

Synthesis, characterization and reactions of $[\text{Tc}(\text{NS})\text{X}_4]^-$ complexes ($\text{X} = \text{Cl}, \text{Br}, \text{NCS}$)

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Abstract

The anions $[\text{Tc}(\text{NS})\text{X}_4]^-$ ($\text{X} = \text{Cl}, \text{Br}$ or NCS) can be prepared from the reaction of TcCl_6^{2-} and TcBr_6^{2-} , respectively, with trithiazyl chloride, $(\text{NSCl})_3$. The equatorial ligands are kinetically labile and the complexes undergo ligand exchange reactions to form $[\text{Tc}(\text{NS})\text{Cl}_n\text{Br}_{4-n}]^-$ mixed-ligand complexes ($n = 1-3$) or the isothiocyanate analogue $[\text{Tc}(\text{NS})(\text{NCS})_4]^-$. The new compounds have been studied by EPR and the obtained parameters have been used to describe bonding properties. $[\text{Tc}(\text{NS})\text{Cl}_4]^-$ and $[\text{Tc}(\text{NS})\text{Br}_4]^-$ are instable in solution. Spontaneous decomposition results in nitridotechnetium(VI) complexes. The products have been characterized by EPR and X-ray diffraction.

Introduction

Thionitrosyl complexes of technetium are known with the metal in the oxidation states '+1' to '+3' [1–8]. Most of them are synthesized from nitrido complexes and disulfur dichloride. Recently, the formation of *mer*- $\text{Tc}(\text{NS})\text{Cl}_2(\text{L})_3$ ($\text{L} = \text{pyridine}$ or 4-picoline) was described as a result of the reaction of TcNCl_4^- , the pyridine ligand and sodium dithionite [8].

Another facile approach to obtain transition metal thionitrosyl compounds is given with the use of trithiazyl chloride, $(\text{NSCl})_3$ [9]. The ring of the trimeric compound is opened by the interaction with Lewis-acidic metal ions. In dependence on the metal and the reaction conditions in a first step chlorothionitrenes or cyclothiazenes are formed [10]. These compounds can undergo further reactions. In a simple case the cleavage of the sulfur–chlorine bonds occurs and thionitrosyl compounds are formed. In this paper, we describe the isolation of new technetium thionitrosyl complexes following this general synthetic route and show that the

formed $[\text{Tc}(\text{NS})\text{X}_4]^-$ anions are not stable in solution and undergo a secondary reaction to yield nitridotechnetium(VI) compounds.

Experimental

Health precautions

All manipulations with the long-lived radioactive isotope ^{99}Tc (half-lifetime $t_{1/2} = 2.1 \times 10^5$ years) were done in laboratories approved for the use of low levels of radioactive materials. EPR spectra were measured in sealed glass tubes to avoid contaminations. ^{99}Tc is only a weak β^- -emitter ($E_{\text{max}} \approx 0.3$ MeV) and normal glassware provides adequate shielding. Secondary X-rays (bremsstrahlung) are not a significant problem with small quantities but must be taken into consideration if working with ^{99}Tc on a larger scale (≥ 20 mg).

Synthesis

$(\text{Ph}_4\text{As})_2\text{TcCl}_6$ and $(\text{Ph}_4\text{As})_2\text{TcBr}_6$ were prepared by heating ammonium pertechnetate in conc. HCl and 40% HBr, respectively, and subsequent precipitation

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of the complex anions by addition of a concentrated aqueous Ph_4AsCl solution. The products were recrystallized from acetonitrile/xylene.

$(\text{NSCl})_3$ was prepared from NH_4Cl , S_2Cl_2 and Cl_2 according to a standard procedure [11].

$(\text{Ph}_4\text{As})[\text{Tc}(\text{NS})\text{Br}_4]$

130 mg (0.1 mmol) $(\text{Ph}_4\text{As})_2\text{TcBr}_6$ were dissolved in 50 ml CH_2Cl_2 and 9 mg (0.035 mmol) $(\text{NSCl})_3$ were added in CH_2Cl_2 . After standing overnight at room temperature the solvent was removed in vacuum and the solid residue was dissolved in 10 ml acetonitrile. 2 ml 40% HBr were added and the mixture was refluxed for 5 min. Addition of about 20 ml of a 4% HBr led to the separation of a dark red oil which was extracted with CH_2Cl_2 . The extracts were dried with Na_2SO_4 and the solvent was removed. The product was recrystallized from acetonitrile/xylene to yield red-brown microcrystals which were contaminated with a few purple blocks of $(\text{Ph}_4\text{As})\text{TcNBr}_4$ which could be removed manually. Yield 47 mg (55% based on Tc). *Anal.* Found: C, 34.3; H, 2.4; N, 1.2; S, 3.5; Tc, 11.5. *Calc.* for $\text{C}_{24}\text{H}_{20}\text{NSBr}_4\text{AsTc}$: C, 34.0; H, 2.4; N, 1.7; S, 3.8; Tc, 11.7%. IR: N=S 1214 cm^{-1} .

$(\text{Ph}_4\text{As})[\text{Tc}(\text{NS})\text{Cl}_4]$

104 mg (0.1 mmol) $(\text{Ph}_4\text{As})_2\text{TcCl}_6$ were dissolved in 50 ml CH_2Cl_2 and 9 mg (0.035 mmol) $(\text{NSCl})_3$ were added in CH_2Cl_2 . The solution was stirred for 1 h at room temperature and the solvent was removed in vacuum. The residue was dissolved in a minimum amount of acetonitrile and reprecipitated by addition of cold xylene to give a yellow powder. Attempts which were made to recrystallize the complex by slow evaporation of acetonitrile, acetone or CH_2Cl_2 solutions of the complex led to considerable formation of $(\text{Ph}_4\text{As})[\text{TcNCl}_4]$. Yield 25 mg (36% based on Tc). *Anal.* Found: C, 42.5; H, 2.7; N, 2.5; S, 4.5; Tc, 14.3. *Calc.* for $\text{C}_{24}\text{H}_{20}\text{NSCl}_4\text{AsTc}$: C, 43.0; H, 3.0; N, 2.1; S, 4.8; Tc, 14.8%. IR: N=S 1219 cm^{-1} .

$(\text{Ph}_4\text{As})[\text{Tc}(\text{NS})(\text{NCS})_4]$

85 mg (0.1 mmol) $(\text{Ph}_4\text{As})[\text{Tc}(\text{NS})\text{Br}_4]$ were dissolved in 50 ml acetonitrile and 2 ml of a saturated solution of $(\text{NH}_4)\text{SCN}$ were added with stirring. The mixture was refluxed for 15 min and 100 ml water were added. The product was extracted with CH_2Cl_2 . After drying with Na_2SO_4 the solvent was removed and the residue was recrystallized from acetonitrile/xylene. Purple microcrystals. Yield 63 mg (83% based on Tc). *Anal.* Found: C, 45.0; H, 2.7; N, 9.7; S, 20.3; Tc, 13.5. *Calc.* for $\text{C}_{28}\text{H}_{20}\text{N}_5\text{S}_5\text{AsTc}$: C, 44.2; H, 2.6; N, 9.2; S, 21.1; Tc, 13.0%. IR: N=S 1232 cm^{-1} .

Physical measurements

IR spectra were recorded in nujol mulls on a Bruker IFS 88 FTIR spectrometer.

EPR spectra were recorded in the X-band ($\nu \approx 9.3$ GHz) in the temperature range $130 \leq T \leq 295$ K. Acetonitrile and CHCl_3 were used as solvents.

The technetium contents of the samples were determined by bremsstrahlung measurements with a well-type $\text{Na}(\text{Ti})\text{I}$ -scintillator according to a standard procedure [12].

X-ray diffraction

X-ray data of $(\text{Ph}_4\text{As})[\text{TcNBr}_4]$ were collected at $T = 185$ K on an Enraf-Nonius CAD 4 diffractometer.

Results and discussion

$(\text{Ph}_4\text{As})_2[\text{TcX}_6]$ ($\text{X} = \text{Cl}, \text{Br}$) complexes react with trithiazyl chloride in CH_2Cl_2 to give $(\text{Ph}_4\text{As})[\text{Tc}(\text{NS})\text{X}_4]$ compounds. Whereas the yellow $[\text{Tc}(\text{NS})\text{Cl}_4]^-$ anion is rapidly formed with $[\text{TcCl}_6]^{2-}$ as starting material, the use of $[\text{TcBr}_6]^{2-}$ leads to the formation of thionitrosyl technetium(II) mixed-ligand complexes of general formula $[\text{Tc}(\text{NS})\text{Cl}_n\text{Br}_{4-n}]^-$ ($n = 0-4$). The composition of this mixture can easily be estimated using EPR spectroscopy. A typical spectrum is given in Fig. 1. The general feature of the spectrum and spectral parameters will be discussed in detail *vide infra*. Addition of HBr/ acetonitrile to the $[\text{Tc}(\text{NS})\text{Cl}_n\text{Br}_{4-n}]^-$ mixture yields $(\text{Ph}_4\text{As})[\text{Tc}(\text{NS})\text{Br}_4]$ which can be isolated in the form of red-brown needles.

$(\text{Ph}_4\text{As})[\text{Tc}(\text{NS})\text{Br}_4]$ and $(\text{Ph}_4\text{As})[\text{Tc}(\text{NS})\text{Cl}_4]$ react with $(\text{NH}_4)\text{SCN}$ under ligand exchange. From the dark solution deep purple crystals of $(\text{Ph}_4\text{As})[\text{Tc}(\text{NS})(\text{NCS})_4]$ can be isolated.

The tetraphenylarsonium salts of the title complexes are easily soluble in polar organic solvents such as acetonitrile, acetone or CH_2Cl_2 . The use of tetrabutylammonium cations only led to the formation of oils which could not be solidified.

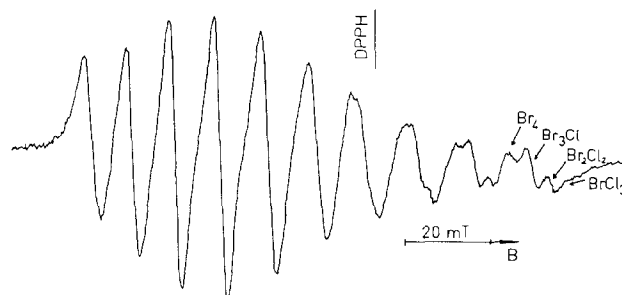


Fig. 1. Room temperature X-band EPR spectrum of the $\text{TcBr}_6^{2-}/(\text{NSCl})_3$ reaction mixture.

In the IR spectra of the compounds the $\nu(\text{NS})$ vibrations can be observed between 1214 and 1232 cm^{-1} which falls into the typical range for the metal thionitrosyl frequencies [9, 10]. In the spectrum of $(\text{Ph}_4\text{As})[\text{Tc}(\text{NS})(\text{NCS})_4]^-$ additional intense bands can be found at 2105 and 2050 cm^{-1} . They can be assigned as $\nu(\text{NS})$ stretching vibrations of the ligands. Their high intensity and the position of the NCS-deformation vibration at a relatively high position (501 cm^{-1}) suggest the coordination of the NCS ligands via nitrogen [13, 14]. This is in accordance with all known NCS^- complexes of technetium and the results of the EPR spectroscopic studies.

The electronic configuration of the title compounds ($4d^5$ 'low spin') with one unpaired electron enables the observation of well-resolved EPR spectra at room-temperature [15]. The spectrum of $(\text{Ph}_4\text{As})[\text{Tc}(\text{NS})\text{Br}_4]^-$ is given in Fig. 2(a). The typical ten-line pattern is due to the interaction of the unpaired electron with the nuclear spin of ^{99}Tc ($I=9/2$). Ligand hyperfine interactions (due to $^{35,37}\text{Cl}$, $^{79,81}\text{Br}$ or $^{14,15}\text{N}$) are not resolved at room temperature. In frozen solutions the spectra (Fig. 2(b) shows that of $(\text{Ph}_4\text{As})[\text{Tc}(\text{NS})\text{Cl}_4]^-$) are characterized by a typical axially-symmetric pattern with

well-resolved ^{99}Tc hyperfine structures in the parallel and perpendicular parts. They can be interpreted using the spin Hamiltonian (1)

$$\hat{H}_{\text{sp}} = \beta_e [g_{\parallel} H_z S_z + g_{\perp} (H_x S_x + H_y S_y)] + A_{\parallel}^{\text{Tc}} S_z I_z + A_{\perp}^{\text{Tc}} (S_x I_x + S_y I_y) + \sum S A^{\text{L}} I^{\text{L}} \quad (1)$$

where $g_{\parallel}$, $g_{\perp}$, $A_{\parallel}^{\text{Tc}}$ and $A_{\perp}^{\text{Tc}}$ are the principal values of the tensors $\tilde{g}$ and $\tilde{A}^{\text{Tc}}$. The obtained values are summarized in Table 1. They were obtained using second order expressions of the perturbation theory [16]. In addition to the ^{99}Tc couplings, in the perpendicular part of the frozen solution spectrum of $(\text{Ph}_4\text{As})[\text{Tc}(\text{NS})\text{Br}_4]^-$, interactions with the ligand nuclei $^{79,81}\text{Br}$ can be observed. In the spectra of $[\text{Tc}(\text{NS})\text{Cl}_4]^-$ and $[\text{Tc}(\text{NS})\text{NCS}_4]^-$ ligand hyperfine interactions due to $^{35,37}\text{Cl}$ or $^{14,15}\text{N}$ could not be resolved. From linewidth considerations these interactions can be estimated to be of a magnitude of about $2\text{--}6 \times 10^{-4} \text{ cm}^{-1}$.

The derived EPR parameters can be used to discuss the bonding situation in the complexes under study using a molecular orbital approach following the formalism of McGarvey [17]. The application on technetium(II) complexes is explained in detail in ref. 15. The molecular orbital of the unpaired electron is of 'in-plane- π -type' and can be described by eqn. (2)

$$\Psi_{\text{MO}} = \beta |4d_{xy}\rangle - \beta' |\Phi_L\rangle \quad (2)$$

where β^2 is a measure for the covalency of the equatorial metal-ligand bonds in this MO and $|\Phi_L\rangle$ describes the linear combination of mainly the p-orbitals of the four equatorial ligands. The bonding parameters which can be obtained from these considerations are summarized in Table 2 together with the values for the corresponding technetium(II) nitrosyl complexes [15]. From the β^2 values a considerable covalency of the equatorial Tc-ligand bonds can be concluded. The large extent of covalency in the NCS and phosphine complexes can

TABLE 1. EPR parameters of $[\text{Tc}(\text{NS})\text{X}_4]^-$ complexes ($\text{X} = \text{Cl}, \text{Br}, \text{NCS}$). Coupling constants in 10^{-4} cm^{-1} ^a

	$[\text{Tc}(\text{NS})(\text{NCS})_4]^-$	$[\text{Tc}(\text{NS})\text{Cl}_4]^-$	$[\text{Tc}(\text{NS})\text{Br}_4]^-$
g_0	1.999	2.021	2.072
$g_{\parallel}$	1.929	1.984	2.105
$g_{\perp}$	2.036	2.041	2.056 ^b
a_0^{Tc}	154.9	168.0	140.8
$A_{\parallel}^{\text{Tc}}$	235.1	264.1	222.9
$A_{\perp}^{\text{Tc}}$	105.3	119.9	99.8 ^b
$A_{\perp}^{\text{L}}$	^c	^c	29

^aExperimental error: $g_{0,\parallel} \pm 0.004$; $g_{\perp} \pm 0.005$; $a_0^{\text{Tc}}, A_{\parallel}^{\text{Tc}} \pm 2.0$; $A_{\perp}^{\text{Tc}} \pm 3.0$. ^b $g_{\perp}$ and $A_{\perp}^{\text{Tc}}$ derived from $g_{\perp} = (3g_0 - g_{\parallel})/2$ and $A_{\perp}^{\text{Tc}} = (3a_0^{\text{Tc}} - A_{\parallel}^{\text{Tc}})/2$. ^cNot resolved.

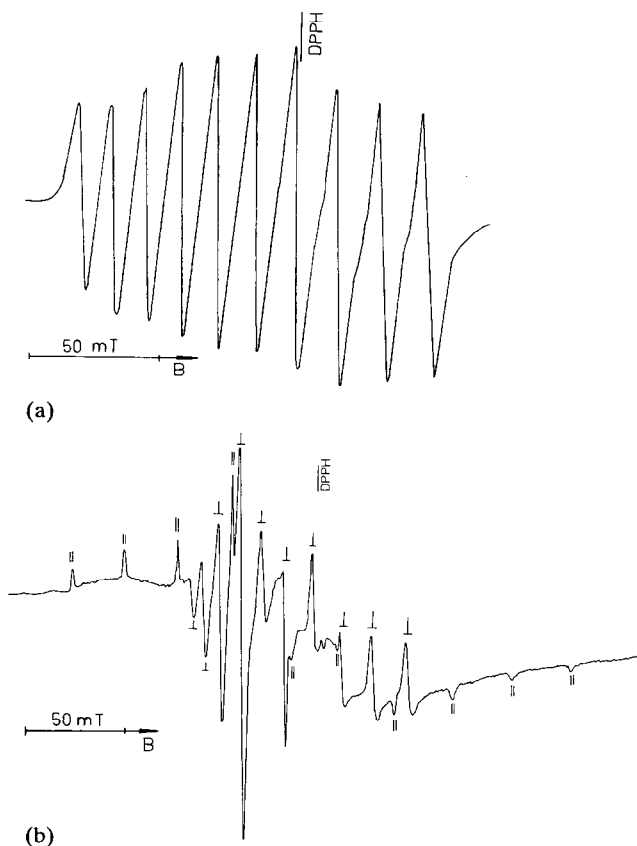


Fig. 2. X-band EPR spectra of (a) $[\text{Tc}(\text{NS})\text{Br}_4]^-$ at room temperature in CH_2Cl_2 and (b) $[\text{Tc}(\text{NS})\text{Cl}_4]^-$ in frozen solution at $T=130 \text{ K}$ in acetonitrile.

TABLE 2. Experimentally derived bonding parameters for nitrosyl [15] and thionitrosyl technetium complexes (K = Fermi-contact interactions in 10^{-4} cm^{-1})

	$[\text{Tc}(\text{NS})\text{Cl}_4]^-$ $[\text{Tc}(\text{NO})\text{Cl}_4]^-$	$[\text{Tc}(\text{NS})\text{Br}_4]^-$ $[\text{Tc}(\text{NO})\text{Br}_4]^-$	$[\text{Tc}(\text{NS})(\text{NCS})_4]^-$ $[\text{Tc}(\text{NO})(\text{NCS})_4]^-$	$[\text{Tc}(\text{NS})\text{Cl}_3(\text{Me}_2\text{PhP})(\text{Me}_2\text{PhPO})]$ [3] $[\text{Tc}(\text{NO})\text{Cl}_3(\text{Me}_2\text{PhP})_2]$ [3]
K	+171.6 +163.8	+154.6 +149.1	+147.9 +145.8	156.0 +140.3
β^2	0.86 0.88	0.82 0.83	0.66 0.72	0.77 0.77

be understood by the π -acceptor behaviour of these ligands.

In analogy to nitrosyl technetium(II) [15, 18] and nitrido technetium(VI) complexes [19, 20] a linear dependence of the EPR parameters is found on the composition of the equatorial coordination sphere. This is illustrated for the isotropic parameters in Fig. 3, which also contains the values of the corresponding nitrosyl compounds. The composition of the equatorial coordination sphere is expressed by the spin-orbit coupling constants λ_L of the donor atoms ($\lambda_N = 76$, $\lambda_{\text{Cl}} = 586$ and $\lambda_{\text{Br}} = 2460 \text{ cm}^{-1}$). The proportionality which is given in eqn. (3)

$$g_0, g_{\parallel}, a_0^{\text{Tc}}, A_{\parallel}^{\text{Tc}} \sim \sum_{i=1}^4 \lambda_{L(i)} \quad (3)$$

holds true if there are no significant differences concerning the structure and bonding properties of the complexes considered and can be used to derive the coordination spheres of species which cannot be isolated. Deviations from the linear dependence (especially of the ^{99}Tc coupling constants a_0^{Tc} and $A_{\parallel}^{\text{Tc}}$) have been found if the ligands possess pronounced π -acceptor properties (e.g. for the NCS^- ligand or phosphines) or if chelate ligands have been used [21].

From eqn. (3) it follows that if the g and/or A parameters of the parent complexes are known the corresponding mixed-ligand complexes can be estimated

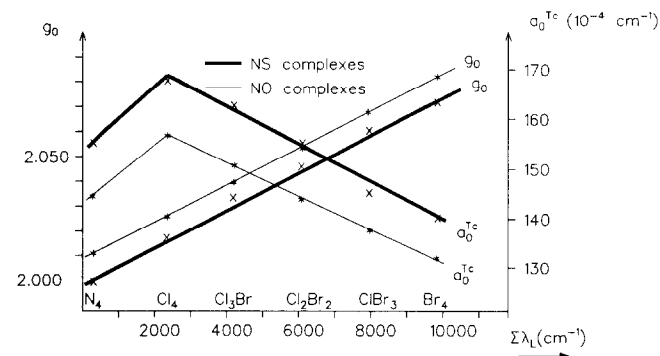


Fig. 3. Dependence of the isotropic EPR parameters of $[\text{Tc}(\text{NS})\text{X}_n\text{Y}_{4-n}]^-$ complexes ($X, Y = \text{Cl}, \text{Br}, \text{NCS}$) on the composition of the equatorial coordination sphere.

from simple relations which are given in eqn. (4), where g and A^{Tc} stand for the principal values g_0 , $g_{\parallel}$, a_0^{Tc} and $A_{\parallel}^{\text{Tc}}$, respectively.

$$g, A^{\text{Tc}}_{[\text{Tc}(\text{NS})\text{Br}_4-p\text{Cl}_p]} \cong \left(\frac{1}{4}\right)(4-p)g, A^{\text{Tc}}_{[\text{Tc}(\text{NS})\text{Br}_4]} + \left(\frac{1}{4}\right)p g, A^{\text{Tc}}_{[\text{Tc}(\text{NS})\text{Cl}_4]} \quad (4)$$

Using this dependence the complex EPR spectrum of the $\text{TcBr}_6^{2-}/(\text{NSCl})_3$ reaction mixture (Fig. 1) can be understood as a superimposition of the spectra of mixed-ligand $[\text{Tc}(\text{NS})\text{Cl}_n\text{Br}_{4-n}]^-$ complexes. An assignment of the signals of the individual complexes is given in the high field part of the spectrum; in the low field part they coincide. Table 3 contains the experimentally derived isotropic spectral parameters g_0 and A_0^{Tc} of the individual mixed-ligand complexes together with the calculated values following eqn. (4). It can be seen that the experimental values are well-reproduced by eqn. (4).

It should be noted that a sixth ligand (halide or solvent) may be coordinated *trans* to the thionitrosyl ligand. However, according to several EPR studies on other d^5 'low-spin' [3, 5, 6, 15, 18] or d^1 systems [19–22] of technetium there will be no noticeable influence on the EPR quantities under discussion.

The title complexes are indefinitely stable as solids. In solution, however, they undergo a marked decomposition by cleavage of the nitrogen-sulfur bond and

TABLE 3. Experimentally obtained^a and calculated (eqn. (4)) isotropic EPR parameters of mixed-ligand $[\text{Tc}(\text{NS})\text{Cl}_n\text{Br}_{4-n}]^-$ complexes (coupling constants in 10^{-4} cm^{-1})

	g_0		a_0^{Tc}	
	Found	Calculated	Found	Calculated
$[\text{Tc}(\text{NS})\text{Br}_4]^-$	2.072		140.8	
$[\text{Tc}(\text{NS})\text{ClBr}_3]^-$	2.060	2.059	145.8	147.6
$[\text{Tc}(\text{NS})\text{Cl}_2\text{Br}_2]^-$	2.049	2.047	155.0	154.4
$[\text{Tc}(\text{NS})\text{Cl}_3\text{Br}]^-$	2.033	2.034	164.8	161.2
$[\text{Tc}(\text{NS})\text{Cl}_4]^-$	2.021		168.0	

^aExperimental error: $g_0 \pm 0.003$; $a_0^{\text{Tc}} \pm 3.0$.

the formation of nitrido technetium(VI) complexes. This reaction can easily be observed by EPR because both oxidation states of technetium (Tc^{6+} : d^1) give well-resolved spectra at room temperature. Typical spectra obtained from the reaction mixture of the chloro complexes are given in Fig. 4. Immediately after the reaction of TcCl_6^{2-} with $(\text{NSCl})_3$ only the signals of $[\text{Tc}(\text{NS})\text{Cl}_4]^-$ can be detected. After standing for 24 h at room temperature more than 80% of this compound have been converted into $[\text{TcNCl}_4]^-$. The reaction can be completed by a short heating of the mixture. The rate of the desulfuration obviously is dependent on the equatorial ligands. Whereas the reaction proceeds rapidly with the chloro complex, with the bromo congener only a few per cent of $[\text{Tc}(\text{NS})\text{Br}_4]^-$ are transferred into TcNBr_4^- on standing at room temperature. The rhombic blocks of $(\text{Ph}_4\text{As})[\text{TcNBr}_4]$ can easily be separated from the bulk of thin needles of $(\text{Ph}_4\text{As})[\text{Tc}(\text{NS})\text{Br}_4]$.

An X-ray diffraction study on the mechanically separated rhombic blocks verifies the product to be $(\text{Ph}_4\text{As})\text{TcNBr}_4$ which crystallizes in the tetragonal space group $P4/n$ with the lattice dimensions (at $T=190\text{ K}$) $a=12.831(5)$, $c=7.920(5)\text{ \AA}$ with $Z=2$. The TcNBr_4^- anion possesses ideal C_{4v} symmetry. An ORTEP plot is shown in Fig. 5. The coordination sphere of the

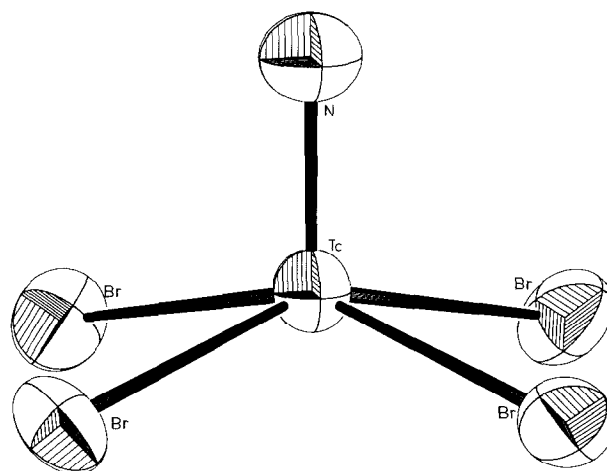
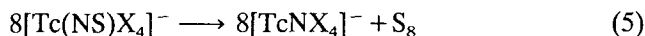


Fig. 5. ORTEP plot of the complex anion in $(\text{Ph}_4\text{As})\text{TcNBr}_4$.

metal is a square pyramid with four Br atoms in the basal plane and the nitrogen at the apex. A Tc–N bond length of $1.63(2)\text{ \AA}$ and Tc–Br bond lengths of $2.476(2)\text{ \AA}$ were found. The main bonding features correspond well to those which were previously reported for a room temperature crystal structure by Baldas *et al.* [23]. See also ‘Supplementary material’. A more detailed discussion of the structure determination and a comparison between the parameters which were obtained at different temperatures is given in ref. 24.

The formation of nitrido technetium(VI) complexes from thionitrosyl compounds according to eqn. (5)



formally represents a four-electron oxidation of the metal. Similar desulfurations have been observed at reactions of $\text{Re}(\text{NS})\text{Cl}_2(\text{Me}_2\text{PhP})_3$ [25] and $\text{Tc}(\text{NS})\text{Cl}_3(\text{Me}_2\text{PhP})(\text{Me}_2\text{PhPO})$ [6] with phosphines. In these cases the formation of phosphine sulfide may be responsible for the cleavage of the thionitrosyl NS bonds. For a mechanistic discussion of the spontaneous decomposition of the title complexes, however, more detailed studies are required. These studies as well as ligand exchange reactions on the $[\text{Tc}(\text{NS})\text{X}_4]^-$ complexes are in progress.

Supplementary material

Further details of our low-temperature crystal structure determination have been deposited with the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, W-7514 Eggenstein/Leopoldshafen 2, as Supplementary Publication No. CSD 56472.

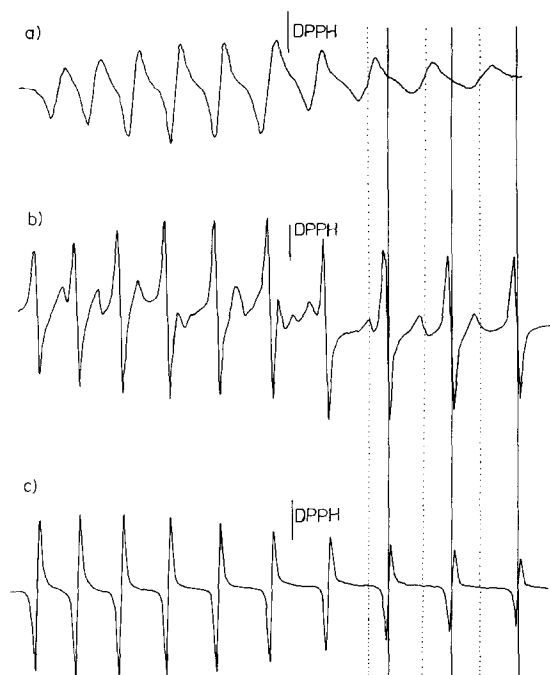


Fig. 4. Room temperature EPR spectra of a reaction mixture during the thermal decomposition of $[\text{Tc}(\text{NS})\text{Cl}_4]^-$: (a) immediately after dissolving the starting compound (only the signals of $[\text{Tc}(\text{NS})\text{Cl}_4]^-$ can be observed), (b) after standing for 24 h at room temperature (the signals of $[\text{Tc}(\text{NS})\text{Cl}_4]^-$ and $[\text{TcNCl}_4]^-$ can be observed), (c) after additional refluxing for 10 min (only the signals of $[\text{TcNCl}_4]^-$ can be observed).

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