

X-ray Structure and Electrochemical Properties of a Tpen-Bridged Hetero-Binuclear Complex *fac*-, *fac*-[Re^{VII}O₃(μ -tpen)Re^I(CO)₃](PF₆)₂ where Tpen Is *N,N,N',N'*-Tetrakis(2-pyridylmethyl)ethylenediamine

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The molecular structure and electrochemical properties of the title complex, **1**, are reported. Single-crystal X-ray diffraction study reveals that complex **1** consists of two distinct metal centers, *fac*-{ReO₃}⁺ and *fac*-{Re(CO)₃}⁺, which are bridged by tpen in a κ^3 - κ^3 coordination mode with a minimal metal-metal interactions (Re...Re = 7.660(1) Å). Complex **1** undergoes irreversible reduction and oxidation in 0.1 M *n*-Bu₄NPF₆-CH₃CN, which are associated with the two metal centers, *fac*-{ReO₃} and *fac*-{Re(CO)₃}⁺.

1. Introduction

N,N,N',N'-tetrakis(2-pyridylmethyl)ethylenediamine (hereafter abbreviated as tpen) affords a versatile array of coordination compounds.¹ It usually coordinates to a metal center as a hexadentate ligand, while some other coordination modes, in which the number of coordinating atoms is limited to five or less, have been also described.²

We have recently reported synthesis and characterizations of a seven-coordinated rhenium-oxo complex [Re^{VO}(tpen)]³⁺ and the one-electron-reduced derivative [Re^{IV}O(tpen)]²⁺, in which tpen coordinates to the {Re^{V/IV}O} with the hexadentate mode,¹ as well as a rhenium-trioxo complex [ReO₃(tpenH)]²⁺ (tpenH is a protonated tpen) which exhibits an unusual κ^3 -coordination mode.³ We have found that the dangling bis(2-pyridylmethyl)amine arm in the [ReO₃(tpenH)]²⁺ complex can coordinate, upon deprotonation, to a single metal center to afford mixed-metal dinuclear complexes. Thus, the reaction of the [ReO₃(tpenH)]²⁺ complex with [Re(CO)₅Br] in refluxing CH₃CN afforded a thermally stable dinuclear complex formulated as [ReO₃(μ -tpenH)Re(CO)₃](ClO₄)₂.³ The *fac*-{Re(CO)₃}⁺ coordination unit adds an additional interest in this dinuclear tpen complex because of its widespread current interest and development of chemistry associated with this structural motif, including ligand-substitution reactions,^{4,5} photoluminescence,⁶ supramolecular assembly formation,^{7,8} self-assembled monolayer formation on solid supports,⁹ photochemical catalysis of CO₂,^{10,11} and therapeutic radiopharmaceuticals.¹²

In this paper, we describe X-ray structure and electrochemical properties of a PF₆⁻ salt of the Re^{VII}O₃-Re^I(CO)₃ complex, *fac*-, *fac*-[ReO₃(μ -tpen)Re(CO)₃](PF₆)₂ (**1**). This work provides the first structurally-determined example of tpen complexes, in which the tpen bridges two nonequivalent metal centers without the support of any additional ligands. Spectroscopic characterizations of **1**, including infrared, UV-Vis, and ¹H NMR spectroscopy, have been reported earlier.³

2. Experimental Section

Materials. The ligand tpen was prepared as described in Reference 13. CH₃CN for electrochemical measurements was distilled from CaH₂ under Ar. *n*-Bu₄NPF₆ used as a supporting electrolyte was recrystallized twice from ethanol. All the other

chemicals were used without further purifications. Complex [ReO₃(tpenH)](ClO₄)₂ was prepared as reported previously.³

Synthesis *fac*-, *fac*-[ReO₃(μ -tpen)Re(CO)₃](PF₆)₂ (1**).** To a CH₃CN solution (20 mL) of [ReO₃(tpenH)](ClO₄)₂³ (97 mg, 0.11 mmol) was added a CH₃CN solution (5 mL) of [Re(CO)₅Br] (47 mg, 0.11 mmol), and the solution was refluxed for 2.5 h. After cooling, the solvent was reduced by a rotary evaporator to ca. 10 mL and filtered. After 4 days, white precipitate thus appeared (30 mg), formulated as [ReO₃(μ -tpen)Re(CO)₃](ClO₄)₂, was collected by filtration. The PF₆⁻ salt **1** was obtained by metathesis between the ClO₄⁻ salt and NaPF₆ in CH₃CN/H₂O. Diffusion of diethyl ether into a CH₃CN solution of **1** afforded single crystals **1**·(CH₃CN)_{0.85}(H₂O)_{0.15} suitable for X-ray diffraction study. Yield, 21 mg (15%, based on [ReO₃(tpenH)](ClO₄)₂). Anal. Calcd. for **1**·(CH₃CN)_{0.85}(H₂O)_{0.15} {C₂₉H₂₈F₁₂N₆O₆P₂Re₂·(CH₃CN)_{0.85}(H₂O)_{0.15}}: C, 29.35; H, 2.47; N, 7.64. Found: C, 29.45; H, 2.52; N, 7.81. ¹H NMR spectrum of **1** (in CD₃CN) was essentially identical to that of [ReO₃(μ -tpen)Re(CO)₃](ClO₄)₂ reported previously.³

Physical Measurements. ¹H NMR spectra were recorded on a JNM-EX270 spectrometer. Infrared spectra were obtained on a JASCO FT/IR-660Plus V spectrophotometer with the KBr method. Cyclic voltammetry was performed under Ar at room temperature with a Hokuto Denko HZ-3000 electrochemical system. The working electrode, counter electrode, and reference electrode were platinum (ϕ = 3 mm), platinum coil, and Ag/AgCl, respectively. The electrolyte solution was 0.1 M *n*-Bu₄NPF₆-CH₃CN and the sample concentration was 1.0 mM. Under our experimental conditions, the half-wave potential (*E*_{1/2}) of the ferrocene/ferricinium couple was 0.45 V vs. Ag/AgCl. Elemental analysis was performed at the Center for Instrumental Analysis, Hokkaido University.

X-ray Diffraction Study. Structural data of a colorless needle-like single crystal (0.250 × 0.025 × 0.012 mm³) were collected on a Rigaku model AFC-7R diffractometer with a Mercury CCD area detector using graphite-monochromated Mo K α radiation (λ = 0.71073 Å) at 153 K and processed using the Crystal Clear software program.¹⁴ Final cell parameters were obtained from a least-squares analysis of reflections of *I* > 10 σ (*I*). The crystal structure was solved by direct methods and expanded using Fourier and difference Fourier techniques. All calculations were performed using the teXsan crystallographic software package.¹⁵ It appeared that the structural similarity of the *fac*-{Re(CO)₃} and *fac*-{ReO₃} caused the partial mixing of two sites in **1**; a model without disordered atoms showed the considerably large densities in D-Fourier

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map and the addition of disordered $\{\text{ReO}_3\}$ and $\{\text{Re}(\text{CO})_3\}$ units appeared to improve R values. A 85% : 15% mixing of the two was admitted in the final structure. Isotropic and anisotropic displacement parameters were applied for the atoms with 0.15 occupancy and for all other non-hydrogen atoms, respectively. Atomic coordinates and displacement parameters were refined by a full-matrix least-squares method. The hydrogen atoms were placed at the calculated positions. Further crystallographic data are provided in Table 1.

The X-ray crystallographic file in CIF format for **1** has been deposited at the Cambridge Crystallographic Data Centre, 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 number CCDC 276472.

TABLE 1: Crystallographic Data of $1 \cdot (\text{CH}_3\text{CN})_{0.85}(\text{H}_2\text{O})_{0.15}$

empirical formula	$\text{C}_{30.7}\text{H}_{30.85}\text{N}_{6.85}\text{O}_{6.15}\text{Re}_2\text{P}_2\text{F}_{12}$
fw	1256.52
crystal system	monoclinic
space group	$P2_1/a$
T , K	153
a , Å	17.219(3)
b , Å	12.648(2)
c , Å	19.591(3)
β , deg	110.191(1)
V , Å ³	4004(1)
Z	4
d_{calcd} , g cm ⁻³	2.09
no. of unique reflections	9139
μ , mm	6.231
$R1$, $wR2^b$	0.055, 0.120

$$^a R1 = \sum |F_o| - |F_c| / \sum |F_o|, wR2 = \{ \sum [w(|F_o|^2 - |F_c|^2)^2] / \sum [w(|F_o|^2)^2] \}^{1/2}, w = \{ \sigma^2(F_o^2) + [0.05(\max(F_o^2, 0) + 2F_c^2)/3] \}^{-1}.$$

3. Results and Discussion

In our previous study,³ synthesis and spectroscopic properties of a ClO_4^- salt of *fac*-, *fac*- $[\text{ReO}_3(\mu\text{-tpen})\text{Re}(\text{CO})_3]^{2+}$ were established. We have found in this study that replacement of the counter anion from ClO_4^- to PF_6^- provides single crystals suitable for X-ray diffraction study (see below). The PF_6^- salt of *fac*-, *fac*- $[\text{ReO}_3(\mu\text{-tpen})\text{Re}(\text{CO})_3]^{2+}$, **1**, gives a satisfactory result of elemental analysis and spectroscopic features that are essentially identical to those of the ClO_4^- salt.

X-ray Structure. The molecular structure of the cationic portion of **1** is presented in Figure 1, and selected interatomic distances and angles are collected in Table 2.¹⁷ The X-ray analysis unequivocally presents dinuclear structure of **1**, in which two heterometallic centers *fac*- $\{\text{Re}^I(\text{CO})_3\}^+$ and *fac*-

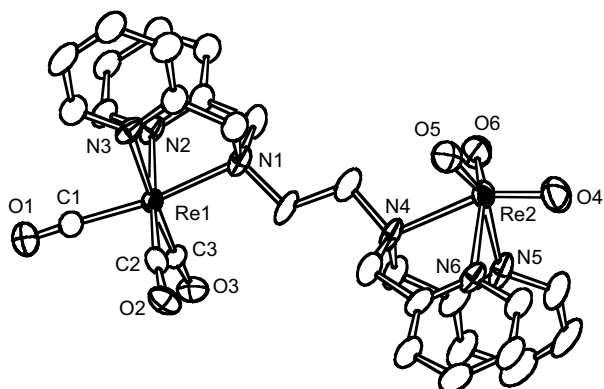


Figure 1. An ORTEP drawing of the cationic portion of $1 \cdot (\text{CH}_3\text{CN})_{0.85}(\text{H}_2\text{O})_{0.15}$ at 50% probability level. Hydrogen atoms are omitted for clarity.

TABLE 2: Selected Interatomic Distances (Å) and Angles (deg) for $1 \cdot (\text{CH}_3\text{CN})_{0.85}(\text{H}_2\text{O})_{0.15}$

Re(1)–C(1)	1.942(9)	Re(2)–O(4)	1.694(7)
Re(1)–C(2)	1.897(8)	Re(2)–O(5)	1.714(6)
Re(1)–C(3)	1.916(7)	Re(2)–O(6)	1.716(6)
Re(1)–N(1)	2.194(7)	Re(2)–N(4)	2.339(7)
Re(1)–N(2)	2.148(6)	Re(2)–N(5)	2.264(8)
Re(1)–N(3)	2.138(6)	Re(2)–N(6)	2.272(7)
Re(1) \cdots Re(2)	7.660(1)		
N(1)–Re(1)–C(1)	171.6(3)	O(4)–Re(2)–O(5)	107.2(3)
N(1)–Re(1)–C(2)	97.4(3)	O(4)–Re(2)–O(6)	107.2(3)
N(1)–Re(1)–C(3)	98.1(3)	O(4)–Re(2)–N(4)	156.7(3)
N(2)–Re(1)–C(1)	94.9(3)	O(4)–Re(2)–N(5)	88.8(3)
N(2)–Re(1)–C(2)	176.7(3)	O(4)–Re(2)–N(6)	88.1(3)
N(2)–Re(1)–C(3)	91.7(3)	O(5)–Re(2)–O(6)	105.8(3)
N(3)–Re(1)–C(1)	94.1(3)	O(5)–Re(2)–N(4)	85.3(3)
N(3)–Re(1)–C(2)	96.5(3)	O(5)–Re(2)–N(5)	155.4(3)
N(3)–Re(1)–C(3)	173.4(3)	O(5)–Re(2)–N(6)	87.9(3)
C(1)–Re(1)–C(2)	88.1(3)	O(6)–Re(2)–N(4)	87.4(3)
C(1)–Re(1)–C(3)	88.3(3)	O(6)–Re(2)–N(5)	86.4(3)
C(2)–Re(1)–C(3)	89.7(3)	O(6)–Re(2)–N(6)	154.7(3)
Re(1)–C(1)–O(1)	175.9(9)		
Re(1)–C(2)–O(2)	172.5(7)		
Re(1)–C(3)–O(3)	177.0(7)		

$\{\text{Re}^{\text{VII}}\text{O}_3\}^+$ are bridged by tpen with a $\kappa^3\text{-}\kappa^3$ coordination mode. The $\text{Re}(1) \cdots \text{Re}(2)$ separation was 7.660(1) Å. This is the first example of structurally-determined tpen-complexes in which heterometallic groups are bridged by a single tpen without the support of any additional ligands.

Each metal center is coordinated by a tridentate bis(2-pyridylmethyl)amine group of tpen, which completes the distorted octahedral geometry around the rhenium centers with a “ C_3N_3 ” donor set for Re(1) and an “ O_3N_3 ” donor set for Re(2). The *fac*- $\{\text{Re}^I(\text{CO})_3\}^+$ and *fac*- $\{\text{Re}^{\text{VII}}\text{O}_3\}^+$ groups show no unusual structural features as compared to the corresponding derivatives in literatures.^{18–21} The $\text{Re-N}_{\text{amine}}$ distances are somewhat longer than the Re-N_{py} distances for both Re centers, resulted from the sp^3 - and sp^2 -hybridized nitrogen donors, respectively. The structure of **1** also illustrates that the coordination of the *fac*- $\{\text{Re}^I(\text{CO})_3\}^+$ core to the *fac*- $[\text{ReO}_3(\text{tpenH})]^{2+}$ complex does not give significant structural perturbation to the *fac*- $\{\text{Re}^{\text{VII}}\text{O}_3\}^+$ core which is present in the opposite end.

Cyclic Voltammetry. Cyclic voltammogram of **1** (1 mM) in the potential range between -2.00 and $+2.20$ V vs. Ag/AgCl in a 0.1 M $n\text{-Bu}_4\text{NPF}_6\text{-CH}_3\text{CN}$ solution is shown in Figure 2.

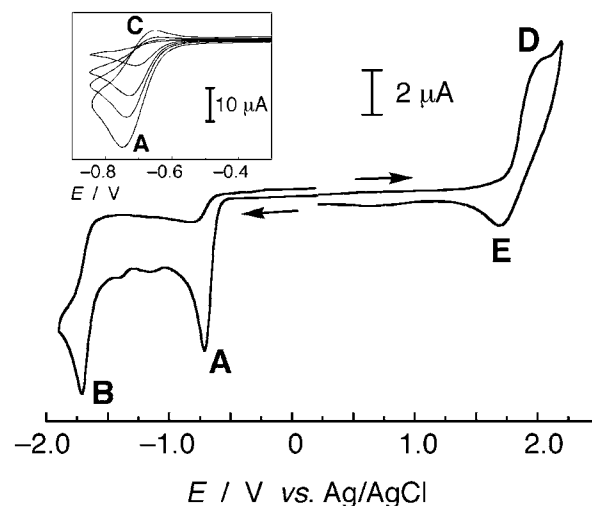


Figure 2. Cyclic voltammogram (CV) of **1** in 0.1 M $n\text{-Bu}_4\text{NPF}_6\text{-CH}_3\text{CN}$ at a scan rate of 0.1 V/s with a process labeling scheme. The inset shows the scan rate dependence (0.1, 0.5, 1.0, and 2.0 V/s) of CVs associated with the first redox process.

On a potential scan from the rest potential (+0.18 V) to the negative direction, two well-defined cathodic peaks, denoted as A and B, are observed at E_p values of -0.72 and -1.71 V. The peak A is irreversible at this scan rate, but at much faster scan rates (inset) a return wave which is denoted as C can be observed at -0.65 V (at 2.0 V/s) when the potential is switched at -0.85 V back to the positive direction, accompanying with a shift of peak A to the negative direction ($\Delta = 0.03$ V upon increase in the scan rate from 0.10 to 2.0 V/s). We attribute the first quasi-reversible couple to the $\{\text{ReO}_3\}^+$ -based redox process, because the parent $[\text{ReO}_3(\text{tpen})]^+$ complex²² displays an irreversible peak at a closely similar potential (-0.70 V) under identical conditions. The second irreversible process can be ascribed to the reduction of either the $\{\text{Re}(\text{CO})_3\}^+$ core, electrochemically-generated $\{\text{ReO}_3\}^0$ core, or an undefined species which is generated upon reduction of **1** during the potential scan.

On a potential scan to the positive direction, an anodic shoulder at +2.02 V, D, and a return peak at +1.73 V with much smaller intensity, E, are observed. This redox wave corresponds most likely to a one-electron oxidation of the $\{\text{Re}(\text{CO})_3\}^+$ core to $\{\text{Re}(\text{CO})_3\}^{2+}$.⁵

4. Conclusion

In this paper, we have described a structurally-determined new coordination type of tpen, which bridges two different metal centers (*fac*- $\{\text{Re}(\text{CO})_3\}^+$ and *fac*- $\{\text{ReO}_3\}^+$) with a κ^3 - κ^3 coordination mode. The bond distances and angles of the *fac*- $\{\text{Re}^{\text{III}}\text{O}_3\text{N}_3\}^+$ center appears to be maintained upon introduction of the *fac*- $\{\text{Re}^{\text{I}}(\text{CO})_3\}^+$ into the dangling arm of the parent complex $[\text{ReO}_3(\text{tpenH})]^{2+}$. Cyclic voltammetric study reveals that complex **1** undergoes irreversible reduction and oxidation which are associated with two unequivalent metal centers involved. In summary, chemical and structural characters of the individual metal centers in **1**, with extreme oxidation states stabilized by two different coordinating ligands (CO and O^{2-}), are essentially unaffected by linking with tpen due most likely to the long-distance, electronically-unconjugated nature of tpen. This characteristics in turn may promise future studies on precise design of geometrical/electronic structures and chemical reactivities of tpen-supported Re and Tc complexes yet prepared.²³ Since the *fac*- $\{\text{Re}^{\text{I}}(\text{CO})_3\}^+$ complexes with a d^6 electronic configuration are, in general, emissive, we are currently studying photoluminescence properties of **1** in the solid state and in solution. Our ongoing study further includes exploration of synthetic ability of $[\text{ReO}_3(\text{tpenH})]^{2+}$ for generating higher-nuclearity clusters by incorporating not only a single metal ion, but also a "metal-oxo-metal" fragment or a metal-metal bonded dimer, which will be reported in due course.

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