X-ray Structure and Electrochemical Properties of a Tpen-Bridged Hetero-Binuclear Complex fac-, fac-[ReVII\(\text{O}_3\)(\(\mu\)-tpen)Re\(\text{V}\)(CO)\text{3}]}(PF\text{6})\text{2}, where Tpen Is \(N,N,N',N'\)-Tetakis(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-\([\text{ReO}_3]\)\text{2} and fac-\([\text{Re(CO)}_3]\)\text{2}, which are bridged by tpen in a \(\kappa^3\)–\(\kappa^1\) coordination mode with a minimal metal–metal interactions (Re\(\text{2+}\)-Re = 7.660(1) Å). Complex 1 undergoes irreversible reduction and oxidation in 0.1 M \(n\)-Bu\(n\)PF\text{6}–CH\text{3}CN, which are associated with the two metal centers, fac-\([\text{ReO}_3]\) and fac-\([\text{Re(CO)}_3]\)\text{2}.

1. Introduction

\(N,N,N',N'\)-tetrakis(2-pyridylmethyl)ethylenediamine (hereafter abbreviated as tpen) affords a versatile array of coordination compounds.\textsuperscript{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.\textsuperscript{2}

We have recently reported synthesis and characterizations of a seven-coordinated rhenium-oxo complex \([\text{ReO}_3\text{(tpen)}]\)\text{2}\text{+} and the one-electron-reduced derivative \([\text{ReVIII}(\text{tpen})]\)\text{2}\text{+}, in which tpen coordinates to the \([\text{ReVII}\text{O}_3]\) with the hexadentate mode,\textsuperscript{3} as well as a rhenium-trioxo complex \([\text{ReO}_3(\text{tpenH})]\)\text{2} which exhibits an unusual \(\kappa^3\)-coordination mode.\textsuperscript{4}

We have found that the dangling bis(2-pyridylmethyl)amine arm in the \([\text{ReO}_3(\text{tpenH})]\)\text{2} complex can coordinate, upon deprotonation, to a single metal center to afford mixed-metal dinuclear complexes. Thus, the reaction of the \([\text{ReO}_3(\text{tpenH})]\)\text{2} complex with \([\text{Re(CO)}_3]\)Br in refluxing CH\text{3}CN afforded a thermally stable dinuclear complex formulated as \([\text{ReO}_3(\text{\(\mu\)}-\text{tpenH})\text{Re(CO)}_3]\)(\text{ClO}_4)\text{2}.\textsuperscript{5} The fac-\([\text{Re(CO)}_3]\)\text{2} coordination unit adds an additional interaction in this tpen tpen complex because of its widespread current interest and development of chemistry associated with this structural motif, including ligand-substitution reactions,\textsuperscript{6,7} photoluminescence,\textsuperscript{8} supramolecular assembly formation,\textsuperscript{9} self-assembled monolayer formation on solid supports,\textsuperscript{10} photocatalytic chemical of CO\text{2},\textsuperscript{11} and therapeutic radiopharmaceuticals.\textsuperscript{12}

In this paper, we describe X-ray structure and electrochemical properties of a PF\text{6}– salt of the \([\text{ReO}_3\text{(tpenH)}\text{Re(CO)}_3]\)(\text{ClO}_4)\text{2}.\textsuperscript{13} This work provides the first structurally-determined example of tpen complexes, in which the tpen bridges two unequivalent metal centers without the support of any additional ligands. Spectroscopic characterizations of 1, including infrared, UV-Vis, and \(^1\text{H}\) NMR spectroscopy, have been reported earlier.\textsuperscript{13}

2. Experimental Section

Materials. The ligand tpen was prepared as described in Reference 13. CH\text{3}CN for electrochemical measurements was distilled from CaH\text{2} under Ar. \(n\)-Bu\(n\)PF\text{6} used as a supporting electrolyte was recrystallized twice from ethanol. All the other chemicals were used without further purifications. Complex \([\text{ReO}_3(\text{tpenH})]\)(\text{ClO}_4)\text{2} was prepared as reported previously.\textsuperscript{14}

Synthesis fac-, fac-[\text{ReO}_3(\text{\(\mu\)}-\text{tpen})\text{Re(CO)}_3](\text{PF}_6)\text{2}. (1). To a CH\text{3}CN solution (20 mL) of \([\text{ReO}_3(\text{tpenH})]\)(\text{ClO}_4)\text{2} (97 mg, 0.11 mmol) was added a CH\text{3}CN solution (5 mL) of \([\text{Re(CO)}_3]\)Br (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 \([\text{ReO}_3(\text{\(\mu\)}-\text{tpen})\text{Re(CO)}_3](\text{ClO}_4)\text{2} was collected by filtration. The PF\text{6}– salt 1 was obtained by metathesis between the Cl\text{O}– salt and NaPF\text{6} in CH\text{3}CN/H\text{2}O.

Diffusion of ethyl ether into a CH\text{3}CN solution of 1 afforded single crystals 1·(CH\text{3}CN)\text{6}(\text{H}_2\text{O})\text{15} suitable for X-ray diffraction study. Yield, 21 mg (15%, based on \([\text{ReO}_3]\)).\textsuperscript{15} Anal. Calcd. for \([\text{C}_2\text{H}_9\text{F}_2\text{N}_2\text{O}_3\text{P}_2\text{Re}_2(\text{CH}_3\text{CN})_6(\text{H}_2\text{O})_{15}]: \text{C}, 29.35; \text{H}, 2.47; \text{N}, 7.64. Found: C, 29.45; H, 2.52; N, 7.81. \(^1\text{H}\) NMR spectrum of 1 (in CD\text{3}CN) was essentially identical to that of \([\text{ReO}_3(\text{\(\mu\)}-\text{tpen})\text{Re(CO)}_3]\)(\text{ClO}_4)\text{2 reported previously.\textsuperscript{16}}

Physical Measurements. \(^1\text{H}\) 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 (\(d = 3 \text{ mm} \)), platinum coil, and Ag/AgCl, respectively. The electrolyte solution was 0.1 M \(n\)-Bu\(n\)PF\text{6}–CH\text{3}CN 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 mm\textsuperscript{3}) were collected on a Rigaku model AFC-7R diffractometer with a Mercury CCD area detector using graphite-monochromated Mo K\(\text{r}\) radiation (\(\lambda = 0.71073 \text{ Å} \)) at 153 K and processed using the Crystal Clear software program.\textsuperscript{17} Final cell parameters were obtained from a least-squares analysis of reflections of \(I > 10I(I)\). 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.\textsuperscript{18} It appeared that the structural similarity of the fac-\([\text{Re(CO)}_3]\)\text{2} and fac-\([\text{ReO}_3]\)\text{2} 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 [ReO$_3$] and [Re(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·(CH$_3$CN)$_{0.85}$(H$_2$O)$_{0.15}$

<table>
<thead>
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<th>Parameter</th>
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<tr>
<td>R1, wR$_2$</td>
<td>0.055, 0.120</td>
</tr>
</tbody>
</table>

R$_1 = \sum|F_o| - |F_c|\sum|F_o|$, wR$_2 = \{\sum w|F_o|^2 - |F_c|^2\}^2/\sum w|F_o|^2$.

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

### 3. Results and Discussion

In our previous study,$^3$ synthesis and spectroscopic properties of a ClO$_4^-$ salt of fac-, fac-[ReO$_3$(µ-tpen)Re(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-[ReO$_3$(µ-tpen)Re(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-(Re$^4$(CO)$_3$)$_2^+$ and fac-(Re$^{110}$O$^3$)$_2^+$ are bridged by tpen with a $\kappa^2$–$\kappa^2$ coordination mode. The Re(1)...Re(2) separation was 7.660(1) Å. This is an unusual structural features as compared to the corresponding derivatives in literatures.$^{18-21}$ The Re–N$_{amine}$ distances are somewhat longer than the Re–N$_{py}$ distances for both Re centers, resulted from the sp$^2$- and sp$^3$-hybridized nitrogen donors, respectively. The structure of 1 also illustrates that the coordination of the fac-[Re(CO)$_3$]$^+$ core to the fac-[ReO$_3$(tpenH)$_2$]$^{2+}$ complex does not give significant structural perturbation to the fac-[Re$^{110}$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-Bu$_4$NPF$_6$–CH$_3$CN solution is shown in Figure 2.

![Figure 1](image1.png)

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

![Figure 2](image2.png)

*Figure 2.* Cyclic voltammogram (CV) of 1 in 0.1 M n-Bu$_4$NPF$_6$–CH$_3$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 20 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 (Δ = 0.03 V) upon increase in the scan rate from 0.10 to 2.0 V/s. We attribute the quasi-reversible couple to the $\{\text{ReO}_3\}^{2+}$-based redox process, because the parent $\{\text{ReO}_3(tpen)\}^{2+}$ complex 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 $\{\text{Re(CO)}_5\}^{2+}$ core, electrochemically-generated $\{\text{ReO}_3\}^{3+}$ core, or an undefined species which is generated upon reduction of I 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 $\{\text{Re(CO)}_5\}^{2+}$ core to $\{\text{Re(CO)}_5\}^{3+}$.

4. Conclusion

In this paper, we have described a structurally-determined new coordination type of tpen, which bridges two different metal centers ($\text{fac-}\{\text{Re(CO)}_5\}^{2+}$ and $\text{fac-}\{\text{ReO}_3\}^{2+}$) with a $\kappa^2-\kappa^3$ coordination mode. The bond distances and angles of the fac-$\{\text{ReO}_3\}^{2+}$ center appears to be maintained upon introduction of the fac-$\{\text{Re(CO)}_5\}^{2+}$ into the dangling arm of the parent complex $\{\text{ReO}_3(tpen)\}^{2+}$. Cyclic voltammetric study reveals that complex I undergoes irreversible reduction and oxidation which are associated with two unequivocal metal centers involved. In summary, chemical and structural characters of the individual metal centers in I, with extreme oxidation states stabilized by two different coordinating ligands (CO and O$^-$), are essentially unaffected by linking with tpen due most likely to the long-distance, electronically-unconjugated nature of tpen. This characteristic 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. Since the fac-$\{\text{Re(CO)}_5\}^{2+}$ complexes with a d$^1$ electronic configuration are, in general, emissive, we are currently studying photoluminescence properties of I in the solid state and in solution. Our ongoing study further includes exploration of synthetic ability of $\{\text{ReO}_3(tpen)\}^{2+}$ 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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References


(17) The small extent (15%) of disorder was observed in the crystal as mentioned in the experimental part. The discussion of structure is based on the major component.


(22) The deprotonated form, $\{\text{ReO}_3(tpen)\}^{2+}$, was prepared in situ by adding an equivalent mole of triethylamine into the solution of $\{\text{ReO}_3(tpen)\}^{2+}$.

(23) For example, Y. Sasaki, an article in this issue.