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Lipophilic Technetium Complexes.
III. Chelate Complexes of Technetium(V) Containing the Tc-nitrido Core*

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Because of the increasing interest in preparation and characterization of new technetium complexes [2, 3], Tc(V)-nitrido compounds are considered as a potential approach to lipid-soluble technetium species.

The first technetium(V)-nitrido complex, bis(diethyldithiocarbamato)nitridotechnetium(V) was reported by Baldas *et al.* [4]. The same compound and a series of phosphine complexes having the Tc≡N core were independently reported by Kaden *et al.* [5]. More recently a series of alkyl varied bis(dialkyldithiocarbamato)nitridotechnetium(V) compounds has been described [6] as well as the first Tc≡N complex having an additional acetonitrile ligand in *trans*-position to the nitrido nitrogen, *trans, trans*-acetonitriledi-isothiocyanato(nitrido)bis(triphenylphosphine)technetium(V) [7].

The aim of the present study is to investigate the ability of the Tc≡N core to form complexes with various coordination spheres. Thus, Tc≡N complexes with the dichalcogeno ligands diphenyldithiophosphinate (ph_2dtpi^-), diisopropyldithiophosphate ($i\text{-}prop_2dtp^-$), diethyldiselenocarbamate (et_2dsc^-), diethylthioselenocarbamate (et_2tsc^-), 2-N-isopropylaminocyclopent-1-ene-1-dithiocarboxylate (i-propcptc$^-$) and maleonitriledithiolate (mnt^{2-}), as well as with the ditertiary phosphine bis(diphenylphosphino)ethan (DPPE) have been synthesized and characterized.

Experimental

Ligands were either prepared as previously [8–11] or obtained commercially. The technetium complexes can be synthesized as described in ref. [4]. Better yields (especially for acid-sensitive and water-insoluble ligands) can be obtained by using $TcNCl_2(Ph_3P)_2$ as precursor [5]. A typical preparation is given for $TcN(ph_2dtpi)_2$.

$TcN(ph_2dtpi)_2$

100 mg $TcNCl_2(Ph_3P)_2$ was stirred for one hour in 10 ml of an acetone/ethanol mixture (1:1 v/v) containing about 1 g of Hph_2dtpi. The resulting clear solution was then halved in volume by vacuum evaporation. After cooling to 0 °C yellow needles were deposited. The crude product was recrystallized from $CHCl_3$/i-propanol.

$[TcN(mnt)_2]^{2-}$ was isolated as tetraethylammonium salt and recrystallized from acetone/i-propanol.

Infrared spectra were recorded in KBr-pellets with an UR 20-instrument and the UV/Vis. spectra with a SPECORD M 40 from Carl-Zeiss-Jena (G.D.R.). NMR measurements were carried out using a WX 90 DS (Bruker spectrospin). EPR spectra were recorded in the X-band using an E-112 spectrometer (Varian, U.S.A.). Tc and selenium analyses were performed by neutron activation analysis.

Results and Discussion

Neutral, anionic and cationic complexes of the general formula $[TcNL_2]^{0,-2,+2}$ (Fig. 1) were obtained by ligand exchange reaction of $TcNCl_2(Ph_3P)_2$ with chelate ligands in acetonic or ethanolic solutions, and also by reduction of pertechnetate with hydrazine and subsequent addition of ligand as described in [4]. The latter procedure involves some problems owing to the lesser stability of the dithiophosphato and selenium containing ligands in acidic media and the water insolubility of Hph_2dtpi and Hi-propcptc, respectively. The yields are almost

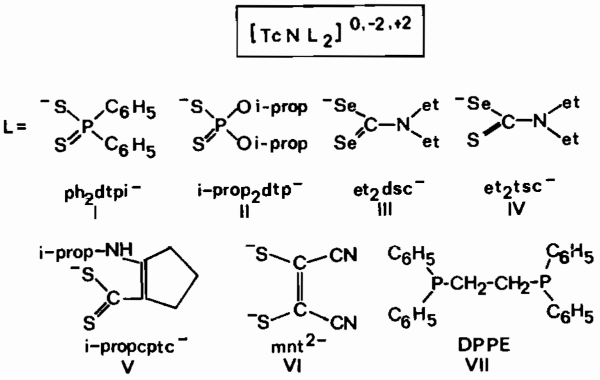

Fig. 1. Neutral, anionic and cationic complexes of the general formula $[TcNL_2]^{0,-2,+2}$.

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*For Part II see ref. 1.

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lower than those of the ligand exchange reactions.

It should be indicated that the Tc≡N core is able to form stable neutral as well as anionic (VI) and cationic (VII) complexes depending on the net charge of the ligands. If chelate ligands were used, no tendency to yield six-coordinated species could be observed.

Analytical data and melting points of the prepared compounds are summarized in Table I. The isolated chelates are yellow to orange crystalline compounds. They are highly soluble in organic solvents like chloroform or methylene chloride, soluble in acetone and benzene and almost insoluble in water and hydrocarbons. Solutions of the nitrido complexes are air-stable for several days.

The extraordinary stability of the Tc–N triple bond is confirmed by the reaction of the Tc(V) complexes with an excess of chlorine or bromine at 50 °C. In the Tc(VI) species obtained the organic ligands are substituted by Cl$^-$ and Br$^-$, respectively, however, the Tc≡N core is maintained. The reason for this could be shown. All chlorine oxidation products show identical EPR-spectra (Fig. 2), which should be assigned to the $[TcNCl_5]^{2-}$ anion [12]. Moderately oxidation conditions gave very complex EPR spectra, probably due to the presence of several mixed ligand species with organic ligands as well as halogenide coordinated.

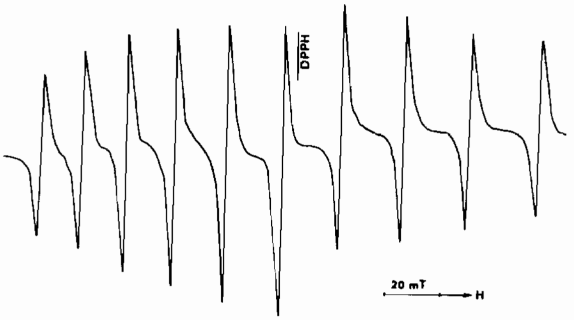

Fig. 2. X-band EPR-spectrum of $[TcNCl_5]^{2-}$ at T = 295 K in $CHCl_3$.

TABLE II. Infrared Spectral Results (cm^{-1}).

Compound	Tc≡N	Others
I	1089	
II	1081	
III	1071	C=N 1529
IV	1075	C=N 1548
V	1076^a	NH 3300
VI	1055	C≡N 2210 C=C 1491
VII	b	

^{a}Overlapped with ligands bands. ^{b}Not detectable unambiguously.

All complexes under study showed strong absorption in the electronic spectra around 370 nm. The presence of the Tc≡N triple bond is confirmed from the infrared spectra in the 1000–1100 cm^{-1} region by a new intensive band (see Table II). In the spectra of the selenium containing complexes a noticeable bathochromic shift of the infrared bands can be seen if the sulphur donors of the dithiocarbamate ligand are substituted stepwise by selenium. This behaviour is as expected and can be explained by the decrease

TABLE I. Analytical Data and Melting Points of the Prepared Tc(V) Nitrido Complexes.

Compound	Melting Point (°C)	Yield (%)	Analytical Data (calc./found) (%)						
			C	H	N	S	P	Se	Tc
I	269	65	47.13	3.27	2.29	20.95	10.14		16.20
			47.02	3.10	2.09	20.93	9.92		15.41
II	132–5	60	26.72	5.19	2.60	23.75	11.50		18.37
			27.71	5.26	2.13	23.61	10.97		17.97
III	276–7	75	20.10	3.35	7.04			52.93	16.58
			19.95	3.27	6.93			52.5	16.83
IV	264–5	80	23.86	3.98	8.35	12.72		31.41	19.68
			23.28	3.92	7.77	12.15		29.9	19.40
V	360	84	42.11	5.46	8.19	24.95			19.30
			39.49	5.12	7.29	23.81			19.21
VI^a	167–8	81	44.10	6.13	15.00	19.60			15.16
			44.07	6.03	14.73	19.80			15.16
VII	216–20	60	63.67	4.90	1.43		12.65		10.10
			61.61	5.28	1.39		11.98		10.06

^{a}As tetraethylammonium salt.

TABLE III. NMR Data of the Tc(V) Nitrido Complexes.

Compound	Chemical shift^a, multiplicity (intensity)	
I^b	^{31}P NMR:	128s
II^b	^{1}H NMR:	CH_3 –1.37d (6H); CH –4.61m (1H)
	^{31}P NMR:	115.9s
III^b	^{1}H NMR:	CH_3 –1.38tr (3H); CH_2 –3.89qu (2H)
IV^b	^{1}H NMR:	CH_3 –1.30tr (3H); CH_2 –3.88qu (2H)
V^c	^{1}H NMR:	CH_3 –1.34d (6H); CH –3.76m (1H); $>CH_2$ –1.93m (2H); $=CH_2$ –2.79m (4H); NH –9.48 (1H)
VII^c	^{1}H NMR:	CH_2 –3.02m (1H); Phenyl –7.32m (5H)
	^{31}P NMR:	38

^{a}In ppm relatively to TMS and H_3PO_4, respectively. ^{b}In $CDCl_3$. ^{c}In dmso-d_6.

of the ligand field from sulphur to selenium. This has been observed previously for a series of geminal dichalcogeno ligand complexes [9, 13, 14]. In the spectrum of $[TcN(DPPE)_2]Cl_2$, the Tc≡N band could not be assigned because of its complexity in the appropriate frequency range.

Further support for this structure is given by the NMR data (Table III). All spectra recorded, with exception of those for $[TcN(DPPE)_2]Cl_2$, show small linewidths, as expected for diamagnetic square-pyramidal complexes of Tc(V) [15]. For $[TcN(DPPE)_2]Cl_2$ a ^{1}H NMR spectrum with linewidths of around 45 Hz was detected as well as a ^{31}P NMR spectrum with a linewidth of about 500 Hz. These spectra are measured in dmso-d_6 and exchange interactions may have caused the observed line broadening. However, the influence of a weak paramagnetism could also be responsible.

Finally, it should be noted that the ^{31}P NMR spectra show a considerable downfield shift of the signals compared with those of other transition metal complexes of the same ligands [16]. In order to investigate the influence of the Tc≡N core on the electronic deshielding of the chelate ring heteroatoms, the well known bis(diethyldithiocarbamato)nitridotechnetium(V) complex was prepaed using a ligand ^{13}C-labeled in CS_2-position (^{13}C-enrichment approx. 30%). The ^{13}C-chemical shift of 218 ppm (relatively to TMS) obtained for the chelate ring C-atoms is the highest ever measured for dithiocarbamato complexes [17]. This confirms the assumption that the strong acceptor behaviour of the nitrido ligand is mainly responsible for the observed strong downfield shift of the chelate ring NMR signals.

The results reported herein demonstrate the ability of the Tc≡N core to form very stable chelates with a broad spectrum of soft donor atom chelate ligands. It would appear useful to include this type of compound in detailed radiopharmacological investigations.

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