FORMATION OF NITRIDOTECHNETIUM(VI) $\mu$-OXO DIMER COMPLEXES WITH EDTA AND EDDA

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Received 6 September 1994
Accepted 23 September 1994

Reactions of $[^{99}\text{TcCl}_4]^-$ with ethylenediaminetetraacetic acid (EDTA) and ethylenediamine-$N,N'$-diacetic acid (EDDA) in a mixture of water and acetone gave $\text{Tc}^{\text{VII}}\text{N}$-EDTA and $\text{Tc}^{\text{VII}}\text{N}$-EDDA complexes. The infrared spectra of both reaction products showed the existence of the $\text{Tc}=\text{N}$ and $\text{C}=\text{O}$ groups. The elemental analysis indicated the 1:1 TcN-ligand ratio in the EDTA and EDDA complexes. Electrophoresis showed that the $\text{Tc}^{\text{VII}}$-EDTA complex was an anionic species in a perchlorate solution. For the $\text{Tc}^{\text{VII}}$-EDDA complex, neutral and anionic species were formed, depending on the pH of the solution. Formation of the $\mu$-oxo dimer complexes was suggested from the UV-Vis absorption spectra.

INTRODUCTION

Growing interest has been directed toward the preparation of nitridotechnetium complexes, since the oxidation state of technetium in nitridotechnetium complexes ranges

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from +5 to +7 and the nitridotechnetium core (Tc^VII) is stable toward hydrolysis and ligand exchange reactions. The formation of nitridotechnetium complexes like dichloronitridobis(triphenylphosphine)-technetium(V) \([\text{TcNCl}_2(\text{PPh}_3)_2]\) and bis(diethylidithiocarbamato)nitridotechnetium(V) \([\text{TcN}(\text{Et}_2\text{dtc})_2]\) was first reported by Kaden et al. and by Baldas et al., respectively. The latter authors investigated interconversion between the monomer, \(\mu\)-oxo dimer and di(\(\mu\)-oxo) dimer of nitridotechnetium(VI) complexes in aqueous solution. They have pointed out that the \(\mu\)-oxo and di(\(\mu\)-oxo) dimers are favorably formed in moderate conditions and the monomer tends to be formed only under highly acidic conditions in the presence of coordinating anions. The \(\mu\)-oxo dimers showed an intense visible absorption peak in the region around 470-510 nm due to a transition in the linear Tc-O-Tc three-center \(\pi\)-bond system. For monomers and di(\(\mu\)-oxo) dimers, no absorption peaks were observed in the same region.

In a previous paper, we have reported the formation of a new Tc^VIN-EDTA complex, in which the Tc^VIN core to ligand ratio was one to one. The UV-Vis absorption peak of this Tc^VIN-EDTA complex was found in the same region as that of the \(\mu\)-oxo dimer complexes synthesized by Baldas et al. The result suggests that the Tc^VIN-EDTA complex has a Tc-O-Tc structure in the frame. Furthermore, from the reaction of Tc^VIN core with EDDA in a mixture of water and acetone at room temperature, we have obtained a Tc^VIN-EDDA complex with a composition different from the Tc^VIN-EDDA complex synthesized by Chappuis et al. This paper reports the synthesis and properties of newly synthesized \(^{99}\)Tc^VIN-EDTA and \(^{99}\)Tc^VIN-EDDA complexes.