

# Synthesis of Technetium Complexes in High Oxidation State I: Formation of Nitridotechnetium(VI) $\mu$ -oxo Dimer Complexes with Edta and Edda

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## II. 2. Synthesis of Technetium Complexes in High Oxidation State I: Formation of Nitridotechnetium(VI) $\mu$ -oxo Dimer Complexes with Edta and Edda

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### Introduction

Growing interest has been paid to preparation of nitridotechnetium complexes, because the oxidation state of technetium in nitridotechnetium complexes ranges from +5 to +7 and the nitridotechnetium core ( $\text{Tc}\equiv\text{N}$ ) is stable toward hydrolysis and ligand exchange reactions<sup>1-4</sup>).

The formation of nitridotechnetium complexes like  $[\text{TcNCl}_2(\text{PPh}_3)_2]$  and  $[\text{TcN}(\text{Et}_2\text{dtc})_2]$  was first reported by Kaden *et al.*<sup>5</sup>) and by Baldas *et al.*<sup>6</sup>). The latter authors investigated interconversion between the monomer,  $\mu$ -oxo dimer and di( $\mu$ -oxo) dimer of nitridotechnetium(VI) complexes in aqueous solution<sup>7,8</sup>). They have pointed out that the  $\mu$ -oxo and di( $\mu$ -oxo) dimers are favorably formed under moderate conditions and the monomer tends to be formed only under high acidic conditions in the presence of coordinating anions. The  $\mu$ -oxo dimers shows an intense visible absorption peak in the region around 470-510 nm due to a transition in the linear Tc-O-Tc three center p-bond system. For monomers and di( $\mu$ -oxo) dimers, no absorption peaks are observed in the same region.

We report the synthesis and properties of newly synthesized  $^{99}\text{Tc}^{\text{VI}}\text{N-EDTA}$  and  $^{99}\text{Tc}^{\text{VI}}\text{N-EDDA}$  complexes. The UV-Vis absorption peak of these complexes was found in the same region as that of the  $\mu$ -oxo dimer complexes synthesized by Baldas *et al.*<sup>7,8</sup>). The result suggests that the  $\text{Tc}^{\text{VI}}\text{N-EDTA}$  complex has a Tc-O-Tc structure in the frame.

### Experiental

PREPARATION OF  $\text{Tc}^{\text{VI}}\text{N-EDTA}$ ; SODIUM  $\mu$ -OXO-BIS[(ETHYLENEDIAMINE-N,N,N',N'-TETRAACETATO)NITRIDOTECHNETATE(VI)] PENTAHYDRATE  
 $\text{Na}_4[\text{Tc}_2\text{N}_2(\mu\text{-O})(\text{EDTA})_2] \cdot 5\text{H}_2\text{O}$

The starting material  $[\text{TcNCl}_4]^-$  was prepared in the same manner as described by Baldas *et al.*<sup>11</sup>). Two milliliters of ammonium pertechnetate solution ( $7.60 \times 10^{-2}$  M) was mixed with 10 ml of concentrated hydrochloric acid, and then 1 ml of aqueous solution

containing 0.1 g of sodium azide was added to the mixture. The solution was stirred for 15 min at 50 °C and then evaporated to dryness using a rotary evaporator. The residue was extracted with 10 ml of acetone and the insoluble salts were filtered off. The color of acetone solution obtained was orange.

When 60 mg of Na<sub>2</sub>H<sub>2</sub>edta, dissolved in 2 ml of water, was added to the orange acetone solution, the color of the solution changed immediately to reddish purple and the similar colored precipitate was formed. The precipitate was filtered, washed with acetone, and dried *in vacuo*. The yield of the product was 41.8 mg (55%). The product was recrystallized from a minimum amount of NaClO<sub>4</sub> solution. The addition of ethanol gave fine reddish purple powder which was soluble in water but insoluble in a variety of organic solvents (Found: C, 23.1; H, 3.36; N, 8.25; Tc, 20.7. C<sub>20</sub>H<sub>34</sub>N<sub>6</sub>O<sub>22</sub>Na<sub>4</sub>Tc<sub>2</sub> requires C, 24.0; H, 3.43; N, 8.40; Tc, 19.8%).

#### PREPARATION OF Tc<sup>VI</sup>N-EDDA; $\mu$ -OXO-BIS[(ETHYLENEDIAMINE-N,N'-DIACETATO)NITRIDO-TECHNETIUM(VI)]PENTAHYDRATE [Tc<sub>2</sub>N<sub>2</sub>( $\mu$ -O)(EDTA)<sub>2</sub>] • 5H<sub>2</sub>O

When 30 mg of H<sub>2</sub>edda dissolved in 2 ml dil NaOH solution was added to the acetone solution of [TcNCl<sub>4</sub>]<sup>-</sup> at room temperature, the color of the mixture rapidly changed to dark purple and then a purple precipitate appeared in 15 min. The precipitate collected by filtration was washed with acetone and dried *in vacuo*. The yield of the product was 33.6 mg (65%). The final product was slightly soluble in water, but insoluble in a variety of organic solvents (Found: C, 21.2; H, 4.04; N, 12.6; Tc, 29.5. C<sub>12</sub>H<sub>30</sub>N<sub>6</sub>O<sub>14</sub>Tc<sub>2</sub> requires C, 21.2; H, 4.44; N, 12.4; Tc, 29.1%).

### Results and Discussion

The infrared spectrum of the Tc<sup>VI</sup>N-EDTA complex gave absorption bands at 1041 cm<sup>-1</sup> (Tc=N) and 1634 cm<sup>-1</sup> (C=O). The Tc<sup>VI</sup>N-EDDA complex showed the absorption peaks at 1057 cm<sup>-1</sup> (Tc=N) and 1631 cm<sup>-1</sup> (C=O), indicating the formation of nitridotechnetium complexes of EDTA and EDDA. The atomic ratio of C, H, N and Tc was 10 : 17 : 3 : 1 for the Tc<sup>VI</sup>N-EDTA complex and 6 : 15 : 3 : 1 for the Tc<sup>VI</sup>N-EDDA complex. The ratio of technetium nitrido core to the ligand was one to one for both the complexes.

The Tc<sup>VI</sup>N-EDTA complex showed a reddish purple color in aqueous solution, with an absorption maximum at 504 nm ( $\epsilon=4.94 \times 10^3$  M<sup>-1</sup>cm<sup>-1</sup>). The color of the Tc<sup>VI</sup>N-EDDA complex was purple in aqueous solution, with an absorption maximum at 556 nm ( $\epsilon=2.68 \times 10^3$  M<sup>-1</sup>cm<sup>-1</sup>). Both the complexes were stable in aqueous solution for several hours at an ambient temperature. The absorption peaks of these complexes were found in the same region as the  $\mu$ -oxo dimers synthesized by Baldas *et al.*<sup>7,8</sup>, which can easily distinguish from

the monomer and di( $\mu$ -oxo) dimer these have the absorption below 400nm. The fact suggests that both of the  $\text{Tc}^{\text{VI}}\text{N-EDTA}$  and  $\text{Tc}^{\text{VI}}\text{N-EDDA}$  complexes are  $\mu$ -oxo dimers.

Chappuis *et al.* prepared a  $\text{Tc}^{\text{V}}\text{N-EDDA}$  complex starting from  $[\text{TcNCl}_4]^-$  and  $\text{H}_2\text{edda}$  in a mixture of water and acetonitrile<sup>10</sup>). The UV-Vis spectrum of their product showed no absorption attributed to a  $m$ -oxo dimer. Their spectrum is obviously different from that of the  $^{99}\text{Tc}^{\text{VI}}\text{N-EDDA}$  complex prepared in the present work. There is a difference in the oxidation state of Tc between their complex ( $\text{Tc}^{\text{V}}$ ) and ours ( $\text{Tc}^{\text{VI}}$ ), even though both the complexes were synthesized from the same starting materials. It should be pointed out that the solvents used for preparation of these complexes are different. Although the  $\text{Tc}^{\text{V}}\text{N-EDDA}$  complex was prepared in a mixture of water and acetonitrile Chappuis *et al.*, we used a mixture of water and acetone in preparation of the  $\text{Tc}^{\text{VI}}\text{N-EDDA}$  complex.

Electrophoresis of the  $\text{Tc}^{\text{VI}}\text{N-EDTA}$  complex indicated that technetium species moved toward only the anode side. The electrophoretic patterns observed at pH 4 and 10 were similar as shown in Figure 1. In the electrophoresis of  $\text{Tc}^{\text{VI}}\text{N-EDDA}$ , the technetium species were distributed from the neutral to anionic region. When perchlorate solution was used at pH 10, the fraction of neutral species was smaller than that at pH 4 (Figure 2). These results indicate that the neutral  $\text{Tc}^{\text{VI}}\text{N-EDDA}$  changed to an anionic form in the alkaline solution. The migration distance of the peak of anionic  $\text{Tc}^{\text{VI}}\text{N-EDDA}$  was two thirds of  $\text{Tc}^{\text{VI}}\text{N-EDTA}$ . This fact implies that the negative charge of  $\text{Tc}^{\text{VI}}\text{N-EDTA}$  is larger than anionic  $\text{Tc}^{\text{VI}}\text{N-EDDA}$ .

Consequently, it is conceivable that the  $\text{Tc}^{\text{VI}}\text{N-EDTA}$  and  $\text{Tc}^{\text{VI}}\text{N-EDDA}$  complexes are  $\mu$ -oxo dimers, as shown in Figure 3. Although the  $\text{Tc}^{\text{VI}}\text{N-EDDA}$  complex is essentially a neutral species, the coordinated carboxyl group in the trans position of the nitrido ligands is dissociated by the attack of  $\text{OH}^-$  through the strong trans effects. Namely, the neutral  $\text{Tc}^{\text{VI}}\text{N-EDDA}$  complex is converted into the anionic form of  $[\text{Tc}^{\text{VI}}\text{N-EDDA}]^{2-}$  in an alkaline solution as shown in Figure 4.

In conclusion both the  $^{99}\text{Tc}^{\text{VI}}\text{N-EDTA}$  and  $^{99}\text{Tc}^{\text{VI}}\text{N-EDDA}$  complexes obtained in the present work must be the  $m$ -oxo dimeric complexes.

## References

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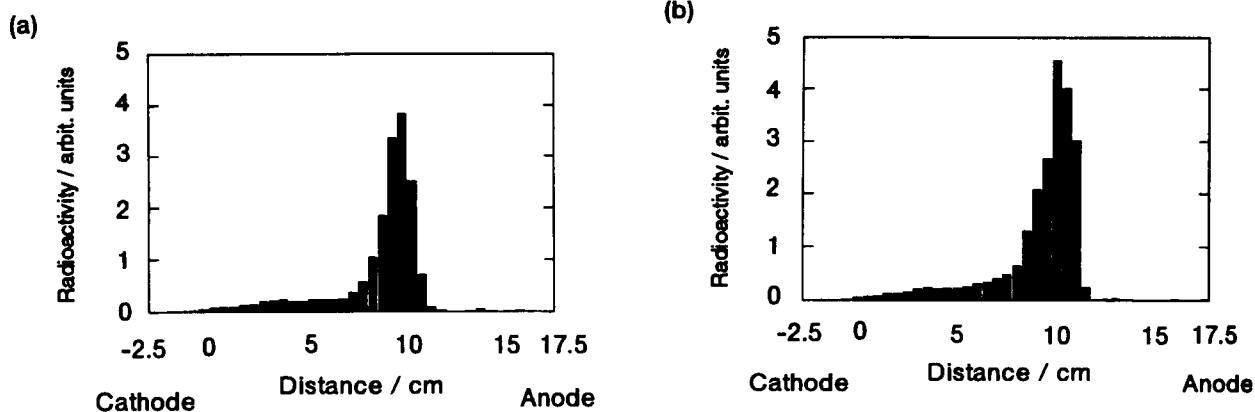


Fig. 1. Electrophoretic patterns of  $Tc^{VI}$ -N-EDTA complex in 0.05M perchlorate solution at (a) pH 4 and (b) pH 10.

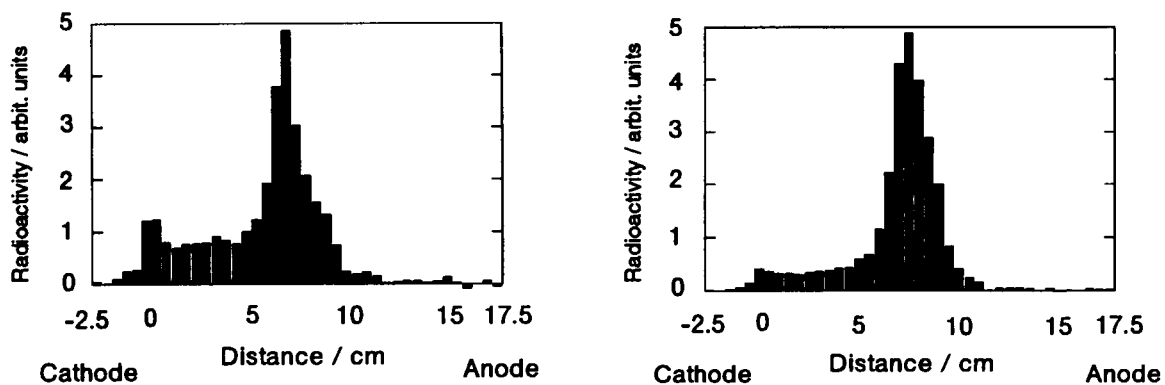


Fig. 2. Electrophoretic patterns of  $Tc^{VI}$ -N-EDDA complex in 0.05M perchlorate solution at (a) pH 4 and (b) pH 10.

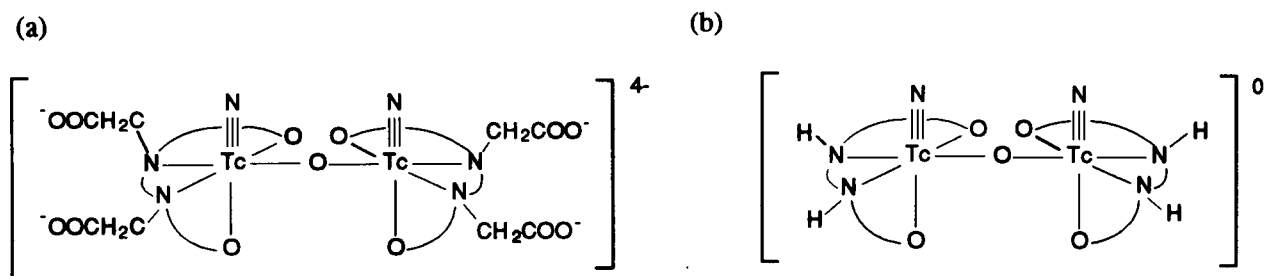


Fig. 3. A possible dimeric form of (a)  $Tc^{VI}$ -N-EDTA and (b)  $Tc^{VI}$ -N-EDDA complexes.

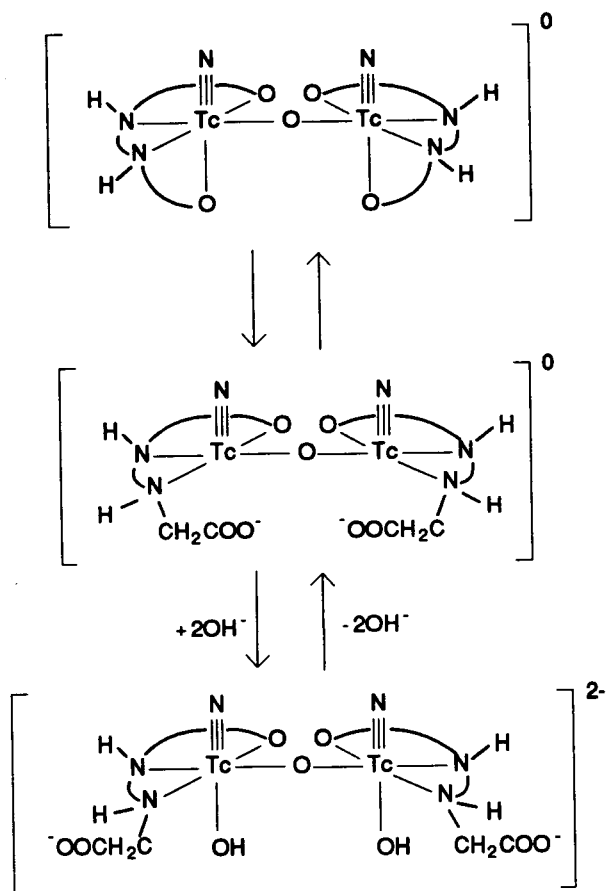


Fig. 4. The conversion of the  $\text{Tc}^{\text{VI}}\text{N}$ -EDDA complex in alkaline solution.