# Synthesis and Structure of Nitridotechnetium(V) Complex of Tetradentate Amine Oxime $[TcN(pnao)(H_2O)]^+$

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Nitridotechnetium complex with a tetradentate amine oxime ligand PnAO (propylene amine oxime; 3,3,9,9-tetramethyl-4,8-diazaundecane-2,10-dione dioxime) was synthesized and its structure was determined by X-ray crystallography.

Knowledge of the technetium chemistry is limited in comparison with that of adjacent transition metals such as Mn, Mo, Ru, and Re, because all of the technetium isotopes are radioactive. The long-lived $^{99}Tc$ ($t_{1/2}$ = 2.1 × $10^5$ y) is an isotope to be used for the synthesis and structural characterization of technetium compounds. Until now, a number of studies have been carried out on technetium complexes including oxotechnetium complexes with the $Tc^V$=O core.[1] Recently, chemical and structural properties of technetium complexes with Tc ≡ N triple bonds have attracted much attention not only in coordination chemistry, but also in nuclear medicine.[2] Although the $[Tc^V{\equiv}N]^{2+}$ core is isoelectronic with the $[Tc^V{=}O]^{3+}$ core, the Tc ≡ N bond is inactive toward hydrolysis and substitution reactions in contrast to the Tc=O bond.[3] Furthermore, it is interesting to compare the structure of nitridotechnetium complexes having tetradentate chelate ligands with that of oxotechnetium analogues. For the $N_4$-type ligand PnAO, the structure has been determined only for the oxo-technetium complex.[4] In this paper, we report the structural properties of the $^{99}$TcN-PnAO complex, $[Tc^VN(pnao)(H_2O)]^+$.

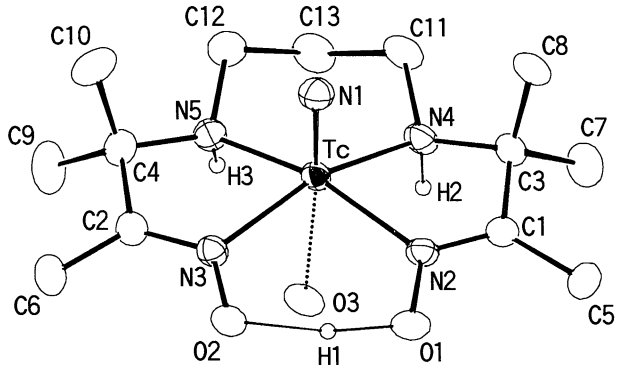
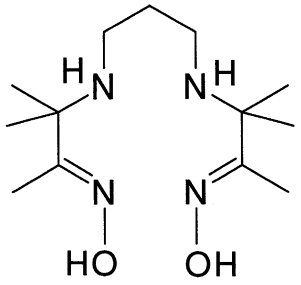



**Figure 1.** Structure of the complex cation $[TcN(pnao)(H_2O)]^+$. Selected bond distances (in Å): Tc-N1 1.610(5); Tc-N2 2.055(3); Tc-N3 2.065(4); Tc-N4 2.094(4); Tc-N5 2.113(4); Tc-O3 2.481(4); N2···N3 3.141(6); N2···N4 2.623(5); N3···N5 2.586(5); N4···N5 3.154(6); O1···O2 2.720(5). Selected bond angles (in deg): N1-Tc-N2 101.9(2); N1-Tc-N3 102.8(2); N1-Tc-N4 98.9(2); N1-Tc-N5 100.5(2); N1-Tc-O3 176.0(2); N2-Tc-N3 99.4(2); N2-Tc-N4 78.4(1); N3-Tc-N5 76.5(2); N4-Tc-N5 97.2(2); N2-Tc-N5 157.6(2); N3-Tc-N4 158.1(2).




Amine oxime ligand, PnAO

The complex TcN-PnAO was synthesized by a ligand exchange reaction. The ligand PnAO was prepared in a similar manner as reported by Lo et al.[5] and Jurisson et al.[6] The starting material $[TcNCl_2(PPh_3)_2]$ (70 mg, 0.099 mmol), prepared in the same way as described by Baldas et al.,[7] was dissolved in 20 $dm^3$ of a $CH_2Cl_2$/ethanol (3:1) mixture. After the pink solution was gently heated to 40 °C, 40 mg of PnAO (0.15 mmol) in 10 $dm^3$ of ethanol was added to the solution. The solution was stirred for 30 min until the color turned yellow, and then evaporated to dryness with a rotary evaporator. The residue was dissolved in water to remove triphenylphosphine, and an aqueous solution of sodium tetraphenylborate was added. The yellow precipitate was filtered, and washed with water and then with ethanol. The compound was recrystallized from an acetone-ethanol solution as ethanol solvate. The ethanol was lost upon drying *in vacuo*, and the product was $[Tc^VN(pnao)(H_2O)][BPh_4]$ (yield 74 %).[8]

TcN-PnAO is stable in aqueous solution, because the UV-Vis spectrum exhibited no practical change even after 3 days. The IR spectrum with absorption at 1061 $cm^{-1}$ indicated the existence of the TcN triple bond in this complex.

Single crystals of the complex suitable for X-ray analysis were grown by slow evaporation of an acetone-ethanol solution. The crystals contain two ethanol molecules in every $[TcN(pnao)(H_2O)][BPh_4]$ and are present as solvates of crystallization. A perspective view of TcN-PnAO, $[TcN(pnao)(H_2O)]^+$, is shown in Figure 1.[9] The coordination around technetium atom is the distorted octahedral; the four N atoms of the PnAO ligand are in the equatorial plane, and the nitrido and $H_2O$ ligands at the apical positions. The Tc atom is placed at 0.399 Å toward the nitrido ligand from the least-squares plane defined by the four N basal atoms.

**Table 1.** Bond distances in nitridotechnetium complexes having an aqua ligand in the trans position of the nitrido ligand

| complex | Tc ≡ N / Å | Tc-$O_{trans}$ / Å | Ref. |
|---|---|---|---|
| $[TcN(pnao)(H_2O)]^+$ | 1.610(5) | 2.481(4) | this work |
| $[TcNBr_4(H_2O)]^-$ | 1.599(9) | 2.443(7) | 11 |
| $[TcN(L^1)(H_2O)]^0$ | 1.612(4) | 2.688(4) | 12 |
| | 1.621(4) | 2.947(4) | |
| $[TcN(HL^2)(H_2O)]^+$ | 1.614(2) | 2.560(2) | 13 |

$H_2L^1$ : 1,4,8,11-tetraazacyclotetradecane-5,7-dione.
$H_2L^2$ : 1,4,8,11-tetraazacyclotetradecane-5-one.

The Tc-N1 bond distance, 1.610(5) Å, is consistent with the TcN triple bond distances reported in most of Tc(V)-nitrido complexes.[10,11,12,13] The N1-Tc-O3 arrangement is approximately linear (176.0(2) °), and the Tc-O3 bond (2.481(4) Å) in this complex is fairly lengthened by the strong trans influence of the nitrido ligand. The length does not conflict with that of the nitridotechnetium complexes having an aqua ligand in the trans position of the nitrido ligand (Table 1).[11,12,13]

The distance between two oxime oxygen atoms (O1···O2), 2.720(5) Å, suggests the loss of an oxime proton and the formation of intramolecular hydrogen bond (O···H···O). The O1···O2 distance is rather long in comparison with that in PnAO complexes of Tc=O as well as transition metals such as Co, Cu, Ni, Pd, and Rh. The O···O distances in the latter complexes are 2.409(10)-2.475(4) Å.[4,14]

The Tc-N4 and Tc-N5 bond distances (2.094(4), 2.113(4) Å) are longer than those of the TcO-PnAO complex (1.908(3), 1.917(3) Å). These long distances in TcN-PnAO would imply a weak interaction between the Tc and the $N_{amine}$, because two amine protons of the ligand remain on coordination to Tc in TcN-PnAO, while amine protons are lost in TcO-PnAO.[4,6,15]

## References and Notes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8 $^1$H-NMR (90 MHz, $CDCl_3$) δ 1.54 (6H, s), 1.68 (6H, s), 2.23 (6H, s). Anal. Found: C, 61.63; H, 7.10; N, 9.75; Tc, 13.94%. Calcd for $C_{37}H_{49}BN_5O_3Tc$: C, 61.59; H, 6.84; N, 9.71; Tc, 13.72%.

9 Crystal data for $[TcN(pnao)(H_2O)][BPh_4]\cdot 2C_2H_5OH$; $C_{41}H_{61}BN_5O_5Tc$, *F.W.* = 813.77, triclinic, space group $P\bar{1}$, $a$ = 14.897(2), $b$ = 17.075(3), $c$ = 9.737(1) Å, α = 104.50(1), β = 104.39(1), γ = 62.12(1)°, $V$ = 2094.3(4) Å$^3$, $Z$ = 2, $D_{calcd}$ = 1.29 gcm$^{-3}$, μ(Mo-Kα) = 3.90 cm$^{-1}$. Data were collected on a Rigaku AFC-6A fourcircle diffractometer at room temperature with graphite-monochromated Mo-Kα (λ = 0.71073 Å) radiation. 12210 unique reflections were collected using the ω-2θ scan technique in the range $3°\leq 2\theta \leq 60°$, with 9008 ($|F_o| > 3\sigma(|F_o|)$) used in calculations. The final reliability factors converged $R$ = 0.067 and $R_w$ = 0.096.

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