A Novel Seven-coordinate Technetium(IV) Complex: Synthesis and Characterization of $[TcO(tpen)]^{2+}$ (tpen = *N*,*N*,*N*′,*N*′-Tetrakis(2-pyridylmethyl)ethylenediamine)

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(Received September 7, 2005; CL-051150)

The 1:1 reaction of $[TcOCl_4]^-$ with tpen (tpen = *N*,*N*,*N*′,*N*′-tetrakis(2-pyridylmethyl)ethylenediamine) led to the formation of $[TcO(tpen)]^{2+}$ which is the first example both of seven-coordinate technetium(IV) and oxotechnetium(IV). The coordination geometry of the Tc(IV) ion is a monocapped trigonal prism.

The coordination chemistry of oxotechnetium complexes which are the mononuclear mono-oxo technetium has attracted much interest, because of radio-pharmaceutical utilization.[1] A large number of oxotechnetium complexes with various donor elements have been synthesized and it has been recognized that almost of the oxotechnetium complexes take their oxidation state +5 and five-coordinate square pyramidal or six-coordinate octahedral structures.[1] Recently, several seven-coordinate rhenium complexes have been prepared by the 1:1 reaction of various oxorhenium(V) with polydentate polypyridyl ethylenediamine ligands.[2] These complexes are interesting in structural chemistry as well as in rich substitutable and redox activity.[2] Among the technetium compounds, several seven-coordinate structures have been found.[3] The most of these seven-coordinate complexes were found as Tc(III).[3a–3g] While the higher oxidation state than +3 are still limited to two structural types in the technetium complexes.[3h,3i] One example is the Tc(VII) nitridoperoxo complex $[\{TcN(O_2)_2\}_2(oxalate)]$.[3h] The other is the mono-oxo Tc(V) $[Tc^{V}O(edta)]^-$ which has only been reported about the crystallographic study, no other properties have been available.[3i] The study about the relation of the structure and properties between technetium and rhenium in the seven-coordinate complex having the higher oxidation state is still unexplored. As our part of goal to develop the coordination chemistry of the technetium complexes, it is interesting to study about the structure and properties of the seven-coordinate technetium complex with high oxidation state. Thus, we decided to investigate whether the reaction of oxotechnetium(V) with the polydentate polypyridyl ethylenediamine ligand is an appropriate method to produce the seven-coordinate structure for technetium. The reaction was found to give $[Tc^{IV}O(tpen)]^{2+}$ ($[\mathbf{1}]^{2+}$) which is the first example both of seven-coordinate technetium(IV) and oxotechnetium(IV) complex. In this paper, we wish to report the formation, characterization, and spectroscopic and redox properties of $[\mathbf{1}]^{2+}$.

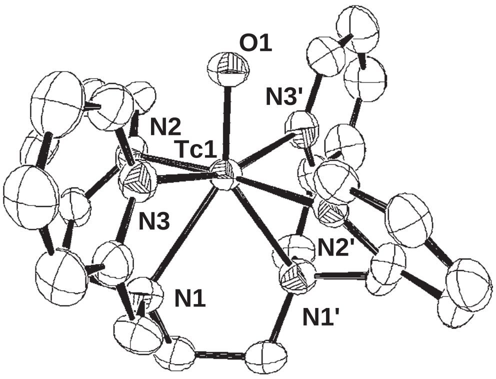

Figure 1. A perspective view of the complex cation of $[\mathbf{1}](ClO_4)_2\cdot(CH_3)_2CO$ with labeling scheme. Hydrogen atoms are omitted for clarity.

Treatment of ethanol solution of $((n\text{-}C_4H_9)_4N)[^{99}TcOCl_4]$ with tpen in a 1:1 molar ratio at room temperature gave a brown solution, from which the seven-coordinate technetium complex ($[\mathbf{1}](ClO_4)_2$; 44% yield) was isolated by adding an aqueous solution of $NaClO_4$.[4] The reaction condition to produce $[\mathbf{1}]^{2+}$ is milder than those of the seven-coordinate rhenium complexes. In case of the rhenium complex, the preparation of $[Re^{IV}O(tpen)]^{2+}$ required to heat to reflux for 10 h in ethanol by using $Cs_2[Re^{V}OCl_5]$ as the starting material.[2a] A facile reaction of $((n\text{-}C_4H_9)_4N)[Tc^{V}OCl_4]$ with tpen in ethanol at room temperature is responsible to the substitution lability of technetium and rhenium ion. Slow evaporation of acetone/toluene solution for $[\mathbf{1}](ClO_4)_2$ provided brown crystals suitable for X-ray analysis.[5] The divalent structure in $[\mathbf{1}]^{2+}$ (Figure 1) indicates that the oxidation state of the Tc ion is +4 (d^3), and a magnetic moment of 1.86 μ_B using the Evans method[6] in CD_3CN at 293 K suggests that the electronic configuration of the d-orbitals for $[\mathbf{1}]^{2+}$ is $(d_{xy})^2(d_{xz},d_{yz})^1(d_{x^2-y^2})(d_{z^2})$ which follows the ordinary ordering of the d-orbitals for oxometal complexes.[7] In $[\mathbf{1}]^{2+}$, six nitrogen atoms of tpen and a terminal oxygen atom are coordinated to the Tc atom to form a seven-coordinate monocapped trigonal prism with the capping oxygen atom. The four pyridyl nitrogen atoms are located at the equatorial positions to Tc=O bond (O–Tc–N(py) = 80.8(2) and 92.4(2)°) and the two aliphatic nitrogen atoms (N1 and N2) are nearly *trans* position of Tc=O bond (O–Tc–N(amine) = 144.2(1)°). The displacement of the Tc atom from the mean plane that consists of four nitrogen atoms of the pyridyl moiety is 0.152(5) Å, indicating that the pyridyl nitrogen atoms and the technetium atom are almost coplanar. The bond distances of Tc–N(py) (2.164(5) and 2.221(5) Å) are within the range of the known Tc–N(py) bond distances,[1d] while the Tc–N1 distance (2.368(6) Å) is ca. 0.2 Å longer compared with the equatorial Tc–N(py) distances owing to the *trans* influence of the Tc=O bond. The Tc^{IV}=O bond length (1.746(7) Å) in $[\mathbf{1}]^{2+}$ is longer than Tc^{V}=O distance (1.593(8)–1.73(2) Å) of the known oxotechnetium(V) complexes,[1b] because of the lower oxidation state of $[\mathbf{1}]^{2+}$. The fact that the Tc^{IV}=O stretching vibration band of $[\mathbf{1}]^{2+}$ (851 cm^{-1}) appears smaller wave number than that of Tc^{V}=O (890–1025 cm^{-1}) supports the long Tc^{IV}=O bond. The overall geometry of $[\mathbf{1}]^{2+}$ is very similar to that of the seven-coordinate rhenium complex, $[Re^{IV}O(tpen)]^{2+}$.[2a] The

Tc–N(amine) bond distance (2.368(6) Å) of $[\mathbf{1}]^{2+}$ is somewhat shorter than the Re–N(amine) lengths (2.395(4) Å) of $[\mathrm{Re^{IV}O(tpen)}]^{2+}$, suggesting that the *trans* influence of the oxo ligand on Tc(IV) functions weaker compared with that on Re(IV).

The electrochemical study of $[\mathbf{1}]^{2+}$ was performed in 0.1 M $((n\text{-}C_4H_9)_4N)PF_6$–acetonitrile solution by the cyclic voltammetry. A reversible one electron redox couple was observed at $E_{1/2} = +0.83$ V vs Ag/AgCl (+0.38 V vs $\mathrm{Fc/Fc^+}$). This redox wave is assignable to Tc(IV/V) process. The redox potential of Tc(IV/V) for $[\mathbf{1}]^{2+}$ is the most positive among the known oxotechnetium complexes, besides the significant difference of the Tc(IV/V) redox potential exists between $[\mathbf{1}]^{2+}$ and the known oxotechnetium complexes of which the Tc(IV/V) processes show the ranges from −0.44 to −1.02 V vs Ag/AgCl.[8] The Tc(IV/V) redox potential of $[\mathbf{1}]^{2+}$ shifts 0.52 V more positive than that of the rhenium(IV) congener $[\mathrm{Re^{IV}O(tpen)}]^{2+}$ (Re(IV/V) = +0.31 V vs Ag/AgCl),[2a] suggesting that the metal-centered orbitals of $[\mathbf{1}]^{2+}$ are stabilized compared with those of the rhenium complex. In the known oxotechnetium and oxorhenium complexes having the same ligands and coordination geometry, the redox potentials of the oxotechnetium complexes were observed 0.19–0.52 V more positive than those of the oxorhenium analogues.[8] Thus, the difference of the redox potential between $[\mathbf{1}]^{2+}$ and the oxorhenium congener is one of the largest among the oxotechnetium and oxorhenium complexes.

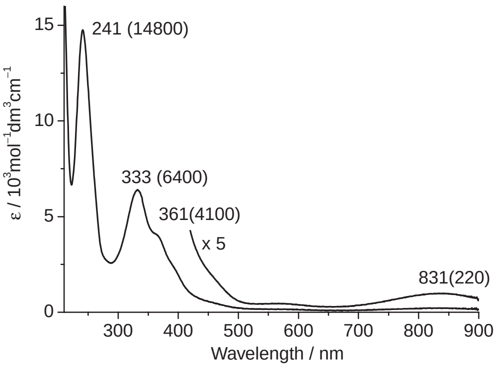

Figure 2. Electronic absorption spectra for $[\mathbf{1}](\mathrm{ClO_4})_2$ in acetonitrile.

Electronic absorption spectrum of $[\mathbf{1}]^{2+}$ in acetonitrile (Figure 2) shows weak transition bands in the visible region.[4] The peak position of the band at 831 nm in $[\mathbf{1}]^{2+}$ assignable to d–d transition is similar at 836 nm[2a] in $[\mathrm{Re^{IV}O(tpen)}]^{2+}$, suggesting that the ligand field splitting of the d-orbital of the technetium(IV) and the rhenium(IV) in the seven-coordinate structure resembles each other. Intense bands (361 and 333 nm) are assignable to charge transfer origin.[4] The peak maxima of these charge transfer bands of $[\mathbf{1}]^{2+}$ shift to higher energy than those of the Re(IV) analogue (428, 381, and 361 nm).[2a] It seems that the stabilization of the technetium-centered orbitals causes to give larger MLCT transition energy compared with that of $[\mathrm{Re^{IV}O(tpen)}]^{2+}$.

In the present study, the first seven-coordinate Tc(IV) complex $[\mathrm{TcO(tpen)}]^{2+}$ was found from the reaction of $[\mathrm{TcOCl_4}]^-$ with tpen, which implies that treatment of the oxometal complex with hexadentate polypyridyl ethylenediamine ligand is a suitable method to synthesize the seven-coordinate complex. Interestingly, $[\mathrm{TcO(tpen)}]^{2+}$ was the first example of the oxotechnetium complex possessing Tc(IV). The synthesis of the seven-coordinate complexes with Tc(V) is currently underway.

Financial supports from Foundation Osaka University Supporters Association and from Sasakawa Grants for Science Fellows (SGSF) of The Japan Science Society are gratefully acknowledged. We are grateful to Dr. H. Miyake and Dr. H. Sugimoto of Osaka City University for valuable discussion.

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4 Anal. Found: C, 42.71; H, 3.98; N, 11.14; Tc, 13.80%. Calcd for $\mathrm{C_{26}H_{28}N_6O_9Cl_2Tc}$: C, 42.29; H, 3.82; N, 11.38; Tc, 13.41%. The elemental analysis of Tc was performed by using the radioactivity measurement with a liquid scintillation counter. Electronic absorption spectrum in acetonitrile [$\lambda_{\max}$/nm (ε/mol^{-1} dm^3 cm^{-1})]: 831 (220), 569 (100), 361 (sh 4100), 333 (6400), 241 (14800).

5 Crystal data for $[\mathbf{1}](\mathrm{ClO_4})_2\cdot 2(\mathrm{CH_3})_2\mathrm{CO}$, fw 852.61, orthorhombic, space group *Aba*2, $a = 12.546(1)$ Å, $b = 25.351(4)$ Å, $c = 11.584(2)$ Å, $V = 3684.3(9)$ Å^3, $Z = 4$. $D_{\mathrm{calcd}} = 1.537$ g cm^{-3}, $\mu(\mathrm{Mo\,K\alpha}) = 5.98$ cm^{-1}, $T = 296$ K, $R1 = 0.043$ ($wR2 = 0.138$) for 1723 unique reflections with a goodness-of-fit of 1.06. Data were collected on a Rigaku AFC7R diffractometer with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å). The structure was solved by direct methods and refined by the SHELX-97 program. All calculations were performed by using TEXSAN.

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Published on the web (Advance View) November 8, 2005; DOI 10.1246/cl.2005.1624