Chemistry of technitium nitrido complexes

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Abstract – The Tc≡N bond is remarkably stable to hydrolysis and technetium nitrido complexes have been prepared in the +5, +6 and +7 oxidation states. Useful starting materials are R[TcNCl$_4$], Cs$_2$[TcNCl$_5$] and nitridotechnetic(VI) acid. Solutions of nitridotechnetic(VI) acid in p-toluenesulphonic acid are of particular interest since these contain a cationic species which is probably a dimeric oxo–bridged technetium nitridoaqua ion. Reaction of Cs$_2$[TcNCl$_5$] with hydrogen peroxide gives Cs[TcN(O$_2$)$_2$Cl], the first example of a transition metal nitridoperoxo complex.

INTRODUCTION

In recent years there has been an upsurge of interest in the coordination chemistry of technetium, largely due to the widespread use of the short–lived ^{99m}Tc isotope ($t_{1/2}$ = 6 h) in diagnostic nuclear medicine. Much work has been directed towards the development of new organ–specific radiopharmaceuticals, in particular for brain and heart imaging (ref. 1). The use of the long–lived ^{99}Tc isotope ($t_{1/2}$ = 2.12 x 10^5 years) allows technetium compounds to be isolated and studied by conventional chemical and spectroscopic techniques. Complexes based on the [Tc^{V}O]$^{3+}$ core are common and are of importance in nuclear medicine (ref. 1). The nitrido ligand (N^{3-}) is isoelectronic with the oxo ligand (O^{2-}) and is a powerful π–electron donor which stabilises transition metals in high oxidation states. The Tc≡N bond has been shown to be remarkably resistant to hydrolysis and to form the basis of an extensive chemistry, particularly in the +5 oxidation state.

Tc(V) AND Tc(VI) NITRIDO COMPLEXES

The Tc(VI) nitrido complexes R[TcNX$_4$] (R = NBu$_4$, AsPh$_4$; X = Cl, Br) and M$_2$[TcNX$_5$] (M = Cs, Rb; X = Cl, Br) are readily prepared by the reaction of ammonium pertechnetate with sodium azide in the refluxing hydrohalic acid followed by precipitation by the cation (ref. 2 and 3). The (AsPh$_4$)[TcNCl$_4$] complex is a useful starting material for the preparation of Tc≡N complexes by ligand exchange in organic solvents. However, the [Tc^{VI}N]$^{3+}$ core is readily reduced to [Tc^{V}N]$^{2+}$ especially by thiolate and phosphine ligands. Thus, for example, reaction of (AsPh$_4$)[TcNCl$_4$] with Na[S$_2$CNEt$_2$] results in the formation of [TcN(S$_2$CNEt$_2$)$_2$].

The reaction of (AsPh$_4$)[TcNCl$_4$] or Cs$_2$[TcNCl$_5$] with KCN and added AsPh$_4$Cl gave yellow water-soluble crystals of (AsPh$_4$)$_2$ trans-[Tc^{V}N(CN)$_4$(OH$_2$)].5H$_2$O in good yield. The geometry of the [TcN(CN)$_4$(OH$_2$)]$^{2-}$ anion is distorted octahedral with a rather short Tc≡N bond distance of 1.596(10) Å and the technetium atom displaced by 0.35 Å above the plane of the four equatorial cyano ligands. The Tc–OH$_2$ bond is exceptionally long at 2.559(9) Å, a manifestation of the strong trans influence of the nitrido ligand. Solutions of Cs$_2$[TcNCl$_5$] in aqueous KCN did not show e.s.r. signals. Addition of conc. HCl resulted in the formation of [TcNCl$_4$]$^-$, [TcNCl$_3$(CN)]$^-$ and [TcNCl$_2$(CN)$_2$]$^-$ which were identified in the e.s.r. spectrum. On standing, the latter two species converted to [TcNCl$_4$]$^-$. These results show that the conversion of the [Tc^{V}N]$^{2+}$ core to the [Tc^{VI}N]$^{3+}$ core may be effected by conc. HCl and that in the case of [TcN(CN)$_4$(OH$_2$)]$^{2-}$ oxidation to Tc(VI) appears to occur only after two of the cyano ligands have been replaced by chloride.

Solutions of Cs$_2$[TcNCl$_5$] in 3 – 11.3 M HCl contain [TcNCl$_4$]$^-$ (λ_{max} 398 nm) as the only technetium species (ref. 4). In 0.5 M HCl a pink species (λ_{max} 540 nm) is formed. Addition of one volume of water to Cs$_2$[TcNCl$_5$] followed by two volumes of 5 M HCl results in the formation of a deep-blue species (λ_{max} 558 nm) which converts to [TcNCl$_4$]$^-$ on standing. E.s.r. studies and magnetic susceptibility measurements in solution by the n.m.r. method indicate that both the pink and blue species are diamagnetic. Hydrolysis of Cs$_2$[TcNCl$_5$] by water results in loss of all five chloride

ions and the formation of a brown precipitate of nitridotechnetic(VI) acid, $[TcN(OH)_3]_n$ (ref. 5). The i.r. spectrum shows peaks at 1054 (Tc≡N) and 708 (Tc–O–Tc) cm^{-1} indicating that the product is probably a polymeric oxo–bridged hydrate.

Nitridotechnetic(VI) acid has proved to be a useful starting material, particularly in cases where competition by chloride is to be avoided. Thus, solutions of $Cs_2[TcNCl_5]$ in 50 percent HF have been shown by e.s.r. spectroscopy to contain $[TcNF_4]^-$, $[TcNCl_4]^-$ and the three mixed species. Solutions of nitridotechnetic(VI) acid in 50 percent HF showed only the presence of $[TcNF_4]^-$. Addition of potassium fluoride resulted in loss of the e.s.r. signal, probably due to the formation of diamagnetic fluoro–bridged dimeric or polymeric species. Similarly, solutions of $Cs_2[TcNCl_5]$ in 10 M potassium fluoride gave no e.s.r. signals. Nitridotechnetic(VI) acid readily dissolves in 1 M p–toluenesulphonic acid (HPTS) to give a yellow solution. Paper electrophoresis using 0.5 M HPTS as the supporting electrolyte has shown the presence a single cationic species and the absence of any neutral or anionic species. This is good evidence for the presence of a technetium nitridoaqua cation in solution. The structure of this cation is being investigated. A possibility is the oxo–bridged dimer $[(H_2O)_4Tc^{VI}N–O–Tc^{VI}N(OH_2)_4]^{4+}$, the $[NTc–O–TcN]^{4+}$ core of which has been established in the cyclic tetramer $(AsPh_4)_4 [Tc_4N_4(O)_2(ox)_6]$ (ox = oxalate). The structure of the anion consists of two $[(ox)Tc^{VI}N–O–Tc^{VI}N(ox)]$ units joined by two quadridentate oxalato ligands (ref. 6).

A Tc(VII) NITRIDOPEROXO COMPLEX

Slow evaporation of a solution of $Cs_2[TcNCl_5]$ in 10 percent hydrogen peroxide resulted in the deposition of yellow–orange crystals of $Cs[Tc^{VII}N(O_2)_2Cl]$, the structure of which was established by X–ray diffraction. This is the first example of a transition metal nitridoperoxo complex and the first peroxo complex to be reported for technetium.

99mTc NITRIDO COMPLEXES

Extensive high performance liquid chromatographic studies have established that ^{99m}TcN–complexes are formed by ligand exchange of $[^{99m}TcNCl_4]^-$ at the ~10^{-8} to 10^{-7} M ^{99m}Tc concentration level. The biological behaviour in mice of ^{99m}TcN–preparations is different to those utilising the same ligand but with stannous chloride or sodium dithionite as the reducing agent for ^{99m}Tc–pertechnetate (ref. 7).

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