

Mixed-ligand Complexes of Technetium

IX.* Oxidative Ligand Exchange Reactions on Tetraphenylarsonium-bis(dithiooxalato)nitridotechnetate(V), $(\text{Ph}_4\text{As})_2[\text{TcN}(\text{dto})_2]$. X-ray Crystal Structure of a Further Modification of $(\text{Ph}_4\text{As})_2[\text{TcN}(\text{dto})_2]$

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Abstract

$(\text{Ph}_4\text{As})_2[\text{TcN}(\text{dto})_2]$ can be prepared starting from TcNCl_4^- or $\text{TcNCl}_2(\text{Ph}_3\text{P})_2$. The compound crystallizes in at least two modifications: as well as a triclinic form (S. F. Colmanet and M. F. Mackay, *Inorg. Chim. Acta*, 147 (1988) 173) a monoclinic one has been found (space group $C2/c$, $Z = 4$, $a = 19.424(3)$, $b = 11.254(2)$, $c = 24.958(3)$ Å, $\beta = 107.68(1)^\circ$; $R = 0.048$). Distances and angles in the complex anions in both modifications are almost identical within experimental error. Oxidation of $[\text{TcN}(\text{dto})_2]^{2-}$ by Cl_2 produces the Tc(VI) complex TcNCl_4^- exclusively, whereas during the Br_2 oxidation technetium(VI) intermediates are generated containing mixed Br/dto coordination spheres which can be monitored easily by EPR spectroscopy.

Introduction

Stimulated by the wide use of $^{99\text{m}}\text{Tc}$ radiopharmaceuticals ($^{99\text{m}}\text{Tc}$: γ -emitter with $E_\gamma = 140$ keV, half-lifetime $t_{1/2} = 6$ h) in diagnostic nuclear medicine [2, 3] the coordination chemistry of this first man-made element entered the centre of interest [4–6]. The availability of the long-lived nuclide ^{99}Tc (β^- -energy of about 0.3 MeV, $t_{1/2} = 2.1 \times 10^5$ years) from fission products enables conventional chemical studies.

Since the first preparation of a nitrido complex of technetium, bis(diethylthiocarbamate)nitridotech-

netium(V), which was published in 1981 [7, 8], a large number of Tc(V) and Tc(VI) compounds with central $\text{Tc}\equiv\text{N}$ units have been prepared and characterized [9, 10–12]. The Tc(V) complexes can be oxidized by excess chlorine or bromine yielding finally $\text{Tc}^{\text{VI}}\text{NCl}_4^-$ and $\text{Tc}^{\text{VI}}\text{NBr}_4^-$, respectively [10, 13–15]. These Tc(VI) products can be detected easily by EPR spectroscopy (Tc^{6+} : 4 d^1 -configuration with $S = \frac{1}{2}$).

In this paper the preparation and X-ray structure of a monoclinic modification of bis(tetraphenylarsonium)-bis(dithiooxalato)nitridotechnetate(V) is described as well as its ligand exchange behaviour when reacting with Br_2 and Cl_2 .

Experimental

Health Precautions

All manipulations were carried out in a fume cupboard with gloves. EPR spectra were measured in sealed glass tubes to avoid contamination.

^{99}Tc is only a weak β^- -emitter and normal glassware gives adequate protection against the low energy β^- -radiation. Secondary X-rays (bremsstrahlung) must be taken into consideration only if working with ^{99}Tc on a larger scale (>20 mg).

Preparation

(a) $(\text{Ph}_4\text{As})_2[\text{TcN}(\text{dto})_2]$ can be prepared following the route of Colmanet and Mackay [16] from $(\text{Ph}_4\text{As})[\text{TcNCl}_4]$, Ph_4AsCl and potassium dithiooxalate.

(b) Another synthesis has been performed via ligand exchange starting from $\text{TcNCl}_2(\text{Ph}_3\text{P})_2$ [7]. Seventy mg (0.1 mmol) of $\text{TcNCl}_2(\text{Ph}_3\text{P})_2$ were

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suspended in 5 ml acetone and 200 mg of K_2dto dissolved in 2 ml H_2O were added followed by 1 ml of a saturated aqueous Ph_4AsCl solution. Overnight deep purple crystals were precipitated. The product was isolated by suction filtration, washed successively with water, methanol and ether, and dried. Yield 92 mg (81% based on Tc). Melting point: 142–144 °C. *Anal.* Found: C, 54.7; H, 3.1; N, 0.9; S, 12.3; Tc, 8.8. Calc. for $C_{52}H_{40}NO_4S_4Tc$: C, 55.8; H, 3.6; N, 1.3; S, 11.5; Tc, 8.8%. IR: $Tc\equiv N$ 1045 cm^{-1} , $C=O$ 1620 cm^{-1} . UV–Vis (λ_{max} (lg ϵ)): 528 nm sh (2.7), 485 (2.8), 312 (4.0), 272 (4.2), 265 (4.2), 260 (4.2).

Oxidation of $(Ph_4As)_2[TcN(dto)_2]$

Samples of 11 mg of $(Ph_4As)_2[TcN(dto)_2]$ were dissolved in 0.5 ml $CHCl_3$ and mixed with 0.5, 1, 2, 3 and 5 equivalents of Br_2 in 0.5 ml $CHCl_3$, respectively. The reaction mixtures were studied by EPR immediately after mixing the reactants, after 3 min and 30 min.

Similar experiments as outlined for Br_2 were carried out using $CHCl_3$ solutions of Cl_2 .

Physical Measurements

UV–Vis spectra were recorded at ambient temperature on a Specord M 40 (Carl-Zeiss-Jena). IR measurements were carried out for KBr pellets on a UR 20 instrument. EPR spectra were recorded at room temperature and at $T = 130$ K in the X-band on an E-112 spectrometer (Varian).

The technetium content of the complex was determined by liquid scintillation measurements.

X-ray Structure Determination

Crystals suitable for diffraction studies were grown by slow evaporation of an acetone/2-propanol solution.

A prismatic crystal with the approximate dimensions $0.18 \times 0.20 \times 0.44$ mm was used for data collection on an Enraf-Nonius CAD-4 diffractometer with graphite monochromatized $Mo K\alpha$ radiation. Lattice parameters were determined by a least-squares treatment of 75 θ values in the range $10 \leq \theta \leq 15^\circ$ using the $Mo K\alpha_1$ wave length with a value of 0.70926 Å. A hemisphere of data with $k \leq 0$ was measured at room temperature (293(1) K). Crystal stability was monitored by periodic measuring of three standard reflections every 10 000 s of scanning time; there was no evidence of crystal deterioration. A change of intensities of standard reflections was observed and a correction applied. Owing to the low value of the linear absorption coefficient no absorption correction was applied.

The technetium atom position was determined by a Patterson map. All remaining non-hydrogen atoms were located from successive Fourier maps. The hydrogen atoms were placed at calculated positions

with isotropic temperature factors of the attached atoms and included as fixed atom contributions in the structure factor calculations. Two blocks matrix least-squares refinement on F magnitudes with anisotropic temperature factors for all non-hydrogen atoms, using the empirical weighting function $w = 0.5 \times W_f \times W_s$ where $W_f(|F_o| < 42.0) = |F_o|/42.0$, $W_f(|F_o| > 75.0) = (75.0/|F_o|)^{1.5}$, $W_f(42.0 < |F_o| < 75.0) = 1.0$ and $W_s(\sin \theta < 0.34) = (\sin \theta/0.34)^3$, $W_s(\sin \theta > 0.36) = (0.36/\sin \theta)^5$, $W_s(0.34 < \sin \theta < 0.36) = 1.0$ to keep $\Sigma w(\Delta F)^2$ uniform.

Atomic scattering factors for hydrogen atoms were taken from Stewart *et al.* [17], for other neutral atoms from Cromer and Mann [18] and dispersion corrections from Cromer and Liberman [19]. All calculations were performed on a DEC-10 computer at RCU-Ljubljana using the XRAY76 [20] system of crystallographic programs.

A summary of the crystal data, data collection and refinement parameters is given in Table 1.

Results and Discussion

The title compound can be prepared from $TcNCl_2 \cdot (Ph_3P)_2$ by ligand exchange. This is an alternative way to the synthesis from $TcNCl_4^-$ described by Colmanet and Mackay [9]. Recrystallization from acetone/2-propanol gives deep purple crystals with a melting point which differs significantly from that of the pale purple crystals which were obtained by the Australian group (215 °C, recrystallized from acetonitrile/ethanol). The reasons for this unusual behaviour are different crystal modifications. Investigation of the pale purple crystals reveals a triclinic space group $P\bar{1}$ with $Z = 2$ (unit cell parameters: $a = 14.225(5)$, $b = 17.778(2)$, $c = 10.993(3)$ Å, $\alpha = 101.52(2)$, $\beta = 111.74(2)$, $\gamma = 100.68(2)^\circ$), whereas the unit cell found for the deep purple modification is monoclinic (space group $C2/c$). The unit cell parameters are given in Table 1. Figure 1 shows a stereo view of the monoclinic unit cell containing four $(Ph_4As)_2[TcN(dto)_2]$ molecules.

The bonding parameters of the roughly square pyramidal complex anion are summarized in Table 2 (the atom numbering scheme is given in Fig. 2). The bond distances and angles show no significant deviations from those in the triclinic modification but in our case only two different Tc–S bond lengths were detected. The technetium–sulphur distances (2.389(1) and 2.398(2) Å) are somewhat longer than found for the triclinic case [9] (2.391(2), 2.390(2), 2.387(2) and 2.378(2) Å) and agree very well with the values for $TcN(et_2dtc)_2$ (2.392(2)–2.405(2) Å [8]) having also a $TcNS_4$ coordination sphere. The Tc–S bond lengths measured for $[TcN(dto)_2]^{2-}$ contradict the assumption that the Tc–S distances in complexes with $R-S^{-1/2}$ ligands as dithiocar-

TABLE 1. Crystal data, data collection and refinement parameters

Formula	C ₅₂ H ₄₀ As ₂ NO ₄ S ₄ Tc
Formula weight	1119.89
Temperature (K)	293(1)
Crystal system	monoclinic
Space group	C2/c (No. 15)
<i>a</i> (Å)	19.424(3)
<i>b</i> (Å)	11.254(2)
<i>c</i> (Å)	24.958(3)
β (°)	107.68(1)
<i>V</i> (Å ³)	5198(2)
<i>Z</i>	4
<i>D</i> _{calc} (Mg m ⁻³)	1.430
Radiation	Mo K α (0.71069 Å)
Linear absorption coefficient (mm ⁻¹)	1.72
θ_{\max} (°)	28
Scan method	ω -2 θ
Scan width (°)	0.7 + 0.3 \times tg θ
Aperture (mm)	2.4 + 0.9 \times tg θ
Scan rate (°/min)	min. 1.03, max. 5.49
Maximum scan time (s)	60
Background	$\frac{1}{4}$ of the scan at each limit
Reference reflections	-10, 0, 2, 3, -5, 3; -3, -5, -3
Intensity change (%)	+2.34
Measured reflections	12703
Averaged reflections	6244
Average, <i>R</i> _{int}	0.028
Observed reflections <i>I</i> > 2.5 σ	2644
Unobserved reflections	3600
<i>R</i>	0.048
<i>R</i> _w	0.043
Contributing reflections ^a	3944
No. variable parameters	290
Scale factor	0.978
Data(<i>m</i>)-to-variable(<i>n</i>) ratio	13.6
$[\Sigma w(\Delta F)^2/(m-n)]^{1/2}$	1.75
Average shift/error	0.023
Maximum shift/error	0.342
Residual density (e/Å ³)	max. 1.6, min. -1.1

^aIncluded are those unobserved reflections for which *F*_c is greater than *F*_o.

bamates are generally larger than those in Tc complexes with R-S⁻¹ ligands [11].

Due to the smaller N-Tc-S angles (104.8(1)°) a shorter distance of the technetium atom from the basal plane of the four sulphur atoms of 0.611 Å arises for the (Ph₄As)₂[TcN(dto)₂] modification under discussion.

The observed small differences should, most probably, be attributed to crystal packing effects. This, however, indicates the problems which arise if solid state structural data are used for the discussion of minor electronic and steric effects in coordination compounds.

The diamagnetic (Ph₄As)₂[TcN(dto)₂] can be oxidized by elemental chlorine or bromine. These reactions occur under ligand exchange to give finally the Tc(VI) complexes TcNCl₄⁻ and TcNBr₄⁻, respectively. Due to the d¹-configuration (*S* = $\frac{1}{2}$) technetium(VI) complexes can be detected easily by EPR spectroscopy [13–15, 21–26]. The room temperature spectra (see Fig. 3(a)) consist of 10-line multiplets due to the interaction of the unpaired electron of the nuclear spin of technetium (⁹⁹Tc: *I* = 9/2). The frozen solution spectra show typical axially-symmetric patterns with ⁹⁹Tc-multiplets in parallel and perpendicular parts (Fig. 3(b)) and can be described by the spin Hamiltonian (1) where *g*_∥, *g*_⊥, *A*_∥^{Tc} and *A*_⊥^{Tc} are the principal values of the \tilde{g} and ⁹⁹Tc-hyperfine interaction tensor \tilde{A}^{Tc} .

$$\mathcal{H}_{\text{sp}} = \beta_e [g_{\parallel} B_z \hat{S}_z + g_{\perp} (B_x \hat{S}_x + B_y \hat{S}_y)] + A_{\parallel}^{\text{Tc}} \hat{S}_z \hat{I}_z + A_{\perp}^{\text{Tc}} (\hat{S}_x \hat{I}_x + \hat{S}_y \hat{I}_y) \quad (1)$$

Recently, we have shown that EPR parameters of [TcNCl_nBr_{4-n}]⁻ complexes (*n* = 0–4) can be used for structural assignment of the mixed-ligand complexes because of a linear dependence on the composition of the ‘equatorial’ coordination sphere [23]. This dependence results from the proportionality which is given in eqn. (2), where $\lambda_{L(i)}$ are the spin-orbit coupling constants of the equatorially coordinated atoms. This proportionality holds true if there are no significant differences concerning the structure and bonding properties of the complexes considered.

$$g, A^{\text{Tc}} \sim \sum_{i=1}^4 \lambda_{L(i)} \quad (2)$$

Deviations (especially in the ⁹⁹Tc coupling constants *a*₀^{Tc} and *A*_∥^{Tc}) have been found if the ligands possess pronounced π -acceptor properties or if chelate ligands are used [24, 25].

The oxidation of [TcN(dto)₂]²⁻ by Cl₂ yields the Tc(VI) complex TcNCl₄⁻ exclusively. Figure 3 shows typical EPR spectra obtained from such reaction mixtures. In all cases, independent of the Cl₂/complex ratio, no mixed-ligand intermediates can be detected by EPR. This result is in contrast to those found for similar reactions of TcN complexes containing four-membered [24] and six-membered chelate rings [27] but comes close to results which were obtained on another five-membered chelate ring complex: [TcN(mnt)₂]²⁻ (mnt = maleonitriledithiolate) [15]. Variation of the Cl₂ amount added results only in a change of the signal intensity of the EPR lines. Apparently, the stability of mixed-ligand Tc(VI) intermediates depends on the chelate ring size. TcN five-membered ring chelates seem to be unable to stabilize mixed-ligand species if they are oxidized by chlorine.

In contrast to the results which were obtained by Cl₂ during the reaction with the weaker oxidant Br₂

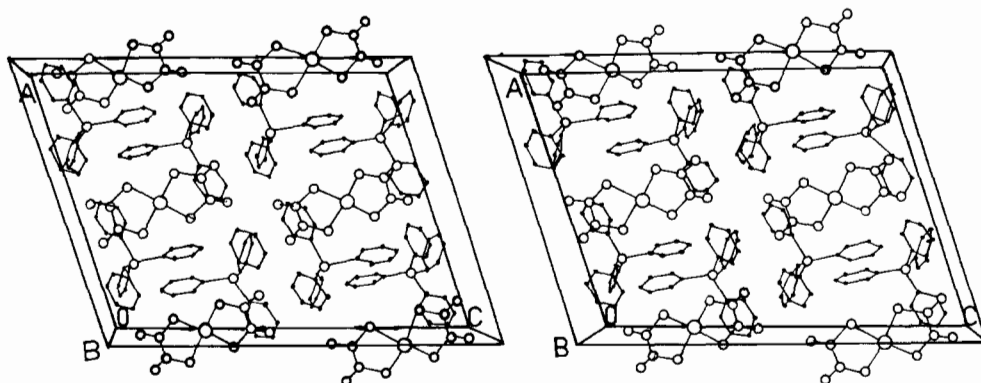


Fig. 1. Unit cell of the monoclinic modification of $(\text{Ph}_4\text{As})_2[\text{TcN}(\text{dto})_2]$.

TABLE 2. Selected bond lengths and angles in $(\text{Ph}_4\text{As})_2[\text{TcN}(\text{dto})_2]$

Bond lengths (Å)			
Tc–N	1.606(7)	S(2)–C(2)	1.745(5)
Tc–S(1)	2.390(1)	C(1)–C(2)	1.558(9)
Tc–S(2)	2.398(2)	C(1)–O(1)	1.211(7)
S(1)–C(1)	1.735(7)	C(2)–O(2)	1.210(9)
Bond angles (°)			
S(1)–Tc–N	104.94(5)	S(1)–Tc–S(2')	86.34(5)
S(2)–Tc–N	104.58(5)	S(2)–Tc–S(1')	86.22(5)
S(1)–Tc–S(2)	86.22(5)	Tc–S(1)–C(1)	106.4(2)
S(1)–Tc–S(1')	150.13(7)	Tc–S(2)–C(2)	106.7(2)
S(2)–Tc–S(2')	150.85(7)		

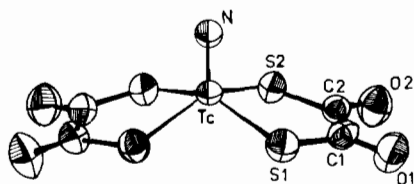


Fig. 2. Complex anion of $(\text{Ph}_4\text{As})_2[\text{TcN}(\text{dto})_2]$.

mixed-ligand species of Tc(VI) with dto/halide coordination sphere could be detected by EPR. The number of individual species and their intensities depend (i) on the $\text{Br}_2/[\text{TcN}(\text{dto})_2]^{2-}$ ratio used and (ii) the reaction time. Figure 4 shows a typical frozen solution EPR spectrum with the signals of five individual species as can clearly be derived from their parallel part lines in the high-field region of the spectrum. The perpendicular part is very complex due to many line overlappings and should not be evaluated.

Table 3 summarizes the spin Hamiltonian parameters of all complexes observed. Species with low g values dominate at short reaction times and low $\text{Br}_2/[\text{TcN}(\text{dto})_2]^{2-}$ ratios. The main product which is obtained with a large Br_2 excess as well as at longer reaction times (30–60 min) is TcNBr_4^- (indicated

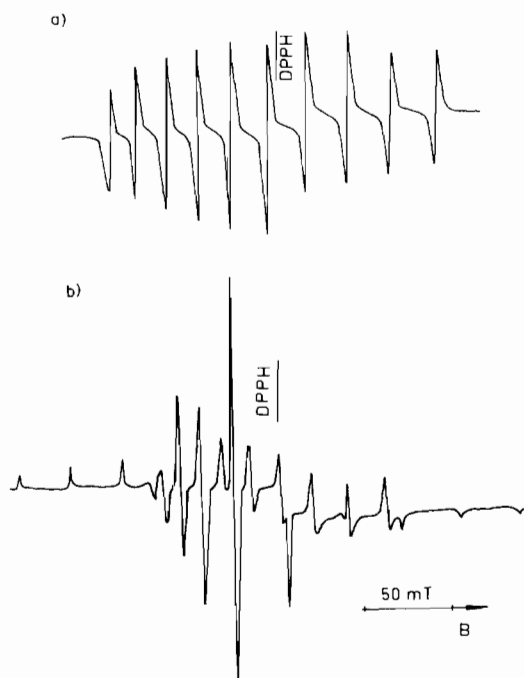


Fig. 3. EPR spectra of an oxidation mixture of $(\text{Ph}_4\text{As})_2[\text{TcN}(\text{dto})_2]$ with Cl_2 ; (a) at room temperature, (b) at $T = 130$ K (solvent: CHCl_3). Only the signals of TcNCl_4^- can be observed.

with 'o'), the EPR parameters of which are well known [15, 23, 26]. The signals of the main products at low $\text{Br}_2/\text{complex}$ ratios are labelled with (□) and (×) and should be assigned to complexes containing mainly sulphur in the coordination sphere as expected from the spin Hamiltonian parameters. Surprisingly, a nearly linear dependence of the g and A^{Tc} values on the number of coordinated halide ions has been found despite the fact that chelating ligands are also present in the coordination sphere. This should mainly be due to the large λ_L difference between bromine (2460 cm^{-1}) and sulphur (382 cm^{-1}). Thus, the EPR parameters of the mixed-ligand complexes appear to be dominated by the Br^-

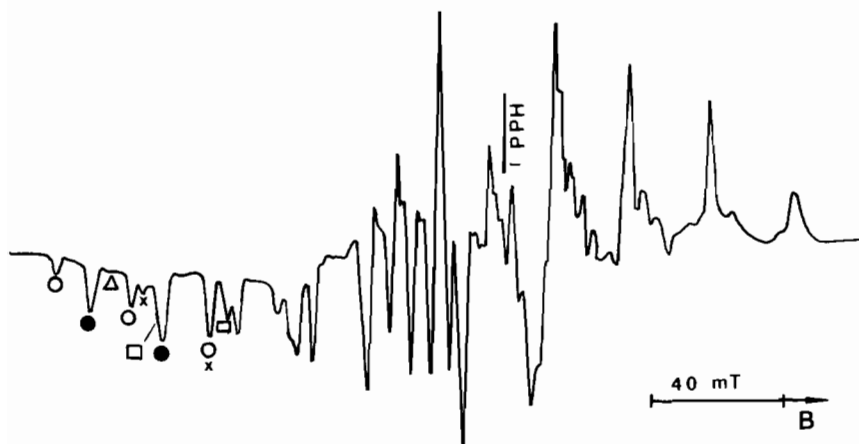


Fig. 4. Frozen solution EPR spectrum of the oxidation products of $(\text{Ph}_4\text{As})_2[\text{TcN}(\text{dto})_2]$ with Br_2 (molar ratio 1:1; reaction time 3 min) in CHCl_3 .

TABLE 3. EPR spectral parameters of the Tc(VI) compounds observed for the reaction of $[\text{TcN}(\text{dto})_2]^{2-}$ with Br_2 (coupling constants in 10^{-4} cm^{-1})^a

Coordination sphere (sign)	g_{\parallel}	$A_{\parallel}^{\text{Tc}}$
S_4 (□)	2.037	206.0
S_3Br (×)	2.073	206.4
S_2Br_2 (△)	2.097	224.4
SBr_3 (●)	2.111	234.4
Br_4 (○)	2.151	249.5

^aExperimental error: $g_{\parallel} \pm 0.003$, $A_{\parallel}^{\text{Tc}} \pm 1.5$.

contributions. The influence of the chelating ligands, which has been found to be important for the EPR values of products generated by Cl_2 oxidation of $\text{TcN}(\text{i-prop}_2\text{dtp})_2$ ($\text{i-prop}_2\text{dtp}^- = \text{O}, \text{O}'\text{-diisopropyldithiophosphate}$) [24], is not significant in bromine oxidation reactions under study.

Finally, it should be noted that all attempts failed to isolate any crystalline mixed-ligand Tc(VI) complex.

Supplementary Material

Atom coordinates, anisotropic thermal parameters, hydrogen atom coordinates and short intermolecular contacts are available from author L.G. (University of Ljubljana) on request.

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