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Mixed-ligand Complexes of Technetium VI*. Nitridotechnetium(V) Complexes with Equatorial $\widehat{O\,N\,O}$,P-Coordination Sphere

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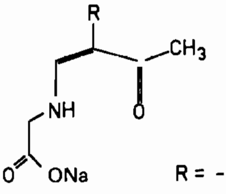
The widespread use of ^{99m}Tc-radiopharmaceuticals (^{99m}Tc: γ-emitter, $E_\gamma = 140$ keV, half-life $t_{1/2} = 6$ h) in diagnostic nuclear medicine has stimulated further development of the coordination chemistry of this man-made element [1–3]. Most chemical studies have been carried out with the long-lived isotope ^{99}Tc (weak β^--emitter, $E_{\max} = 0.3$ MeV, $t_{1/2} = 2.1 \times 10^5$ years) which is available in macroscopic amounts from fission products and can be handled with conventional chemical equipment.

Bidentate, tridentate and tetradentate azomethine ligands have been shown to form various stable complexes with transition metal ions [4, 5]. In this paper we report the synthesis and characterization of nitridotechnetium(V) complexes containing triphenylphosphine and tridentate azomethine ligands (I) derived from glycine.



R = -COOEt, -COCH$_3$

I

Experimental

The ligands sodium *N*-(2-ethoxycarbonyl-3-oxobut(1)en(1)yl)aminoacetate (NaHaeba) and sodium *N*-(2-acetyl-3-oxobut(1)en(1)yl)aminoacetate (NaHaoba) were synthesized from sodium glycinate and 2-(ethoxymethylene)acetoacetate and 3-(ethoxymethylene)pentane-2,4-dione, respectively, in ethanol [6]. TcNCl$_2$(Ph$_3$P)$_2$ was prepared by a standard procedure [7, 8].

All manipulations involving technetium were carried out in a low-level radioactivity laboratory with gloves.

IR spectra were recorded on a UR 20 instrument (Carl Zeiss Jena) with KBr pellets. ^{1}H NMR spectra were measured on a WX 90 DS spectrometer (Bruker) in CDCl$_3$. Fast atom bombardment (FAB) mass spectra were recorded on a VG ZAB-HSQ spectrometer in glycerol matrix. Argon was used as a primary beam gas (8 kV, 100 μA).

TcN(aeba)(Ph$_3$P)

TcNCl$_2$(Ph$_3$P)$_2$ (70 mg; 0.1 mmol) was suspended in 20 ml acetone/methanol (1:1). After addition of 120 mg (0.5 mmol) NaHaeba in 5 ml methanol, the mixture was refluxed for 2 h. The resulting clear orange–red solution was filtered, halved in volume and placed in a refrigerator. A crystalline solid was formed overnight which was filtered off, washed with cold methanol and dried to give orange–red plates. Yield 52 mg (85% based on Tc), melting point (m.p.) 113–115 °C. *Anal.* Calc. for C$_{27}$H$_{26}$N$_2$O$_5$PTc: C, 55.1; H, 4.5; N, 4.8; Tc, 16.8. Found: C, 54.3; H, 4.9; N, 5.2; Tc, 17.0%.

TcN(aoba)(Ph$_3$P)

The complex was synthesized as outlined above to give orange–red crystals. Yield 50 mg (85%), m.p. 151–154 °C. *Anal.* Calc. for C$_{26}$H$_{24}$N$_2$O$_4$PTc: C, 55.9; H, 4.3; N, 5.0; Tc, 17.7. Found: C, 54.9; H, 4.9; N, 4.8; Tc, 17.7%.

Results and Discussion

TcNCl$_2$(Ph$_3$P)$_2$ has been shown to be a convenient starting material for the synthesis of Tc(V)N chelate complexes [8–11]. Using tridentate azomethine ligands of type I, one triphenylphosphine is retained in the equatorial coordination sphere and mixed-ligand complexes of the general formula TcNL(Ph$_3$P) are formed. The azomethine ligands coordinate with deprotonation of the NH group via the $\widehat{O\,N\,O}$ donor set. Similar complexes have been reported recently with tridentate dithiocarbazates possessing an equatorial $\widehat{O\,N\,S}$,P coordination sphere [10].

The products are orange–red, crystalline solids which are easily soluble in chloroform and benzene, and insoluble in water. As solids they are stable in air; a slow decomposition occurs in solution.

The Tc≡N band in the infrared spectra cannot be assigned unambiguously due to many line over-

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TABLE 1. ^1H NMR data[a] of the azomethine ligands and complexes under study

	CH_3(ethyl)	CH_3(C=O)	CH_2(NH)	CH_2(ethyl)	CH	Phenyl
NaHaeba	1.31tr (3H)	2.43s (3H)	3.99s (2H)	4.18qu (2H)	8.08s (1H)	
TcN(aeba)(Ph_3P)	1.31tr (3H)	2.41s (3H)	4.43s (2H)	4.23qu (2H)	8.52s (1H)	7.3–7.8m (15H)
	CH_3	CH_3	CH_2	CH	Phenyl	
NaHaoba	2.30s (3H)	2.43s (3H)	4.04s (2H)	8.07s (1H)		
TcN(aoba)(Ph_3P)	2.37s (3H)	2.39s (3H)	4.43s (2H)	8.34s (1H)	7.3–7.8m (15H)	

[a] Chemical shift relative to TMS, multiplicity (relative intensity).

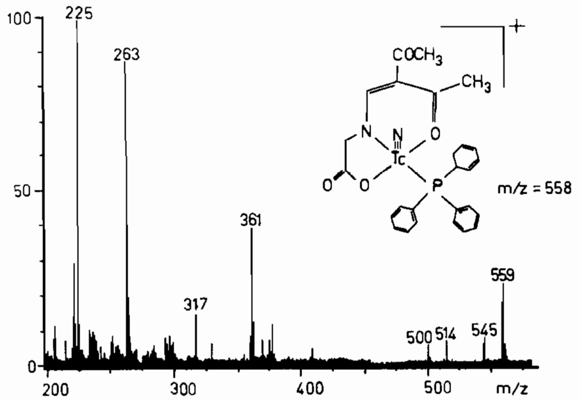

Fig. 1. Molecular ion region of the FAB$^+$ mass spectrum of TcN(aoba)(Ph_3P).

lappings in the 1000–1100 cm^{-1} range. The IR spectrum of TcN(aeba)(Ph_3P) which was ^{15}N-substituted in the nitrido position (^{15}N enrichment: 95%), however, shows an additional band at 1048 cm^{-1}. Assuming a $^{14}N-^{15}N$ bathochromic shift for the compounds under study [12], the Tc≡^{14}N infrared band should be masked by an intense ligand band at 1070 cm^{-1}.

^1H NMR spectral results (Table 1) show a downfield chemical shift of the chelate ring protons in comparison to those of the uncoordinated ligands. This comes close to ^{31}P and ^{13}C chemical shifts in other nitridotechnetium(V) complexes and indicates the electron-withdrawing capacity of the coordinated nitrido ligand.

The FAB mass spectrum of TcN(aoba)(Ph_3P) shows both a molecular ion peak at $m/z = 558$ and a more intense one for the protonated molecular ion, which is evident from the isotope peak $m/z = 559$. The molecular ion region of this spectrum is shown in Fig. 1. Besides the peak of triphenylphosphonium ($m/z = 263$), numerous metal-containing fragments can be detected. They are caused by loss of the nitrido nitrogen (m/z = 544/545, 500, 361) and/or the azomethine ligand (m/z = 375, 361). In the coordinated aoba^{2-} ligand fragmentation takes place in the amino acid part by loss of CO_2 (m/z = 514, 500). Further fragmentations yield the metal-containing fragment $[TcC_6H_7NO_2]^+$ ($m/z = 225$). A surprising result in the mass spectrometric fragmentation of the compound under study is the cleavage of the Tc≡N bond. In other types of nitridotechnetium(V) complexes with bidentate $\widehat{SS}$-, $\widehat{SSe}$- and $\widehat{SN}$-donor ligands the loss of the nitrido ligand occurs only with less abundance [1, 11, 13].

Finally, it should be noted that mixed-ligand complexes of the present type offer the possibility to synthesize numerous derivatives by variation in the molecular frame of the ligands. With this, the polar and lipophilic properties of the complex molecules can be controlled within a wide range and corresponding ^{99m}Tc complexes possibly represent a potential for new radiopharmaceuticals.

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