ac.jp

A pair of seven-coordinate oxorhenium complexes of *N*,*N*,*N*′,*N*′-tetrakis(2-pyridylmethyl)ethylenediamine (tpen), $[Re^{IV}O(tpen)](ClO_4)_2$ (**1**) and $[Re^{V}O(tpen)](ClO_4)_3$ (**2**), and its *R*-1,2-propylenediamine analogue (*R*-tppn), have been prepared. X-ray structural analyses indicate that the structure of complex cation in **1** is best described as a monocapped trigonal prism with the oxo ligand as a cap. The four pyridylmethyl nitrogen atoms are essentially planar. On the other hand, the structure of complex cation in **2** is approximated as a pentagonal bipyramid, in which the four pyridyl nitrogen atoms take a tetrahedrally distorted arrangement. The structural difference is discussed in terms of different d-electron numbers. The μ_{eff} value of **1** at 300 K is 1.99 B.M. which corresponds to $S = 1/2$, while **2** is diamagnetic. The complexes show a reversible redox wave (Re(IV/V)) at +0.31 V vs Ag/AgCl in 0.1 M $(n\text{-}C_4H_9)_4NPF_6$ acetonitrile solution. In acetonitrile–aqueous buffer solution ($2 < pH < 12$), in addition to a pH independent Re(IV/V) wave at +0.18 V vs Ag/AgCl, a pH-dependent quasi-reversible Re(III/IV) wave with a slope of −0.056 V/pH-unit was observed, indicating that the relevant Re(III) species is $[Re(OH)(tpen)]^{2+}$. The weak absorption peaks of **1** (in acetonitrile) at 836 and 511 nm and those of **2** (in water) at 800, 633, and 408 nm may be assigned to d–d transitions, while the peaks at 428, 381, and 361 nm of **1** may be of charge transfer origin.

Coordination compounds of the group 7 transition elements, Mn, Tc and Re, have structural and chemical characteristics of both early and late transition metal complexes. Particularly, the coordination chemistry of the heaviest member Re may be among the richest, since Re takes a wide range of oxidation states and a wide variety of steric structures, including monomers and polynuclear complexes with and without direct metal–metal bonds.[1] The chemistry of Re complexes has only slowly developed, however, due possibly to the limited number of starting materials and the rather inert nature of the complexes in various oxidation states.[1,2]

We have recently shown the versatility of Re complexes by using a single tripodal tetradentate ligand, tris(2-pyridylmethyl)amine (tpa).[3] The Re complexes of tpa so far prepared are as follows: (i) a typical mononuclear complex with Re(III), $[ReCl_2(tpa)]^+$;[4] (ii) an oxo-bridged dinuclear complex with Re(III), $[Re_2(\mu\text{-}O)Cl_2(tpa)_2]^{2+}$;[5] (iii) edge-shared Re–Re bonded dinuclear complexes with Re(IV) and mixed valence analogues, $[Re_2(\mu\text{-}O)_2(tpa)_2]^{3+/4+}$;[6] (iv) mononuclear complexes bearing one free pyridylmethyl arm with Re(V) ($Re^{V}O$) (example, $[ReO(eg)(tpa)]^+$ (eg = ethyleneglycolate)),[7,8] with Re(VII) ($Re^{VII}(O)_3$), $[Re(O)_3(tpa)]^+$,[7] and with Re(I) ($Re^{I}(CO)_3$) $[Re(CO)_3(tpa)]^+$.[9] Except for the last one, the complexes were prepared by using an Re(V) complex, $Re^{V}OCl_3(PPh_3)_2$ ($PPh_3 = P(C_6H_5)_3$), as a starting material. The solubility of the ligand tpa in several non-aqueous solvents enables us to find ways to gain access to such a variety of complexes in various oxidation states.

A hexadentate ligand, *N*,*N*,*N*′,*N*′-tetrakis(2-pyridylmethyl)ethylenediamine (tpen), which is also soluble in various non-aqueous solvents, has donor groups similar to those of tpa, but has a higher dentate number of 6. The coordination mode of tpen is distinctly different from that of tpa. We have conducted the present research in order to find how the structural characteristics of Re complexes are affected by the ligand structure. A similar but hydrophilic ligand EDTA, where four pyridylmethyl groups of tpen are replaced by carboxymethyl groups, is known to give a dinuclear Re(IV) complex, $[Re^{IV}_2(\mu\text{-}O)_2(edta)]^{2+}$, by the reaction with $[Re^{V}OCl_5]^{2-}$ in aqueous media. In this complex, each ligand leaves two carboxymethyl arms uncoordinated.[10] Except for this dinuclear complex, no EDTA complexes in other oxidation states of Re have been reported so far.

A variety of tpen complexes have been prepared with various metal ions. Mononuclear tpen complexes are known with Fe(II),[11,12] Ni(II),[13] Ru(II),[14] Pt(II),[14] Co(III),[15] V(III),[16]

Published on the web June 9, 2004; DOI 10.1246/bcsj.77.1139

Rh(III),[14] V(V),[17] La(III),[18] Eu(III),[19] Sm(III),[20] and Tb(III).[18] Four, six, seven, eight, and ten coordinate species are involved in these mononuclear complexes. Hypodentate coordination of tpen (one and two pyridylmethyl arms remain uncoordinated) is often found.[12,14,16,17] Fully coordinated tpen is found in six, eight, and ten coordinate species, with none, two, and four additional donor atoms, respectively. The tpen ligand is also known to behave as a bridging ligand in some edge-shared bioctahedral complexes of Mo(V),[21–23] W(V),[21,22] Mo(III),[23] V(IV),[24] Cr(III),[25] and mixed valent Mn_2(III,IV),[26] and in dinuclear Cu(I) complexes.[27] In the study of these tpen complexes, the optically active analogue of tpen, *N*,*N*,*N′*,*N′*-tetrakis(2-pyridylmethyl)-(*R*)-propylenediamine (*R*-tppn), where one of the two carbon atoms in the ethylenediamine part is asymmetric by the introduction of a methyl group, has been useful in understanding asymmetric stereochemical distortion of the complexes as well as their electronic structures by referring to the circular dichroism spectra.

The present study revealed a unique set of rhenium complexes, namely a pair of Re(IV) and Re(V) seven-coordinate mononuclear complexes. Several seven-coordinate Re(V) complexes have already been reported, i.e., oxorhenium(V) complexes such as $[Re^{V}O(CH_3O)_2(\text{quartpy})]^+$ (quartpy = 2,2′:6′,2″:6″,2‴-quaterpyridine),[28] $[Re^{V}OCl_2(\text{pmen})]^+$ (pmen = *N*,*N′*-bis(2-pyridylmethyl)ethylenediamine),[29] $[Re^{V}O(\text{bped})]^+$ (H_2bped = *N*,*N′*-bis(2-pyridylmethyl)ethylenediamine-*N*,*N′*-diacetic acid),[29] $[Re^{V}O(\text{bbpen})]^+$ (H_2bbpen = *N*,*N′*-bis(2-hydroxybenzyl)-*N*,*N′*-bis(2-pyridylmethyl)ethylenediamine),[29] and a non-oxo Re(V) complex $[Re^{V}(\text{tpy})(\text{diBucat})_2]^+$ (tpy = 2,2′:6″,2″-terpyridine, diBucatH_2 = 3,6-di-*tert*-butylcatechol).[30] To the best of our knowledge, however, no seven-coordinate Re(IV) complex has been reported.

This pair of seven-coordinate Re complexes, $[Re^{IV}O(\text{tpen})]^{2+}$ and $[Re^{V}O(\text{tpen})]^{3+}$, is unprecedented with respect not only to rhenium chemistry but also to the coordination mode of tpen. A pair of seven-coordinate complexes with neighboring oxidation states has not been reported previously in any metal ion. The new complexes are the first seven-coordinate complexes of fully coordinated hexadentate tpen and its analogues. X-ray structural analyses and various properties of a pair of the tpen complexes are reported in this paper. The *R*-tppn analogues are also described. A seven-coordinate nitridorhenium(V) complex, $[Re^{V}N(\text{tpen})](ClO_4)_2$, is also introduced briefly. During the course of the present study, an Re(VII) tpen complex, $[Re^{VII}(O)_3(\text{tpenH})]^{2+}$, which has an unusual tridentate tpenH^+, has also been separated. This remarkable complex has been reported separately.[31]

Experimental

Materials. The ligands, tpen and *R*-tppn, were prepared from 2-picolylchloride hydrochloride and the corresponding diamine by following the reported procedures.[32] All other reagents were obtained from commercial sources and were used without further purifications.

Preparation of the Complexes. Caution: All the following complexes were isolated as perchlorate salts. Perchlorate salts are potentially explosive, and the complexes must be handled in small portions with extreme care.

$[Re^{IV}O(\text{tpen})](ClO_4)_2$ (1): A mixture of $Cs_2[Re^{V}OCl_5]$[33] (0.50 g, 0.77 mmol) (or $Re^{V}OCl_3(PPh_3)_2$[34] (PPh_3 = $P(C_6H_5)_3$) (0.35 g, 0.80 mmol)) and tpen (0.34 g, 0.80 mmol) in 100 mL of ethanol containing a small amount of water (ca. 1/25) was refluxed for 10 h. The reaction mixture was diluted with 100 mL of water and then loaded on an SP-Sephadex C-25 cation exchange column. The initial red component that was eluted with 0.1 M NaCl was isolated as a perchlorate salt by adding $NaClO_4$ to the eluent. The product was recrystallized from acetone by adding hexane. Red crystals of $[Re^{IV}O(\text{tpen})](ClO_4)_2$ suitable for X-ray structural analysis were obtained. Yield 0.18 g (27%). Anal. Found: C, 37.45; H, 3.51; N, 10.17%. Calcd for $C_{26}H_{28}N_6O_9Cl_2Re$ (MW 825.66): C, 37.82; H, 3.42; N, 10.18%. IR (KBr) 852 cm^{-1} (ν(Re–O)).

$[Re^{V}O(\text{tpen})](ClO_4)_3$ (2): A mixture of $[Re^{IV}O(\text{tpen})](ClO_4)_2$ (0.030 g, 0.036 mmol) and ferrocenium hexafluorophosphate (0.012 g, 0.036 mmol) in 15 mL of water was stirred for 1 h at room temperature. After the filtration to remove insoluble byproducts, sodium perchlorate was added to the filtrate to obtain green solid of $[Re^{V}O(\text{tpen})](ClO_4)_3$. Yield 0.03 g (78%). Anal. Found: C, 33.55; H, 2.99; N, 8.75; Cl, 11.1%. Calcd for $C_{26}H_{28}N_6O_{13}Cl_3Re$ (MW 925.11): C, 33.76; H, 3.05; N, 9.08; Cl, 11.1%. ^{1}H NMR (270 MHz, D_2O (25 °C, in the presence of H_2O_2), TMS) δ pyridyl rings: 6-H and 3-H 9.54 (2H, d, $J = 5.9$ Hz), 8.01 (2H, d, $J = 7.3$ Hz), 7.85 (2H, d, $J = 7.3$ Hz); 4-H and 5-H 8.26 (4H, t), 7.93 (2H, t, $J = 6.2$ Hz); not assigned 7.64 (4H, br); $-CH_2-$ of pyridylmethyl: 5.08 (4H, d, $J = 15.9$ Hz), overlapped signals with the solvent signal; diamine moiety: 4.08 (2H, d, $J = 10.3$ Hz), 3.90 (2H, br). A single crystal used for the X-ray structural analysis was obtained from the aqueous filtrate left after the separation of **1** (vide supra). While the filtrate was kept in air for a week, its color changed from red to dark green by air-oxidation and green crystals of **2** deposited. Their elemental analyses and spectroscopic data were in good agreement with the sample prepared as above.

$[Re^{IV}O(R\text{-tppn})](ClO_4)_2\cdot 0.5H_2O$ (3): This complex was obtained by a method similar to that of **1** except for using *R*-tppn in place of tpen. The yield was 0.18 g (28%) from 0.64 g (0.77 mmol) of $[Re^{V}OCl_3(PPh_3)_2]$ and 0.35 g (0.80 mmol) of *R*-tppn. Anal. Found: C, 38.17; H, 3.27; N, 9.86; Cl, 8.21%. Calcd for $C_{27}H_{31}N_6O_{9.5}Cl_2Re$ (MW 848.69): C, 38.21; H, 3.68; N, 9.90; Cl, 8.35%. The one-electron oxidized analogue of **3**, $[Re^{V}O(R\text{-tppn})](ClO_4)_3$ (**4**), was not obtained in analytically pure form, but the crude product was used for obtaining qualitative spectroscopic data for comparison.

$[Re^{V}N(\text{tpen})](ClO_4)_2\cdot H_2O$ (5): A mixture of $Re^{V}NCl_2(PPh_3)_2$[35] (0.30 g, 0.38 mmol) and tpen (0.16 g, 0.38 mmol) in 30 mL of ethanol containing a small amount of water (ca. 1/15) was refluxed for 10 h and then loaded on an SP-Sephadex C-25 cation exchange column. To the eluent of 0.1 M NaCl was added sodium perchlorate to obtain bright red crystals of a perchlorate salt of the product. Yield 0.057 g (18%). Anal. Found: C, 37.39; H, 3.38; N, 11.69%. Calcd for $C_{26}H_{30}N_7O_9Cl_2Re$ (MW 841.67): C, 37.10; H, 3.59; N, 11.65%. IR (KBr) 1066 cm^{-1} (ν(Re–N)).

Measurements. Electrochemical Measurements: Cyclic voltammetry was performed with a BAS CV-50W potentiostat. The working and the counter electrodes were a glassy-carbon disk and a platinum wire, respectively. Cyclic voltammograms were recorded at room temperature. The sample solutions (0.5–1.0 mM) in 0.1 M $TBAPF_6$ (tetra(*n*-butyl)ammonium hexafluorophosphate) acetonitrile, in acetonitrile–aqueous Britton–Robinson buffer (1:1), or in aqueous acetate buffer (0.1 M NaCl), were deoxygenated with a stream of nitrogen. The reference electrode was Ag/AgCl. The half-wave potential of Fc/Fc$^+$ ($E_{1/2}(\text{Fc}^{0/+})$) vs Ag/

Table 1. Crystallographic Data and Experimental Details for $[Re^{IV}O(tpen)](ClO_4)_2$ (**1**) and $[Re^{V}O(tpen)](ClO_4)_3$ (**2**)

	1	**2**
Empirical formula	$C_{28}H_{28}Cl_2N_6O_9Re$	$C_{26}H_{28}Cl_3N_6O_{13}Re$
M	825.66	925.11
Crystal system	Monoclinic	Monoclinic
Space group	$C2/c$	$P2_1/n$
a/Å	16.112(3)	9.334(3)
b/Å	8.706(1)	18.998(3)
c/Å	20.453(4)	18.789(2)
β/°	90.95(2)	93.76(2)
V/Å^3	2868.4(9)	3324(1)
Z	4	4
T/K	293	296
Crystal size/mm	0.30 × 0.15 × 0.05	0.50 × 0.12 × 0.05
μ/mm^{-1}	4.731	4.017
No. reflections measured	3433	7877
No. reflections observed	3430, $F_o > 3\sigma(F_o)$	4396, $I > 2\sigma(I)$
R[a)]	0.033	0.055
R_w[b)]	0.050	0.047
GOF	3.57	1.39

a) $R = \Sigma \| F_o| - |F_c\| / \Sigma |F_o|$. b) $R_w = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w |F_o|^2]^{1/2}$; $w = 1$ for **1**, $w^{-1} = \sigma^2(|F_o|) + 0.00006|F_o|^2$ for **2**.

AgCl) was 0.453 V.

Other Measurements: Electronic absorption spectra were recorded on a HITACHI U-3000 spectrophotometer. Infrared absorption spectra were measured with KBr discs by using a HITACHI 270-30 spectrophotometer. ^{1}H NMR spectra were obtained at room temperature at 270 MHz by using a JNM-EX270 spectrometer. Magnetic susceptibility data were collected in the temperature range 100–300 K and in applied 10 kG field with the use of a Quantum Design Model MPMS SQUID magnetometer. Powdered samples were contained in a small half of a gelatin capsule, and a phenolic guide (clear soda straw) was used to house the sample holder and was fixed to the end of the magnetometer drive rod.

X-ray Structural Determination. X-ray data for **1** and **2** were collected on a Rigaku AFC4 and a Rigaku AFC5R diffractometer, respectively, using graphite monochromated Mo Kα ($\lambda = 0.71073$ Å) radiation at 293 K. The data were corrected for Lorentz polarization effects. Each unit cell parameter was obtained by least-squares refinement of 25 reflections ($19.4 < 2\theta < 25.0°$ for **1**, $24.8 < 2\theta < 29.8°$ for **2**). The intensities of three standard reflections, monitored every 150 reflections, showed no appreciable decay during the data collection. Absorption corrections were applied for **1**[36] and **2**.[37] The structures of **1** and **2** were solved by the heavy atom method by using UNICS III[36] and by using SAPI91[38] combined with other crystallographic software packages in TEXSAN,[39] respectively. The positional and thermal parameters of non-hydrogen atoms were refined anisotropically by the block-diagonal-matrix least-squares method for **1** and by the full-matrix least-squares method for **2**. The minimized function was $\Sigma w(|F_o| - |F_c|)^2$, where $w = 1$ for **1** and $w^{-1} = \sigma^2(|F_o|) + 0.00006|F_o|^2$ for **2**. Hydrogen atoms were included at calculated positions with fixed displacement parameters (1.2 times the displacement parameter of the host atom). No correction was made for secondary extinction. Further crystallographic data are given in Table 1. Selected bond distances and angles are summarized in Table 2.

Table 2. Selected Bond Distances (Å) and Angles (deg) for $[Re^{IV}O(tpen)](ClO_4)_2$ (**1**) and $[Re^{V}O(tpen)](ClO_4)_3$ (**2**)

	1	**2**
Re–O1	1.752(5)	1.669(6)
Re–N1	2.395(4)	2.312(8)
Re–N2		2.326(8)
Re–N11	2.154(4)	2.259(9)
Re–N21	2.208(4)	2.079(9)
Re–N31		2.265(9)
Re–N41		2.078(9)
O1–Re–N1	144.80(10)	144.4(3)
O1–Re–N2		144.3(3)
O1–Re–N11	89.7(1)	77.5(3)
O1–Re–N21	82.3(1)	99.5(3)
O1–Re–N31		76.8(3)
O1–Re–N41		102.2(3)
N1–Re–N2(N1′)	70.4(2)	71.1(3)
N1–Re–N11	107.1(1)	67.5(3)
N1–Re–N21	69.3(1)	75.9(3)
N1–Re–N31(N11′)	73.5(1)	138.5(3)
N1–Re–N41(N21′)	125.0(1)	87.0(3)
N2–Re–N11		138.1(3)
N2–Re–N21		84.4(3)
N2–Re–N31		67.5(3)
N2–Re–N41		77.3(3)
N11–Re–N21	84.3(1)	91.8(3)
N11–Re–N31(N11′)	179.3(2)	154.0(3)
N11–Re–N41		93.9(3)
N21–Re–N31(N11′)	95.6(1)	96.6(3)
N21–Re–N41(N21′)	164.5(2)	158.2(3)
N31–Re–N41		87.3(3)

X-ray crystallographic files in CIF format for **1** and **2** have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition numbers 239565 and 239566.

Results and Discussion

Preparation of the Complexes. X-ray structural analyses revealed that complex cations in **1** and **2** are both seven-coordinate complexes (vide infra). Although the seven-coordinate structure is known for some $\mathrm{Re^{V}O}$ complexes,[28,29] it is not known for $\mathrm{Re^{IV}}$. Rhenium–rhenium bonded dinuclear structures appear to be rather common to Re(IV).[1,6] The initially isolated product from the reaction mixture of tpen and the Re(V) precursor $\mathrm{Re^{V}OCl_3(PPh_3)_2}$ (or $[\mathrm{Re^{V}OCl_5}]^{2-}$) was Re(IV) complex **1**. We conclude, however, that the coordination of tpen to $\mathrm{Re^{V}O}$ (and even the formation of seven coordinate structure) takes place prior to the reduction to $\mathrm{Re^{IV}O}$. If the reduction of Re(V) occurred first, formation of a dinuclear complex would be more likely. In the case of tpa ligand, the di(μ-oxo)-dirhenium(IV) complex has been isolated from the mixture of Re(V) precursor $\mathrm{Re^{V}OCl_3(PPh_3)_2}$ and tpa.[6] It was suggested that the disproportionation of Re(V) takes place, and the Re(IV) species thus formed converted to the dinculear complex.[6] In the present case also, the disproportionation mechanism is considered as the most plausible one, since Re(VII) complex has been isolated from the reaction mixture.[31] The initially formed seven-coordinate $[\mathrm{Re^{V}O(tpen)}]^{3+}$ is likely to be reduced to $[\mathrm{Re^{IV}O(tpen)}]^{2+}$ in the reaction mixture. Formation of a dinuclear complex was not observed, since the mononuclear complex is stabilized by the firm coordination of tpen. The redox potential (+0.12 V vs Ag/AgCl in water for the Re(IV)/(V)–tpen couple (vide infra)) may play a favorable role for the disproportionation to give this unusual seven-coordinate Re(IV) complex. It was observed that the isolated pure Re(V) complex dissolved in water always undergoes partial reduction to **1**, unless oxidizing reagent $\mathrm{H_2O_2}$ is present. With more basic nitrido-ligand, reduction to Re(IV) is unfavorable as indicated by the more negative redox potential (vide infra); then only the Re(V) complex, $[\mathrm{Re^{V}N(tpen)}]^{2+}$, was isolated.

Crystal Structures. X-ray crystal structures of the two seven-coordinate tpen complexes, $[\mathrm{Re^{IV}O(tpen)}](\mathrm{ClO_4})_2$ (**1**) and $[\mathrm{Re^{V}O(tpen)}](\mathrm{ClO_4})_3$ (**2**), are shown in Fig. 1. The complex cation in **1** has a two-fold axis passing through the rhenium, oxo ligand, and the center of diamine C–C bond. The complex cation may be best described as a monocapped trigonal prism with the terminal oxygen as the cap (Fig. 2a). The four pyridyl nitrogen atoms form a slightly distorted square plane where the torsion angle of N11–N21–N11′–N21′ is 11.1(2)°. The rhenium atom is slightly deviated (0.155 Å) from the mean plane defined by the four pyridyl nitrogen atoms (deviations of the nitrogen atoms are ±0.142 Å) towards the direction of the ethylenediamine ring. The O–Re–N(pyridyl) angles are thus all smaller than 90° (82.3(1), 89.7(1)°). In general, a metal atom in six or five coordinate oxometal complexes is located out of the mean plane of the four equatorial atoms towards the oxo ligand. Two diamine nitrogen atoms in **1** would pull the metal atom downward to cause the unusual displacement.

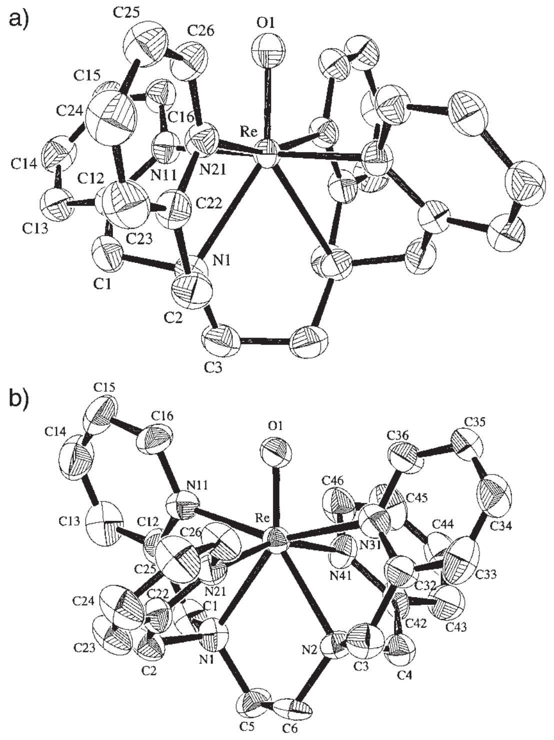


Fig. 1. ORTEP drawings of (a) $[\mathrm{Re^{IV}O(tpen)}]^{2+}$ and (b) $[\mathrm{Re^{V}O(tpen)}]^{3+}$ with the atomic numbering scheme showing 50% probability thermal ellipsoids.

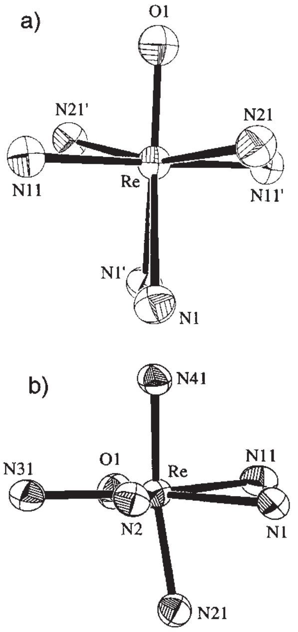


Fig. 2. Core structures of the complex cations, (a) $[\mathrm{Re^{IV}O(tpen)}]^{2+}$ and (b) $[\mathrm{Re^{V}O(tpen)}]^{3+}$.

The structure of complex cation in **2** is significantly different from that in **1**. The four pyridyl nitrogen atoms are distorted tetrahedrally with the torsion angle (N11–N21–N31–N41) of 32.5(3)°.[40] Two of the O–Re–N(pyridyl) angles are larger than 90° (99.5(3) and 102.2(3)°), while the other two are smaller (76.8(3) and 77.5(3)°). The overall structure of the Re(V) complex may be more precisely approximated to a distorted pentagonal bipyramid with two pyridyl nitrogens (N21 and N41) as axial atoms (Fig. 2b). The central rhenium atom sits on the mean plane defined by the five atoms (O1, N1, N2, N11, and N31). The maximum deviation from the mean plane is 0.119(9) Å (N11). The axis perpendicular to the mean plane is bent considerably with the N21–Re–N41 angle of

158.2(3)°. It should be noted here that the structures of all the known seven-coordinate $Re^{V}O$ complexes are expressed by distorted pentagonal bipyramids rather than monocapped trigonal prisms. Three complexes reported by Orvig and co-workers, $[Re^{V}OCl_2(pmen)]^+$, $[Re^{V}O(bped)]^+$, and $[Re^{V}O(bbpen)]^+$, have a common partial structure, i.e., bis(2-pyridylmethyl)-ethylenediamine moiety,[29] which is also common to **2**. Four nitrogen donors of this common fragment together with the oxo ligand form a distorted pentagonal plane in all these complexes. The pentagonal bipyramidal geometry is completed by chlorides, carboxylate oxygens, phenolate oxygens, or 2-pyridylmethyl nitrogens (**2**). The structure of the quartpy complex, $[Re^{V}O(OCH_3)_2(quartpy)]^{+}$[28] is also approximated to a pentagonal bipyramid, where the distorted pentagonal plane is formed by tetrahedrally distorted arrangement of the four pyridyl nitrogens of quartpy and the oxo ligand. Two methoxy oxygens occupy axial positions. Thus, the distorted pentagonal bipyramidal structure is likely to be the most stable one for the seven-coordinate $Re^{V}O$ complexes.

The significant differences in the geometrical structures of a pair of the seven-coordinate oxo-metal complexes **1** and **2** in the neighboring oxidation states will be reasonably explained in the later section in terms of the different d electron number (vide infra).

Further comparison of the bond distances of the two complex cations in **1** and **2** revealed some additional features. The Re–O and Re–N(amino) distances are longer for **1** than the corresponding distances in **2**, as expected from the lower oxidation state of **1**. The Re–N(amino) distances (2.395(4) Å for **1** and 2.312(8) and 2.326(8) Å for **2**) are comparatively long, due possibly to trans influence from the oxo ligand. All the four equatorial Re–N(pyridyl) distances are similar in **1** (2.154(4) and 2.208(4) Å, av 2.181 Å), but these are significantly different in **2** (2.078(9)–2.265(9) Å, av 2.170 Å). In the latter, two sets of the mutually trans Re–N(pyridyl) distances are found. Because the N11 and N31 pyridyl rings in **2** are close to the oxo ligand (O–Re–N, 77.5(3), 76.8(3)°), steric and/or electronic repulsions from the terminal oxygen ligand would cause elongation of the corresponding Re–N bonds. The torsion angles of the diamine part, N–C–C–N, are 53.7(6)° and 57(1)° for **1** and **2**, respectively. They are close to the ideal gauche conformation, suggesting that the coordination of the pyridyl groups does not cause significant strain to the diamine part.

The structures of *R*-tppn complexes **3** and **4** have not been determined, but would be very similar to the corresponding tpen complexes with respect to not only the overall structure but also the tetrahedral distortion of the four pyridyl nitrogens and ligand conformations. The structural similarity between tpen complexes and the corresponding *R*-tppn complexes has been confirmed by the X-ray structural analyses of a pair of $[GdCl_2(tpen)]^+$ and $[GdCl_2(R\text{-tppn})]^+$[41] and a pair of $[Mo_2O_4(tpen)]^{2+}$ and $[Mo_2O_4(R\text{-tppn})]^{2+}$.[21] The difference in these cases is that the two enantiomers (tetrahedral distortion makes the tpen complex asymmetric) exist in equal amounts in the crystal in the tpen complexes, while only one diastereoisomer is found in the *R*-tppn complex, due to fixed conformation of the diamine moiety (λ conformation in this case).

Although the X-ray structural analysis of **5** has not been successful, that of a seven-coordinate nitridorhenium(V) ($Re^{V}N$) complex, $[Re^{V}N(quartpy)(PPh_3)Cl]$ is available.[28] It may be worth mentioning that X-ray structures of some seven coordinate non-oxo rhenium complexes are available. These complexes include rhenium(V) complex $[Re^{V}(tpy)(diBucat)_2]^+$,[29] and some rhenium(III) complexes such as $K_4[Re^{III}(CN)_7]\cdot 2H_2O$,[42] $[Re^{III}X(tpy)_2]^{2+}$ ($X^- = OH^-, Cl^-, NCS^-$),[43] and $[Re^{III}(2,2':6',2'':6'',2''':6''',2''''\text{-quinquepyridine})Cl_2]^+$.[44–46]

^{1}H NMR Spectra. ^{1}H NMR spectrum of **2** in D_2O containing a small amount of H_2O_2 showed two sets of pyridyl signals and the AB pattern of the diamine signals (at 4.08 ppm). The spectrum is consistent with the fixed gauche conformation. Thus the inversion of the tetrahedral distortion accompanied by the diamine conformational change, would be slow with respect to the NMR time scale, if it occurred. Dissociation of one of the four arms in solution is denied, since the dissociation would cause a complicated NMR pattern. Rapid dissociation–recombination of one of the pyridylmethyl arm would be unlikely, since in some $Re^{V}O$ complexes of tpa with a pendant pyridylmethyl arms (typically $[ReO(tpa)(cat)]^+$ ($catH_2$ = catechol)) no sign of the exchange between the coordinated and free pyridylmethyl arms was observed.[7] Thus we conclude that **2** keeps its seven-coordinate structure with the fixed ligand conformation in solution. The reversible redox wave of the Re(IV/V) (vide infra) indicates that rhenium(IV) complex **1** also keeps its seven-coordinate structure in solution.

Electronic States and Geometrical Structures. The $\mu_{\rm eff}$ values of **1** (d^3) at 300 and 100 K were 1.99 and 1.53 B.M., respectively. Such values correspond to $S = 1/2$. ^{1}H NMR spectrum of **2** (d^2) showed signals in the normal region for diamagnetic complexes, indicating that **2** has no unpaired electron ($S = 0$). Similarly, the nitrido complex **5** was found to be diamagnetic as expected for the spin-paired d^2 rhenium(V) oxidation state.

The electronic structure of the present oxo-rhenium complexes is discussed on the basis of general ordering of the d-orbitals for oxometal complexes. If one takes the *z*-axis in the direction of Re=O bond and the *x*- and *y*-axes in the direction of basal ligands perpendicular to the *z*-axis (in the present complexes, the basal ligands situate out of these axes due to distortion), the energy of the d-orbitals would be in the order $d_{xy} \ll d_{xz}, d_{yz} < d_{x^2-y^2} < d_{z^2}$. Since d_{xz} and d_{yz} orbitals, which are nearly degenerated, are destabilized by considerable π interaction with the oxo ligand, d_{xy} orbital should be significantly more stable than them. Tetrahedral distortion would further stabilize the d_{xy} orbital, and would destabilize the vacant (d_{xz}, d_{yz}) orbitals. The complex **2** is diamagnetic as expected from the pairwise occupation of the d_{xy} orbital. The complex **1** must have one additional d-electron in the (d_{xz}, d_{yz}) orbitals. The d_{xz} and d_{yz} orbitals should be more stabilized in the planar arrangement in the d^3 $Re^{IV}O$ ion, as the repulsion of the additional d-electron with the equatorial nitrogen donors would be avoided. Thus the structural difference of the two complexes **1** and **2** is reasonably explained in terms of the different number of d electrons. The diamagnetic nitrido–rhenium complex **5** should have an electronic structure similar to that of **2**.

Electronic Spectra. Absorption spectral data of **1**, **2**, **3**, and **5** are summarized in Table 3. Numerical data of circular dichroism spectrum of **3**, which has an the optically active ligand, are also included in the table. Weak visible absorption bands

Table 3. Numerical Data on Electronic Absorption and Circular Dichroism Spectra of the Seven Coordinate Complexes, $[Re^{IV}O(tpen)]^{2+}$ (**1**), $[Re^{IV}O(R\text{-tppn})]^{2+}$ (**3**), $[Re^{V}O(tpen)]^{2+}$ (**2**), $[Re^{V}N(tpen)]^{2+}$ (**5**)

Complex	UV–vis spectral: λ_{max}/nm (ε/mol^{-1} dm^3 cm^{-1})	CD spectra: λ_{max}/nm ($\Delta\varepsilon$/mol^{-1} dm^3 cm^{-1})	Solvent
1	836 (556); 511sh (1640); 428sh (6070); 381 (7900); 361 (8940); 253 (14100)		CH_3CN
3	836 (551); 518sh (1670); 426sh (5930); 383 (7859); 362 (8468); 254 (14100)	787 (+6.1); 480 (+10.3); 425 (−11.2); 385 (−24.1); 365 (−21.9); 261 (+50.8)	CH_3CN
2	800sh (140); 633sh (272); 408sh (465); 259 (26300)		H_2O
5	830(28); 519 (2600); 394 (9300); 340sh (7000); 254 (17000)		CH_3CN

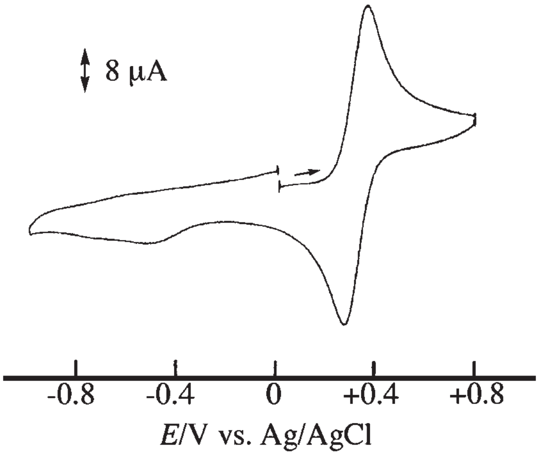


Fig. 3. Cyclic voltammogram of $[Re^{IV}O(tpen)]^{2+}$ in 0.1 M $TBAPF_6$ acetonitrile solution at a scan rate of 200 mV/s.

($\varepsilon < 500$ M^{-1} cm^{-1}) of these complexes may be ascribed as d–d transitions. The shoulder at 511 nm of **1** and the corresponding one in **3** may be also of d–d transition origin. Distinctive CD bands corresponding to the d–d transitions in **3** may reflect the asymmetric arrangement of the nitrogen donors in the equatorial plane. While no strong band is seen in $Re^{V}O$ complex **2**, several strong bands are observed in **1** and **3** (428, 381, and 361 nm for **1**) which may be of charge transfer origin. The metal-to-ligand charge transfer bands of a rhenium(III) complex $[Re^{III}Cl_2(tpa)]^+$ were observed at 503 nm ($\varepsilon = 6440$ M^{-1} cm^{-1}) and 382 nm ($\varepsilon = 4750$ M^{-1} cm^{-1}).[4] Since the d-orbitals are more stabilized in the higher oxidation state of Re(IV), the MLCT bands are expected to have higher transition energy in **1** and **3**. Thus the charge-transfer bands in **1** and **3** may be of MLCT type. Nitrido complex **5** shows some strong visible bands that should be assigned as MLCT associated with the nitrido ligand.

Redox Properties. Figure 3 shows the cyclic voltammogram (CV) of the complex **1** in 0.1 M $TBAPF_6$ acetonitrile solution. The complex **2** shows almost identical CV, suggesting that the two complexes make a redox pair, as expected. The couple shows a reversible one-electron oxidation wave at $E_{1/2} = +0.31$ V vs Ag/AgCl (−0.14 V vs Fc/Fc$^+$). The reduction potential is to our knowledge the most positive among other $Re^{V}O$ complexes regardless of the coordination number. Exceptional cases are proton-coupled redox processes,[47] where the potential shifts to the positive direction on protonation at the ligand in acidic solution. Another seven-coordinate $Re^{V}O$ complex, $[Re^{V}O(quartpy)(OCH_3)_2]^+$ shows a reversible one-electron oxidation wave (Re(V/VI)) at +0.39 V vs Fc/Fc$^+$ in acetonitrile, and no reduction potential is reported.[28] Coordination of the highly basic methoxo ligands makes the reduction to the corresponding $Re^{IV}O$ complex significantly more difficult.

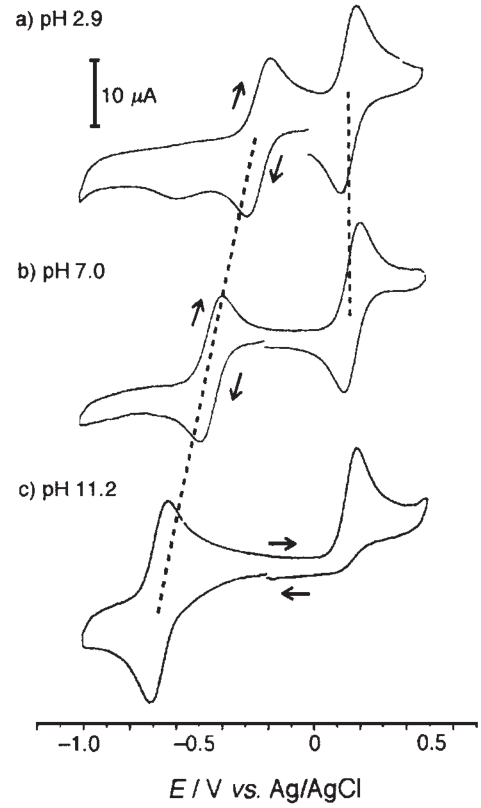


Fig. 4. Cyclic voltammograms of $[Re^{V}O(tpen)]^{3+}$ in 0.05 M $TBAPF_6$ acetonitrile–aqueous Britton–Robinson buffer (1:1) solution at a scan rate of 100 mV/s at various pH′ (apparent pH).

Figure 4 shows the cyclic voltammograms of **1** in 1:1 mixed solvent of acetonitrile and aqueous Britton–Robinson buffer at

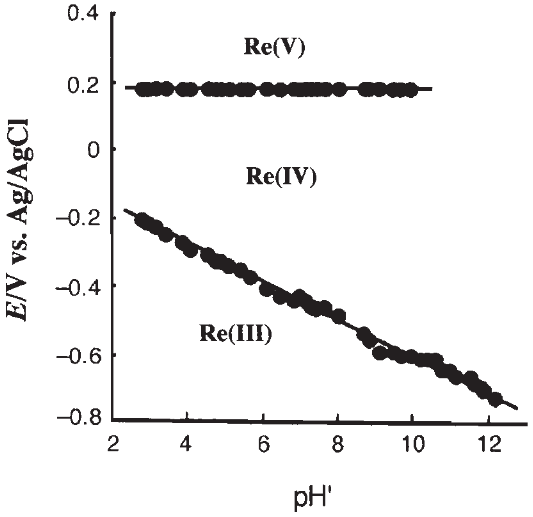
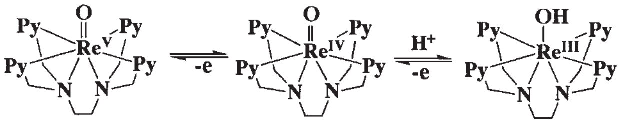


Fig. 5. Dependence of $E_{1/2}$ of the Re(III/IV) and Re(IV/V) processes on pH′.



Scheme 1.

apparent pH (pH′) values of 2.9, 7.0, and 11.2. The mixed solvent was used since the complex is sparingly soluble in water at higher pH. Two redox waves were observed in this mixed solvent. The wave at more positive potential should correspond to Re(IV/V) process as observed in acetonitrile. The redox potential is independent of pH (+0.18 V vs Ag/AgCl), although the reversibility deteriorates at higher pH. The quasi-reversible wave at more negative potential is assigned to the Re(III/IV) process. Interestingly, the potential depends on pH′. The small reduction peak on the negative side of the main Re(III/IV) wave at lower pH may be due to some decomposition of the seven-coordinate species. Figure 5 shows the pH dependence of the two redox waves over the pH′ range of 2–12. The nearly linear dependence of $E_{1/2}$ of the Re(III/IV) process on pH′ with the slope of 0.056V/pH, indicates that the redox process involves one proton. In order to confirm that acetonitrile is not significantly influential on the redox behavior, the cyclic voltammograms were also measured in aqueous acetate buffer solutions without acetonitrile in the pH range of 3.6–4.6, where the complex is just soluble. The two reversible redox waves were observed at +0.12 V vs Ag/AgCl (pH independent) and −0.24 to −0.29 V vs Ag/AgCl (pH dependent). The potentials of the pH dependent process lie nearly on the linear plot in the mixed solvent. It is reasonable to assume that the reduction to rhenium(III) is associated with the protonation at the terminal oxo ligand to give the hydroxo rhenium(III) complex, $[\mathrm{Re^{III}(OH)(tpen)}]^{2+}$, as summarized in Scheme 1. Since there is no clear sign of the curvature of the plot, it is concluded that $\mathrm{p}K_\mathrm{a}$ of $[\mathrm{Re^{III}(OH)(tpen)}]^{2+}$ is higher than 12, and that of the oxo ligand of $[\mathrm{Re^{IV}(O)(tpen)}]^{2+}$ is smaller than 2.

The failure to observe the Re(III/IV) process in acetonitrile is reasonable, since without the protonation the wave is expected to occur at significantly more negative potential. Study of proton-coupled redox reactions of **1** in acetonitrile by adding some proton donors, as we did for some diruthenium complexes,[48–50] was not promising as a clear CV could not be observed in the presence of proton donors probably due to decomposition of the seven-coordinated structure. Attempts to isolate a salt of hydroxo complex, $[\mathrm{Re^{III}(OH)(tpen)}]^{2+}$, are so far unsuccessful.

The nitrido complex **5** showed a reversible oxidation wave (Re(V/VI)) at +0.66 V ($E_{1/2}$, $\Delta E = 70$ mV) and an irreversible reduction wave (Re(IV/V)) at ca. −1.5 V (E_pc). Coordination of the more negative nitrido ligand stabilizes higher oxidation states.

Conclusion

A hexadentate ligand tpen favors the full coordination to one rhenium ion in +5 and +4 oxidation states to give seven-coordinate species with the cooperation of an oxo ligand. The isolation and X-ray structural determination of a pair of seven-coordinate $\mathrm{Re^{IV}O}$ and $\mathrm{Re^{V}O}$ complexes enabled us to discuss the effect of d electron number to the geometrical structures. The tpen ligand in the $\mathrm{Re^{V}O}$ complex (d^2) takes a less strained conformation, namely the tetrahedral distortion of the four pyridyl nitrogens around the rhenium(V) ion. Such distortion is not favorable in the $\mathrm{Re^{IV}O}$ complex due to the repulsion with the additional $\mathrm{d}\pi$ electron, and the more strained planar arrangement is observed. The successful isolation of the unusual seven-coordinate $\mathrm{Re^{IV}O}$ complex is explained by facile reduction of the initially formed $\mathrm{Re^{V}O}$ complex ($E_{1/2}$(Re(IV/V)) = +0.18 V vs Ag/AgCl in acetonitrile–aqueous buffer). Proton-coupled redox waves (Re(III/IV) (2 < pH < 12) (observed in acetonitrile/aqueous Britton–Robinson buffer mixed solvent)) suggest that the reduction must involve seven-coordinate hydroxo–Re(III) complex, $[\mathrm{Re^{III}(OH)(tpen)}]^{2+}$. In the case of the nitrido complex, $[\mathrm{Re^{V}N(tpen)}]^{2+}$, redox potential is unfavorable for the isolation of the Re(IV) analogue.

Financial support from a Grant-in-Aid (No. 15036201) on Priority Area of "Reaction Control of Dynamic Complexes" from the Ministry of Education, Culture, Sports, Science and Technology, is gratefully acknowledged. We are grateful to Professor A. Yamagishi for the measurement of circular dichroism spectra.

References

1 a) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry, 5th Ed," Wiley Interscience, New York (1988). b) F. A. Cotton and R. A. Walton, "Multiple-Bond between Metal Atoms, 2nd Ed," Oxford, New York (1993). c) K. A. Connor and R. A. Walton, In "Comprehensive Coordination Chemistry," ed by G. Wilkinson, R. D. Gillard, and J. A. McCleverty, Pergamon Press, Oxford (1987), Vol. 4.

2 For recent examples, see: a) M. Chabanas, A. Baudouin, C. Coperet, J. M. Baset, W. Lukens, A. Lesage, S. Hediger, and L. Emsley, *J. Am. Chem. Soc.*, **125**, 492 (2003). b) R. Visentin, R. Rossin, M. C. Giron, A. Dolmella, G. Bandoli, and U. Mazzi, *Inorg. Chem.*, **42**, 950 (2003). c) A. R. Cowley, J. R. Dilworth, P. S. Connelly, and J. Woollard-Shore, *Dalton Trans.*, **2003**, 748. d) S. H. Pawlicki, B. C. Noll, J. A. Kanney, and M. R. DuBoix,

Inorg. Chem., **42**, 1556 (2003). e) T. G. Gray, C. M. Rudzinski, E. E. Meyer, R. H. Holm, and D. G. Nocera, *J. Am. Chem. Soc.*, **125**, 4755 (2003). f) W. K. Rybak, A. Skarzynska, and T. Growiak, *Angew. Chem., Int. Ed.*, **42**, 3445 (2003). g) T. Ohashi, Y. Miyashita, Y. Yamada, K. Fujisawa, and K. Okamoto, *Bull. Chem. Soc. Jpn.*, **76**, 1199 (2003). h) T. Yoshimura, Z.-N. Chen, A. Itasaka, M. Abe, Y. Sasaki, S. Ishizaka, N. Kitamura, S. S. Yarovoi, S. F. Solodovnikov, and V. E. Fedorov, *Inorg. Chem.*, **42**, 4857 (2003).

3 H. Sugimoto, H. Miyake, and H. Tsukube, *J. Chem. Soc., Dalton Trans.*, **2002**, 4535.

4 H. Sugimoto, C. Matsunami, C. Koshi, M. Yamasaki, K. Umakoshi, and Y. Sasaki, *Bull. Chem. Soc. Jpn.*, **74**, 2091 (2001).

5 H. Sugimoto, T. Takahira, T. Yoshimura, M. Shiro, M. Yamasaki, H. Miyake, K. Umakoshi, and Y. Sasaki, *Inorg. Chim. Acta*, **337**, 203 (2002).

6 a) H. Sugimoto, M. Kamei, K. Umakoshi, Y. Sasaki, and M. Suzuki, *Inorg. Chem.*, **35**, 7082 (1996). b) T. Takahira, K. Umakoshi, and Y. Sasaki, *Acta Crystallogr., Sect. C*, **50**, 1870 (1994).

7 H. Sugimoto and Y. Sasaki, *Chem. Lett.*, **1997**, 541.

8 H. Sugimoto and Y. Sasaki, *Chem. Lett.*, **1998**, 197.

9 M. Omizo, K. Tsuge, and Y. Sasaki, unpublished.

10 S. Ikari, T. Ito, W. McFarlane, M. Nasreldin, B.-L. Ooi, Y. Sasaki, and A. G. Sykes, *J. Chem. Soc., Dalton Trans.*, **1993**, 2621.

11 H.-R. Chang, J. K. McCusker, H. Toftlund, S. R. Wilson, A. X. Trautwein, H. Winkler, and D. N. Hendrickson, *J. Am. Chem. Soc.*, **112**, 6814 (1990).

12 T. Nagano and T. Hirano, *Farumashia*, **28**, 1119 (1992).

13 D. Da Luz, C. V. Franco, L. Vencato, A. Neves, and Y. P. Mascarenhas, *J. Coord. Chem.*, **26**, 269 (1992).

14 M. Sokolov, K. Umakoshi, and Y. Sasaki, *Inorg. Chem.*, **41**, 6237 (2002).

15 J. B. Mandel and B. E. Douglas, *Inorg. Chim. Acta*, **155**, 55 (1989).

16 K. Kanamori, E. Kameda, and K. Okamoto, *Bull. Chem. Soc. Jpn.*, **69**, 2901 (1996).

17 A. Neves, M. Horner, H. Fenner, and J. Strahle, *Acta Crystallogr., Sect. C*, **49**, 1737 (1993).

18 L. R. Morss and R. D. Rogers, *Inorg. Chim. Acta*, **255**, 193 (1997).

19 R. Hazama, K. Umakoshi, C. Kabuto, K. Kabuto, and Y. Sasaki, *Chem. Commun.*, **1996**, 15.

20 H.-Y. Jin, M. Akiba, K. Umakoshi, Y. Sasaki, and K. Kabuto, *Acta Crystallogr., Sect. C*, **53**, 60 (1997).

21 R. Hazama, K. Umakoshi, A. Ichimura, S. Ikari, Y. Sasaki, and T. Ito, *Bull. Chem. Soc. Jpn.*, **68**, 456 (1995).

22 K. Saito, Y. Sasaki, and R. Hazama, *J. Cluster Sci.*, **6**, 549 (1995).

23 H.-Y. Jin, R. Hazama, M. Yamasaki, K. Umakoshi, and Y. Sasaki, unpublished.

24 A. Neves, K. Wieghardt, B. Nuber, and J. Weiss, *Inorg. Chim. Acta*, **150**, 183 (1988).

25 H. Toftlund, O. Simonsen, and E. Pedersen, *Acta Chem. Scand.*, **44**, 676 (1990).

26 S. Pal, J. W. Gohdes, W. C. A. Wilisch, and W. H. Armstrong, *Inorg. Chem.*, **31**, 713 (1992).

27 R. R. Gagne, R. T. Kresh, J. A. Dodge, R. E. Marsh, and M. McCool, *Inorg. Chem.*, **21**, 254 (1982).

28 C.-M. Che, Y.-P. Wang, K.-S. Yeung, K.-Y. Wong, and S.-M. Peng, *J. Chem. Soc., Dalton Trans.*, **1992**, 2675.

29 L. Xu, I. A. Setyawati, J. Pierreroy, M. Pink, V. G. Young, Jr., B. O. Patrick, S. J. Rettig, and C. Orvig, *Inorg. Chem.*, **39**, 5958 (2000).

30 H. Sugimoto, K. Tsuge, and K. Tanaka, *Chem. Lett.*, **1998**, 719.

31 A. Mitani, M. Abe, K. Tsuge, and Y. Sasaki, *Chem. Lett.*, **34**, 502 (2003).

32 G. Anderegg and F. Wenk, *Helv. Chim. Acta*, **50**, 2330 (1967).

33 J. E. Fergusson and J. L. Love, *Aust. J. Chem.*, **24**, 1054 (1971).

34 N. P. Johnson, C. J. L. Lock, and G. Wilkinson, *J. Chem. Soc.*, **1964**, 1054.

35 J. Chatt, C. D. Falck, G. J. Leigh, and R. J. Paske, *J. Chem. Soc. A*, **1969**, 2288.

36 K. Sakurai and K. Kobayashi, *Rikagaku Kenkyuusho Hokoku (Rep. Inst. Phys. Chem. Res.)*, **55**, 69 (1979).

37 A. C. T. North, D. C. Philips, and F. S. Mathews, *Acta Crystallogr., Sect. A*, **24**, 351 (1968).

38 SAPI91: H. F. Fan, "Structure Analysis Programs with Intelligent Control," Rigaku Corporation, Tokyo, Japan (1991).

39 TEXSAN: "Single Crystal Analysis Software," Molecular Structure Corporation (1995).

40 The deviations of the nitrogen atoms from the mean plane defined by the four pyridyl nitrogens are now as much as 0.46 Å.

41 H.-Y. Jin, R. Hazama, K. Umakoshi, Y. Sasaki, C. Kabuto, and K. Kabuto, unpublished.

42 J.-M. Manoli, C. Potvin, J.-M. Bregeault, and W. P. Griffith, *J. Chem. Soc., Dalton Trans.*, **1980**, 192.

43 J. Rall, F. Weingart, D. M. Ho, M. J. Heeg, F. Tisato, and E. Deutsch, *Inorg. Chem.*, **33**, 3442 (1994).

44 T. H. Lemmen, J. A. Kocal, Y.-K. Lo, M. N. Chen, and L. F. Dqahl, *J. Am. Chem. Soc.*, **103**, 1932 (1981).

45 L. Xu, J. Pierreroy, B. O. Patrick, and C. Orvig, *Inorg. Chem.*, **40**, 2005 (2001).

46 Several seven-coordinate complexes are known for a similar hexadentate ligand EDTA and related ligands with the metal ions having a relatively large ionic size like Ti(III), V(III), and Fe(III). The seventh ligand in these EDTA complexes is usually H_2O. The coordination geometry of the cations depends on the metal ions, and both the distorted pentagonal bipyramid and monocapped trigonal prism have been found. It has been discussed that the ionic radius and d-electron configuration may be important factors to determine whether or not the complexes take the seven-coordinate structure (K. Miyoshi, J. Wang, and T. Mizuta, *Inorg. Chim. Acta*, **165**, 228 (1995)).

47 C.-M. Che and V. W.-W. Yam, *Adv. Transition Met. Coord. Chem.*, **1**, 209 (1996).

48 A. Kikuchi, T. Fukumoto, K. Umakoshi, Y. Sasaki, and A. Ichimura, *J. Chem. Soc., Chem. Commun.*, **1995**, 2125.

49 Y. Sasaki, K. Umakoshi, T. Imamura, A. Kikuchi, and A. Kishimoto, *Pure Appl. Chem.*, **69**, 205 (1997).

50 T. Fukumoto, A. Kikuchi, K. Umakoshi, and Y. Sasaki, *Inorg. Chim. Acta*, **283**, 151 (1998).