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Mixed-ligand complexes of technetium
Part XI*. Nitridotechnetium complexes with tri- and tetradentate azomethines. X-ray molecular and crystal structure of [*N*-(2-ethoxycarbonyl-3-oxo-but-1-en(1)yl)-2-aminophenolato](triphenylphosphine)nitridotechnetium(V), TcN(ecbap)(Ph_3P)

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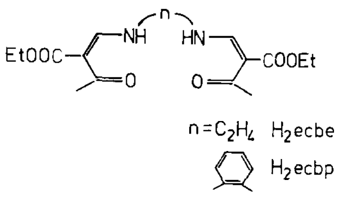
Abstract

Diamagnetic nitridotechnetium(V) complexes with tri- and tetradentate azomethine ligands which possess electron withdrawing groups in their periphery can be prepared starting from $TcNCl_2(Ph_3P)_2$ or (in the case of the tetradentate ligands) $TcNX_4^-$ (X = Cl, Br). The products are air stable compounds which have been characterized by elemental analysis, infrared and UV-Vis spectroscopy, NMR and mass spectrometry. The mixed-ligand complex [*N*-(2-Ethoxycarbonyl-3-oxo-but-1-en(1)yl)-2-aminophenolato](triphenylphosphine)nitridotechnetium(V) ($C_{31}H_{28}N_2O_4PTc$, M_r = 622.5) crystallizes monoclinic in the space group *C2/c*. The coordination geometry is a distorted square pyramid with the nitrido ligand at the apex.

Introduction

The exploration of the coordination chemistry of technetium is strongly connected with the demands of diagnostic nuclear medicine for new ^{99m}Tc radiopharrnaceuticals (^{99m}Tc: y-emitter, E_γ = 140 keV, half-life $t_{1/2}$ = 6 h) [2–4]. Chemical studies are commonly done with the long-lived isotope ^{99}Tc (weak p--emitter, E_{max} = 0.3 MeV, $t_{1/2}$ = 2.12 x 10^5 years) which is available in macroscopic amounts from the fission of uranium and can be handled using conventional laboratory equipment.

Recently, we described the synthesis and characterization of mixed-ligand nitridotechnetium(V) complexes containing azomethine ligands derived from glycine with triphenylphosphine in the equatorial coordination sphere [5]. Now we have extended these studies to other tri- and tetradentate ligands which contain electron withdrawing groups. Such type of ligands are interesting from two different points of view: (i) the electron withdrawing substituents mainly affect the complex formation properties of the ligands [6, 7] and (ii) ligands with ester and/or ether groups are potentially important in the development of new technetium radiopharmaceuticals because of in *vitro* reactivity of such substituents [8–10].



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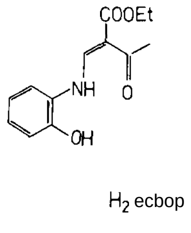

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*For Part X, see ref. 1.

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Experimental

Health precautions

^{99}Tc is only a weak β^--emitter. Normal glassware gives adequate protection; secondary X-rays (bremsstrahlung) play an important role only if one works with larger amounts of technetium. All experiments were carried out in laboratories approved for the use of low-level radioactive material.

Synthesis

The ligands *N,N′*-bis(2-ethoxycarbonyl-3-oxo-but-1-ene(1)yl)-ethylenediamine (**I**, n = C_2H_4; H_2ecbe), *N,N′*-bis(2-ethoxycarbonyl-3-oxo-but-1-ene(1)yl)-1,2-diaminobenzene (**I**, n = *o*-phenylene; H_2ecbp) and *N*-(2-ethoxycarbonyl-3-oxo-but-1-ene(1)yl)-2-aminolphenol (**II**, H_2ecbap) have been described elsewhere [7]. The syntheses of $(Bu_4N)TcNCl_4$ and $TcNCl_2(Ph_3P)_2$ were performed following standard procedures [11, 12].

TcN(ecbe)

(a) 70 mg (0.1 mmol) $TcNCl_2(Ph_3P)_2$ were suspended in acetone/ethanol (1:1, vol./vol.) and 68 mg (0.2 mmol) H_2ecbe added. After addition of 2 drops triethylamine the mixture was refluxed for 2 h. The solvent was removed under vacuum. The oily residue was dissolved in hot ethanol, cooled and diethylether added. After standing overnight a yellow microcrystalline precipitate could be isolated. This purification procedure was repeated twice. Yield: 16 mg (35% based on Tc).

(b) 50 mg (0.1 mmol) $(Bu_4N)TcNCl_4$ were dissolved in 5 ml acetone and, after addition of 68 mg (0.2 mmol) H_2ecbe in 2 ml ethanol and 2 drops triethylamine the mixture refluxed for 2 h. The work-up followed that described in method (a). Yield 18 mg (40%).

Melting point (m.p.) 218–225 °C, *Anal.* Calc. for $C_{16}H_{22}N_3O_6Tc$: C, 42.6; H, 4.9; N, 9.3; Tc, 21.9. Found: C, 43.5; H, 5.3; N, 9.7; Tc 21.5%. ^{1}H NMR (ppm): CH_3(ethyl) 1.21tr (6H); CH_3 2.28s (6H); CH_2 3.95d (4H); CH_2(ethyl) 4.02qu (4H); CH 7.98d (2H).

TcN(ecbp)

The complex was prepared as outlined for TcN(ecbp). Yields: 25 mg (50%) via $(Bu_4N)TcNCl_4$ and 30 mg (60%) via $TcNCl_2(Ph_3P)_2$.

m.p. 215–220 °C. *Anal.* Calc. for $C_{20}H_{22}N_3O_6Tc$: C, 48.1; H, 4.4; N, 8.4; Tc, 19.8, Found: C, 48.8; H, 4.9; N, 7.9; Tc, 18.6%. ^{1}H NMR (ppm): CH_3(ethyl) 1.32tr (6H); CH_3 2.56s (6H); CH_2 4.25qu (4H); phenyl 7.28m (4H), CH 8.40d (2H).

TcN(ecbap)(Ph$_3$P)

70 mg (0.1 mmol) $TcNCl_2(Ph_3P)_2$ were suspended in 10 ml methanol and 100 mg (0.4 mmol) H_2ecbap added. After refluxing for 10 h the reaction mixture was reduced in volume to about 2 ml. The deep green solution was chromatographed on a SEPHADEX LH20 column (20 cm, 1 cm diameter) with ethanol. A first intensely coloured green band is followed by a brown one which contains more than 60% of the radioactivity. The eluate from this second band was reduced in volume to about 3 ml and stored in the refrigerator. Overnight, a yellow-orange product precipitated. After recrystallization from $CHCl_3$/n-heptane orange crystals are formed. Yield: 36 mg (55%).

m.p. 238–240 °C. *Anal.* Calc. for $C_{31}H_{28}N_2O_4PTc$: C, 59.8; H, 4.5; N, 4.8; Tc, 15.9. Found: C, 59.8; H, 4.5; N, 4.3; Tc, 15.7%. ^{1}H NMR (ppm): CH_3(ethyl) 1.31tr (3H); CH_3 2.41s (3H); CH_2(ethyl) 4.23qu (2H); CH_2 4.43s (2H); phenyl 7.3–7.8m (19H); CH8.51s (1H).

Physical measurements

Infrared spectra were recorded for KBr pellets on a UR 20 instrument. ^{1}H NMR measurements were carried out on a Bruker WX 90 DS spectrometer.

Mass spectra were recorded on a VG ZAB HSQ spectrometer. For FAB measurements argon was used as primary beam gas. The ion gun was operated at 8 kV and 100 μA. Glycerol and 3-nitrobenzylalcohol were used as matrices. CID spectra could be obtained with argon as the collision gas.

The technetium contents of the samples were determined by Bremsstrahlung measurements.

X-ray crystal structure determination

Standard experimental and computational details are given elsewhere [13]. The crystal (0.26 × 0.19 × 0.04 mm) which was used for the measurements, at $T = 293$ K with Mo Kα radiation ($\mu = 5.913$ cm^{-1}), was obtained by crystallization from $CHCl_3$/i-PrOH. Unit cell dimensions were obtained from 25 reflections with $5 < \theta < 13°$: $a = 27.480(5)$, $b = 11.4145(10)$, $c = 18.443(3)$ Å; $\beta = 103.22(2)°$; $V = 5631.8(15)$ Å^3; $Z = 8$; $D_x = 1.468$ g cm^{-3}. The space group was determined to be monoclinic; $C2/c$. Intensity data were collected for 27 980 reflections (sphere up to $\theta = 27.5°$), the drift-correction curve showed an intensity decrease to 98%. The semi-empirical absorption correction factors (EMPABS) were in the range 0.93–1.00; the second empirical absorption correction factors (DIFABS) ranged from 0.95–1.09. Of the 6453 unique reflections, 3390 were observed ($R_{\text{marge}} = 0.09$). The position of the Tc atom was easily found from a Patterson synthesis. The rest of the structure was solved by DIRDIF. All non-hydrogen atoms were refined with anisotropic temperature factors. Hydrogen atoms are included on calculated positions. The final conventional agreement factors were $R = 0.047$, $R_w = 0.037$ and S = 1.88 for 3091 observed reflections and 380 variables. The function minimized was $\Sigma w(F_o - F_c)^2$ with $w = 1/[\sigma^2(F_o) + 0.00008F_o^2]$ with $\sigma(F_o)$ from counting statistics. The maximum shift-over-e.s.d. ratio in the last full matrix least-squares cycle was less than 0.024 for atomic positions. Final difference Fourier peaks were less than 0.5 e Å^{-3}. Atomic parameters are given in Table 1. Programs used were EMPABS, DIRDIF, SHELX, DIFABS, PARST; for program references see [13].

TABLE 1. Fractional positional and thermal parameters for $TcN(ecbap)(Ph_3P)$ with e.s.d.s in parentheses

Atom	x/a	y/b	z/c	U_{sq} (Å^2)^a
Tc(1)	0.1924(2)	0.0571(0)	0.4768(0)	2.6(2)
P(1)	0.1172(1)	0.1092(1)	0.3882(1)	2.8(6)
O(1)	0.1564(1)	−0.0723(3)	0.5186(2)	3.4(2)
O(2)	0.2286(1)	0.0891(3)	0.3932(2)	3.4(2)
N(1)	0.1970(2)	0.1715(4)	0.5288(3)	4.2(2)
N(2)	0.2515(2)	−0.0546(4)	0.5178(2)	2.6(2)
C(1)	0.2035(3)	−0.2946(5)	0.6579(4)	4.2(3)
C(2)	0.2539(2)	−0.2934(5)	0.6588(3)	3.6(2)
C(3)	0.2720(2)	−0.2173(5)	0.6124(3)	3.2(2)
C(4)	0.2390(2)	−0.1414(5)	0.5668(3)	2.5(2)
C(5)	0.1878(2)	−0.1434(5)	0.5651(3)	2.8(2)
C(6)	0.1706(2)	−0.2211(5)	0.6124(3)	3.5(2)
C(7)	0.2757(2)	0.0847(5)	0.3958(3)	2.9(2)
C(8)	0.3106(2)	0.0290(4)	0.4526(3)	2.5(2)
C(9)	0.2962(2)	−0.0455(5)	0.5051(3)	2.7(2)
C(10)	0.2884(3)	0.1417(7)	0.3289(4)	5.1(3)
C(11)	0.3641(2)	0.0361(5)	0.4548(4)	3.5(2)
O(3)	0.3846(2)	0.0826(4)	0.4110(2)	5.7(2)
O(4)	0.3912(2)	−0.0169(4)	0.5167(2)	5.1(2)
C(12)	0.4446(2)	−0.0144(7)	0.5266(4)	5.7(3)
C(13)	0.4666(3)	−0.0635(9)	0.6008(4)	7.7(4)
C(14)	0.0599(2)	0.1171(5)	0.4201(3)	2.9(2)
C(15)	0.0632(2)	0.1585(5)	0.4925(4)	4.0(3)
C(16)	0.0205(3)	0.1739(6)	0.5188(4)	5.4(3)
C(17)	−0.0260(2)	0.1489(6)	0.4749(4)	4.8(3)
C(18)	−0.0294(3)	0.1079(6)	0.4045(4)	5.5(3)
C(19)	0.0131(2)	0.0931(6)	0.3772(4)	4.6(3)
C(20)	0.1180(2)	0.2460(5)	0.3373(3)	3.3(2)
C(21)	0.1566(2)	0.3247(5)	0.3574(4)	4.0(3)
C(22)	0.1560(3)	0.4298(6)	0.3187(4)	5.5(3)
C(23)	0.1175(3)	0.4537(7)	0.2602(4)	5.9(3)
C(24)	0.0789(3)	0.3760(7)	0.2393(5)	6.9(4)
C(25)	0.0785(3)	0.2712(6)	0.2776(4)	5.5(3)
C(26)	0.1086(2)	−0.0035(5)	0.3165(3)	3.2(2)
C(27)	0.0859(3)	−0.1087(6)	0.3255(4)	6.1(3)
C(28)	0.0836(3)	−0.1971(7)	0.2726(5)	7.2(4)
C(29)	0.1050(3)	−0.1821(6)	0.2132(4)	5.7(3)
C(30)	0.1283(2)	−0.0796(6)	0.2043(4)	5.2(3)
C(31)	0.1311(2)	0.0096(6)	0.2562(3)	4.2(2)

$^a U_{eq} = \frac{1}{3}\Sigma_i \Sigma_j a_i^* a_j^* \mathbf{a}_i \mathbf{a}_j U_{ij}$.

Results and discussion

Synthesis and characterization

$TcNCl_2(Ph_3P)_2$ has been shown to be a convenient starting material for the synthesis of Tc(V)N chelate complexes [12,14–17]. Using tetradentate ligands of type I the four equatorial ligands are replaced by the azomethine. In the case of the tridentate ligand H_2ecbap one triphenylphosphine is retained in the equatorial coordination sphere. These results are similar to those observed with tri- and tetradentate dithiocarbazates [15] and tridentate Schiff base ligands derived from glycine [5].

The ligands undergo double deprotonation on coordination (two NH protons for type I and OH and NH for type II) to form neutral chelates. Addition of a base increases the rate of the reaction. The same products can also be obtained with the tetradentate ligands H_2ecbe and H_2ecbp starting from $(Bu_4N)TcNCl_4$. This latter technetium(W) complex is reduced during the reaction and finally Tc(V)NL complexes are formed.

The products are yellow or orange and are readily soluble in chloroform and benzene. TcN(ecbe) and TcN(ecbp) are also moderately soluble in ethanol but $TcN(ecbap)(Ph_3P)$ is practically insoluble in this solvent. The compounds are stable in air.

In contrast to other technetium(V) nitrido complexes [11, 12, 14–17] the Tc≡N bands in the IR spectra cannot be assigned unambiguously due to many overlapping vibrations in the 1000-1100 cm^{-1} region. The carbonyl bands of the ligands are not significantly shifted compared with those in the uncoordinated azomethines.

The ^1H NMR spectra of the title compounds are characterized by narrow lines indicating diamagnetism. Due to the strong interaction of the electrons of the nitrido ligand with the metal d_{xz} and d_{yz} orbitals of r-symmetry and the strong u-bonds of the ligands, the energetic separation of the essentially non-bonding d_{xy} orbital containing the two electrons results, giving spin paired complexes. This interpretation follows that which was given for diamagnetic technetium(V) complexes with the TcO moiety [3b]. The NMR signals of the chelate ring protons are downfield shifted in comparison to those in the uncoordinated ligands. This is similar to results obtained for other TcN chelates [5, 14, 16] and may be interpreted by the electron withdrawing capacity of the coordinated nitrido ligand.

The electron impact mass spectra of TcN(ecbe) and TcN(ecbp) show intense molecular ions ($m/z = 451$ and 499) which represent the base peaks in the corresponding spectra. Metal containing fragments are produced by bond cleavages inside the macrocyclic ligand (loss of CH_3CO radicals) and degradation of the substituents on the macrocycle (loss of C_2H_5; OC_2H_5).

In the mass spectrum of TcN(ecbap)(Ph_3P) the base peak ($m/z = 262$) and other intensive fragments are caused by the triphenylphosphine ligand (Fig. 1(a)). Two metal containing fragments can be observed in the electron impact mass spectrum: the molecular ion ($m/z = 622$) and $[M-Ph_3P]^+$ ($m/z = 360$). A quite different picture is given by the MIKE spectrum of mass selected molecular ions of TcN(ecbap)(Ph_3P). The spectrum obtained under metastable conditions (without collision gas, Fig. 1(b)) is dominated by fragmentations of the coordinated chelating ligand:

$m/z = 593$ $[M-{}^{\bullet}C_2H_5]^+$
$m/z = 579$ $[M-CH_3\dot{C}O]^+$
$m/z = 576$ $[M-C_2H_5OH]^+$
$m/z = 549$ $[M-{}^{\bullet}COOC_2H_5]^+$
$m/z = 543$ $[M-{}^{\bullet}COOC_2H_5, -{}^{\bullet}CH_3]^+$
$m/z = 506$ $[M-{}^{\bullet}COOC_2H_5, -CH_3\dot{C}O]^+$
$m/z = 300$ $[M-PPh_3]^+$

The reaction of TcN(ecbap)(Ph_3P) with Me_2PhP in $CHCl_3$ does not result in the formation of TcN(ecbap)(Me_2PhP) but yields the well-known complex $TcNCl_2(Me_2PhP)_3$. The chloro ligands for the formation of this product are abstracted from the solvent chloroform.

X-ray crystal structure of TcN(ecbap)(Ph_3P)

The structure consists of discrete monomeric molecules. The molecular structure together with the crystallographic numbering scheme is given in Fig. 2. Selected interatomic distances and angles are collected in Table 2.

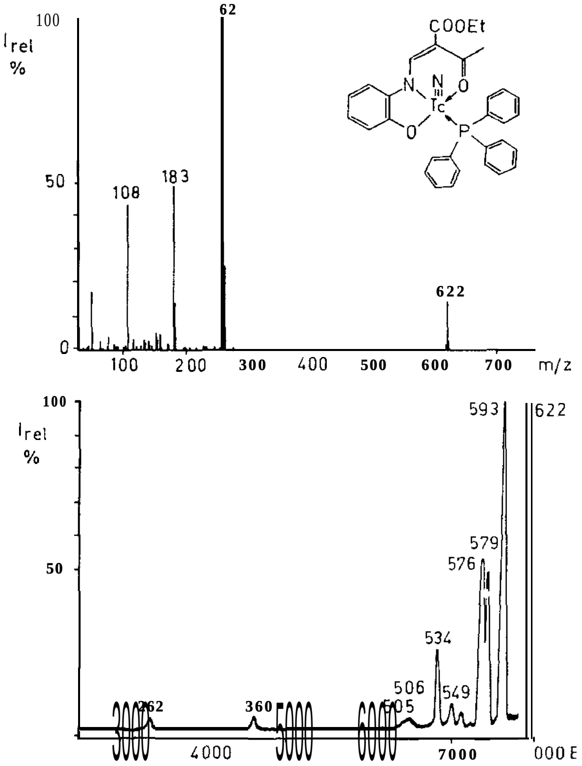

Fig. 1. (a) EI^+ mass spectrum of TcN(ecbap)(Ph_3P) and (b) MIKE spectrum of mass selected molecular ions.

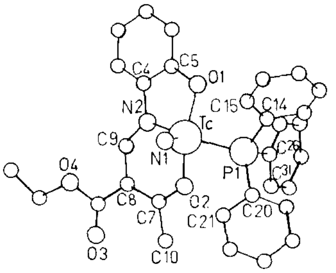

Fig. 2. Pluto plot of the molecular structure of TcN(ecbap)(Ph_3P) and atomic numbering scheme.

The technetium atom is five coordinate with the phosphorus and the ONO donors of the tridentate ligand in the basal plane and the nitrido ligand in the apical position, giving a distorted square-pyramidal environment about the technetium. The metal is displaced by 0.66 Å towards the nitrido nitrogen from the plane defined by the atoms O(l), N(2) and O(2). The same holds true for the phosphorus atom which is placed 0.33 Å out of this plane towards the technetium. This may be caused by steric requirements but may also have electronic reasons due to strong interactions between the metal d_{xy} orbital (which essentially contains the two d electrons) and the charged donor atoms in the chelating ligand. This assumption is confirmed by the fact that N(nitrido)-Tc-P angles (91.3-98.2”) are generally smaller than N(nitrido)-Tc-S(O,N) angles (if the donors are charged) (104.1-110.1”) [15,17–22]. The same trend can be observed for Tc(V) oxo complexes [18].

The Tc(V)–N bond length of 1.605(7) Å falls in the range of similar distances found in other nitrido complexes of technetium(V), 1.591-1.624 Å [15, 17–22] and underlines the multiple bond character of this metal-nitrogen bond. The technetium-(equatorial) donor atom bond lengths are in the range expected [18].

The chelating ligand (with the exception of the ester substituent) is essentially planar. The two oxygen donors of the azomethine together with Tc and the N(1) atom form a plane (deviation less than 0.004 A). The atoms N(l), N(2), P together with Tc have deviations less than 0.04 Å to their least-squares plane. The angle between the two planes is 92.7(1)“. The bonding angles Tc-P-C(Ph) largely deviate from the tetrahedral angle, which reflects a slightly bended bonding of the PPh_3 group. The angle Tc–P–G(Ph_3) is 173.4°, where G(Ph_3) is the centre of gravity of the three phenyl groups. Torsion angles and shortest distances concerning the bonding of PPh_3 groups to Tc are given in Table 3.

TABLE 2. Selected bond lengths (A) and angles (°) of TcN(ecbap)(Ph_3P) with e.s.ds in parentheses

Bond lengths			
Tc-PI	2.398(2)	C7–C8	1.399(7)
Tc–O1	2.027(4)	C8–C9	1.411(8)
Tc-02	2.049(4)	N2–C9	1.306(7)
ToNl	1.608(5)	N2–C4	1.335(7)
Tc-N2	2.067(4)	C4–C5	1.400(8)
O2–C7	1.284(8)	O1–C5	1.342(6)
Bond angles			
N1–Tc–N2	109.6(2)	N1–Tc–O1	110.1(2)
N l-Tc-02	108.6(2)	N l-Tc-P	98.2(2)
Pl-Tc-01	91.2(1)	Pl-Tc-02	86.2(1)
N2–Tc–P	152.2(1)	O1–Tc–O2	141.2(2)
Ol-Tc-N2	79.8(2)	O2–Tc–N2	84.8(2)

TABLE 3. Torsion angles (°) and shortest distances (Å)[a]

Torsion angles	
N(1)–Tc–P–C(14)	−66.6(3)
N(l)-Tc-P-C(20)	58.5(3)
N(1)–Tc–P–C(26)	173.9(3)
N(l)-Tc-P-G(Ph,)	177.9(2)
N(2)–Tc–P–C(26)	−5.7(4)
Shortest distances	
O(2)–C(20)	3.476(7)
O(2)–C(21)	3.315(7)
O(2)-C(26)	3.445(7)
O(2)-C(31)	3.360(7)
N(1)–H(15)[b]	2.742(8)
N(1)–H(21)[b]	2.785(8)

[a] G = Centre of gravity. [b] H(15), H atom bonded on C(15); H(21), H atom bonded on C(21).

Supplementary material

A full list of atomic coordinates and anisotropic thermal parameters (including hydrogen atoms) and F_o–F_c tables are available from author P.T.B. (University of Nijmegen) on request.

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