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$Tc(NX)Y_3(Me_2PhP)_2$ Complexes (X = O or S; Y = Cl or Br). Preparation, Characterization and EPR Studies

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Abstract

The d^5-'low-spin' Tc(II) complexes tribromo-nitrosyl-bis(dimethylphenylphosphine)technetium(II) and tribromo-thionitrosyl-bis(dimethylphenylphosphine)technetium(II) were prepared by ligand exchange starting from the analogous chloro compounds. The complexes were characterized chemically and IR, UV–Vis and EPR spectroscopically.

In the room temperature EPR spectra a well-resolved ^{99}Tc hyperfine splitting is observed indicating a ground state of the unpaired electron which is well separated from the other orbit states. The general features of the spectra at low temperatures are characteristic for an axially symmetric spin Hamiltonian. Analysis of the ^{99}Tc and ^{31}P hfs (hfs = hyperfine splittings) shows a marked covalency of the Tc–ligand bonds. A comparison is given between the chloro and bromo, as well as between the nitrosyl and thionitrosyl complexes.

Introduction

The widespread use of the metastable isotope ^{99m}Tc in diagnostic nuclear medicine is well documented [1–5]. This, in part, is due to the favourable nuclear properties of this isotope (γ-energy: 140 keV, half-lifetime $t_{1/2} = 6$ h) which allow γ-camera images of high resolution to be obtained with a low radiation dose to the patient. During the last decades the availability of macroscopic amounts of the long lived isotope ^{99}Tc (weak β^--emitter, $E_{\max} = 0.29$ MeV, $t_{1/2} = 2.13 \times 10^5$ years) from fission products has enabled substantial progress to be made in the basic chemistry of this element [4, 6–8].

Nitrosyl complexes of technetium which can be isolated with the metal in the low oxidation states '+1' and '+2' are rarely known. To our knowledge there are only a few well characterized complexes of this type, namely $[Tc(NO)(NH_3)_4(H_2O)]^{2+,3+}$ [9–11], $[Tc(NO)X_{4(5)}]^{(2)-}$ with X = Cl, Br, I and NCS [11–15] and the phosphine complex $Tc(NO)Cl_3(Me_2PhP)_2$ [16]. Very recently, Linder *et al.* [17] reported the reaction of hexakis(t-butylisonitrile)technetium(I) with nitrosyling agents to yield $[Tc(NO)(TBI)_5]^{2+}$.

$Tc(NS)Cl_2(et_2dtc)_2$ (et_2dtc^- = *N*,*N*-diethyldithiocarbamate) [18], $Tc(NS)Cl_2(Me_2PhP)_3$ [19] and $Tc(NS)Cl_3(Me_2PhP)_2$ [19] are the only known thionitrosyl compounds of technetium. Whereas the ligand exchange behaviour of the amine and halogeno species have been studied extensively [10–13], that of nitrosyl and thionitrosyl complexes with additional phosphines coordinated must be regarded as unknown up to now.

In this paper we report the reaction of $Tc(NO)Cl_3(Me_2PhP)_2$ and $Tc(NS)Cl_3(Me_2PhP)_2$ with hydrobromic acid to yield the bromo analogues. UV–Vis and EPR spectroscopy are used to monitor these reactions as well as to characterize the structure of the products.

Experimental

Blue–green $Tc(NO)Cl_3(Me_2PhP)_2$ was prepared from the orange–red $TcCl_3(Me_2PhP)_3$ by the reaction with NO gas in benzene as published previously [16]. The red thionitrosyl compound $Tc(NS)Cl_3(Me_2PhP)_2$ can be synthesized by refluxing $TcNCl_2(Me_2PhP)_3$ [20] with an excess of S_2Cl_2 in methylene chloride [19].

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Tc(NO)Br$_3$(Me$_2$PhP)$_2$

$Tc(NO)Cl_3(Me_2PhP)_2$ (51 mg; 0.1 mmol) in 5 ml acetone was refluxed adding 2 ml HBr (40% *v/v*). After 5 h the reaction mixture was diluted with 20 ml cold water and extracted with 4 equivalents of 3 ml chloroform. After drying the extracts over sodium sulphate the solvent was removed *in vacuo* and the residue redissolved in 2 ml chloroform. Addition of 2 ml n-hexane and slow evaporation of the solvents gave green crystals which were collected by filtration, washed with diethylether and dried *in vacuo*. Yield 65 mg (95% based on Tc).

Tc(NS)Br$_3$(Me$_2$PhP)$_2$

$Tc(NS)Br_3(Me_2PhP)_2$ was prepared as outlined above for the nitrosyl complex starting from 56 mg (0.1 mmol) $Tc(NS)Cl_3(Me_2PhP)_2$. Recrystallization from chloroform/n-hexane yields purple crystals. Yield 20 mg (29% based on Tc).

Spectroscopy

UV–Vis spectra were recorded on a SPECORD M 40 (Carl-Zeiss-Jena, G.D.R.) in chloroform. Infrared spectra were determined in KBr discs on an UR 20 spectrometer (Carl-Zeiss-Jena, G.D.R.).

EPR spectra were recorded in the X-band ($\nu \approx 9.3$ GHz) on an E-112 spectrometer (VARIAN, U.S.A.) at $T = 295$ and 140 K in chloroform solutions using sealed glass tubes.

Health Precautions

Due to the radioactivity of ^{99}Tc some health precautions were made. All operations were carried out in a fume cupboard with gloves. ^{99}Tc is an only weak β^--emitter ($E_{max} = 0.29$ MeV, specific activity of 17 μCi/mg) and so no further precautions are necessary provided some elementary ones are taken. Normal glassware gives adequate protection against the weak β^- emission. Secondary X-rays (Bremsstrahlung) only become important if handling ^{99}Tc on a larger scale.

Results

The technetium(II) complex $Tc(NO)Cl_3(Me_2PhP)_2$ (Me_2PhP = dimethylphenylphosphine) can be prepared by reacting $TcCl_3(Me_2PhP)_3$ with NO gas [16]. Due to the lack of an appropriate thionitrosylating agent the analogous thionitrosyl compound $Tc(NS)Cl_3(Me_2PhP)_2$ was prepared by the reaction of the nitrido–technetium(V) complex $TcNCl_2(Me_2PhP)_3$ [20] with an excess of disulphur dichloride [19]. The corresponding bromo species could not be synthesized following the outlined synthetic routes because (i) the Tc(III) complex $TcBr_3(Me_2PhP)_3$ does not react in the manner stated for the chloro compound and (ii) the reaction of $TcNBr_2(Me_2PhP)_3$ [21] with S_2Cl_2 results in the formation of the chloro complex. However, ligand exchange reactions starting from the chloro complexes and HBr yield these complexes in a simple manner. $Tc(NO)Br_3(Me_2PhP)_2$ is a deep green, crystalline solid which is easily soluble in organic solvents as its purple thionitrosyl analogues $Tc(NS)Br_3(Me_2PhP)_2$. Analytical data as well as infrared and UV–Vis spectroscopical results are summarized in Table I.

TABLE I. Analytical Data and IR and UV–Vis Spectroscopical Results (L = Me_2PhP)

	Colour	Melting point (°C)	UV–Vis λ_{max} (nm) (ϵ (l mol^{-1} cm^{-1}))	IR $\nu_{NO, NS}$ (cm^{-1})	Elemental analysis (calc.(found)) (%)				
					C	H	N	Tc	Hal
$Tc(NO)Cl_3L_2$[a]	blue–green	175–7	280(25052) 373(3043) 606(915) 710sh(615)	1770 1975	37.5 (37.4)	4.3 (4.1)	2.7 (2.6)	19.3 (19.2)	20.8 (21.0)
$Tc(NO)Br_3L_2$	green	184–6	253(15405) 292(14011) 398(1260) 449(2396) 642(1382)	1779 1794	29.7 (29.8)	3.4 (3.4)	2.2 (2.2)	15.4 (16.1)	37.2 (38.5)
$Tc(NS)Cl_3L_2$[b]	red	146–9	254(13604) 288(7873) 418(965) 488(1429)	1240	36.4 (37.9)	4.2 (4.2)	2.7 (2.1)	18.8 (17.1)	20.2 (20.1)
$Tc(NS)Br_3L_2$	purple	163–7	281(15440) 412(1407) 572(2385)	1242	29.1 (29.1)	3.3 (3.0)	2.1 (1.8)	15.0 (14.2)	36.3 (36.2)

[a] See also ref. 17. [b] See also ref. 19.

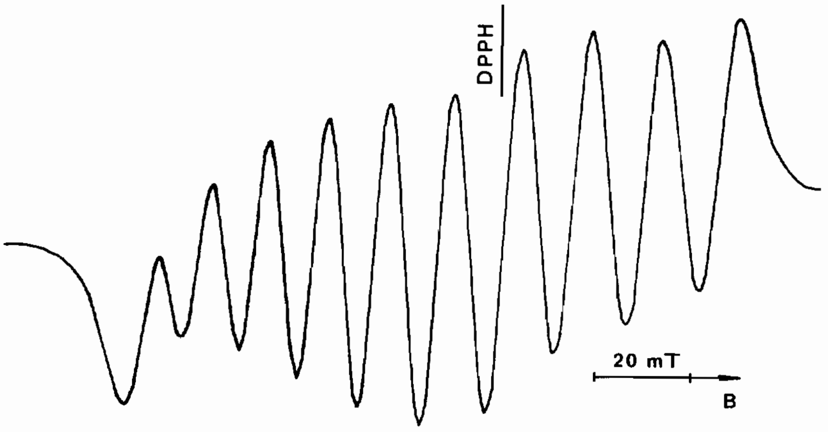


Fig. 1. Room temperature EPR spectrum of $Tc(NS)Br_3(Me_2PhP)_2$ in $CHCl_3$.

Whereas in the infrared spectra the NO and NS stretching frequencies at about 1800 and 1240 cm^{-1}, respectively, are nearly independent on the halogen substitution, in the electronic spectra of the bromo complexes we found the first intense bands in the visible parts to be bathochromically shifted with respect to those in the spectra of the chloro complexes. This is in agreement with the weaker ligand field caused by the bromo ligands.

More detailed information on the electronic structure and the bonding properties of the complexes under study should be available using EPR spectroscopy. EPR should be a valuable method to study technetium compounds with the metal in the oxidation state '+2' due to their 4 d^5-'low-spin' configuration, $S = 1/2$, which should yield well resolved EPR spectra even at room temperature [11–16]. The low substance need, the possibilities given to derive bonding properties of the metal–ligand bonds and the restricting radioactivity of Tc favour EPR spectroscopy for investigation of paramagnetic technetium complexes.

The room-temperature EPR spectra of $CHCl_3$ solutions of the complexes under study (Fig. 1 shows that of $Tc(NS)Br_3(Me_2PhP)_2$) consist of ten hyperfine lines resulting from the hyperfine interaction with the ^{99}Tc nucleus which possesses a nuclear spin $I = 9/2$. Superhyperfine splittings (shfs) due to the interaction of the unpaired electron with the coordinating ^{31}P ($I = 1/2$), $^{35,37}Cl$ ($I = 3/2$), $^{79,81}Br$ ($I = 3/2$) or ^{14}N ($I = 1$) nuclei of the ligands could not be resolved at room temperature. Only the smallest ^{99}Tc-hfs-line of $Tc(NO)Cl_3(Me_2PhP)_2$ shows very poorly resolved splittings which possibly may be caused by a superhyperfine interaction due to the ^{31}P ligand nuclei.

In Fig. 2 the EPR spectrum of a frozen solution of $Tc(NS)Br_3(Me_2PhP)_2$ at $T = 130$ K is given. The general features of this spectrum, as well as those of the other studied nitrosyl and thionitrosyl complexes of Tc(II), are characteristic for an axially symmetric, randomly oriented $S = 1/2$ system with parallel and perpendicular sets of ^{99}Tc hyperfine lines, as can be described by the following spin Hamiltonian

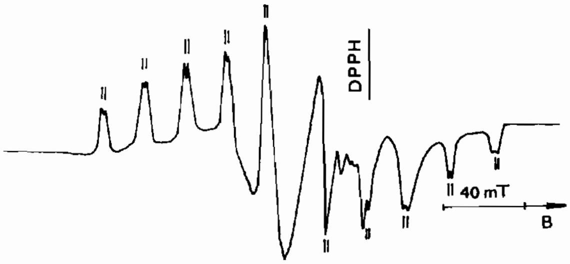


Fig. 2. Frozen solution EPR spectrum of $Tc(NS)Br_3(Me_2PhP)_2$ at $T = 130$ K in $CHCl_3$ (^{99}Tc hyperfine lines of the parallel part of the spectrum indicated with ‖).

$$\mathcal{H}_{sp} = \beta_e [g_\| H_z \hat{S}_z + g_\perp (H_x \hat{S}_x + H_y \hat{S}_y)] + A_\|^{Tc} \hat{I}_z \hat{S}_z + A_\perp^{Tc} (\hat{I}_x \hat{S}_x + \hat{I}_y \hat{S}_y) + Q' [\hat{I}_z^2 - (1/3) I(I+1)] \qquad (1)$$

where $g_\|$, $g_\perp$, $A_\|^{Tc}$ and $A_\perp^{Tc}$ are the principal values of the $\tilde{g}$ and ^{99}Tc hyperfine tensor $\tilde{A}^{Tc}$. Q' represents the ^{99}Tc quadrupole coupling parameter. This interaction is expected to be small and has been neglected.

In the parallel part of the spectra an additional splitting of the ^{99}Tc hyperfine lines can be seen due to the interaction with the ^{31}P nuclei of the equatorially coordinated phosphine ligands. ^{31}P superhyperfine interactions are also resolved in the perpendicular part of the $Tc(NO)Cl_3(Me_2PhP)_2$ spectrum [17]. For the other complexes such kind of shfs-interactions are only poorly resolved.

In Table II the measured spin Hamiltonian parameters are listed. These parameters were obtained by means of the usual second order expressions [22].

Discussion

Synthesis

Ligand exchange reactions starting from the technetium(II) complexes $Tc(NO)Cl_3(Me_2PhP)_2$ or

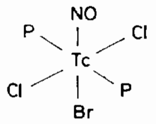
TABLE II. EPR Parameters for $Tc(NX)Y_3(Me_2PhP)_2$ Complexes ($L = Me_2PhP$), Hyperfine Coupling Constants are Given in 10^{-4} cm^{-1} [a]

	$Tc(NO)Cl_3L_2$ [b]	$Tc(NO)Br_3L_2$	$Tc(NS)Cl_3L_2$	$Tc(NS)Br_3L_2$
$g_\parallel$	2.034	2.119	2.027	2.103
$g_\perp$	2.053	2.100	2.039 [c]	2.078 [c]
$\langle g_{av}\rangle$ [d]	2.047	2.106		
g_0	2.045	2.108	2.032	2.086
$A_\parallel{}^{Tc}$	214.5	184.1	236.7	205.1
$A_\perp{}^{Tc}$	88.0	79.0	106.3	94.0 [c]
$\langle a_{av}^{Tc}\rangle$ [d]	130.1	114.0	149.8	
$a_0{}^{Tc}$	124.9	111.3	148.6	131.0
$A_\parallel{}^{P}$	19.1	e	23.7	19.6
$A_\perp{}^{P}$	23.6	e	e	e
$\langle A_{av}^{P}\rangle$ [d]	20.6			

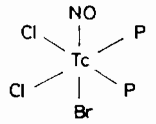
[a] Experimental error: $g_\parallel$ ±0.003; $g_\perp$ ±0.005; g_0 ±0.003; $A_\parallel{}^{Tc}$ ±2.0; $A_\perp{}^{Tc}$ ±5.0; $a_0{}^{Tc}$ ±2.0; $A_\parallel{}^{P}$ ±1.0; $A_\perp{}^{P}$ ±0.5. [b] See also ref. 17. [c] Perpendicular part poorly resolved – values obtained with $g_{av} = g_0 (A_{av} = a_0)$ and $g_\perp = (3g_0 - g_\parallel)/2$ and $A_\perp = (3a_0 - A_\parallel)/2$, respectively. [d] $g_{av} = (g_\parallel + 2g_\perp)/3$ and $A_{av} = (A_\parallel + 2A_\perp)/3$. [e] Not resolved.

$Tc(NS)Cl_3(Me_2PhP)_2$ and hydrobromic acid lead to the corresponding halogen exchanged products tribromo(nitrosyl)bis(dimethylphenylphosphine)technetium(II) and tribromo(thionitrosyl)bis(dimethylphenylphosphine)technetium(II), respectively. No evidence could be found for the formation of noticeable amounts of $[Tc(NO)Br_4]^-$ or its thionitrosyl analogues reflecting a strong Tc–phosphine bond. Whereas the reaction of $Tc(NO)Cl_3(Me_2PhP)_2$ yields the Tc(II) bromo complex nearly quantitatively, in the same reaction of the thionitrosyl complex redox processes seem to play an important role decreasing the yield of $Tc(NO)Br_3(Me_2PhP)_2$ to 20 per cent. It should be noted, that similar results could be found for the preparation of the starting compounds. $Tc(NO)Cl_3(Me_2PhP)_2$ is obtained from $TcCl_3(Me_2PhP)_3$ [23] without evidence for the formation of nitrosyl complexes with the metal in the oxidation states '+1' and '+3', respectively. The reaction of $TcNCl_2(Me_2PhP)_3$ with S_2Cl_2 yields Tc(II) and Tc(I) thionitrosyl compounds in dependence on the reaction conditions used [19]. The preparation of pure samples is difficult and lowers the yields. This behaviour offers the possibility of the formation of additional Tc(I) thionitrosyl products in the ligand exchange reactions studied. Isolation and characterization of these compounds have failed up to now.

Whereas the ligand exchange of the thionitrosyl compound proceeds without detectable intermediates, that of $Tc(NO)Cl_3(Me_2PhP)_2$ seems to yield firstly an intermediate the UV–Vis spectrum of which (283 nm (21 920 l mol^{-1} cm^{-1}), 390 (2698), 435 (2084), 628 (1086) clearly differs from that of the chloro complex. An EPR spectroscopic investigation of this compound, however, results in the detection of only one Tc(II) complex with nearly the same spectral parameters as found for $Tc(NO)Cl_3(Me_2PhP)_2$. This can be understood assuming a structure for $Tc(NO)Cl_3(Me_2PhP)_2$ as given in formula **II** and an initial ligand exchange in *trans* position to the NO ligand. Changes in this coordination position are more difficult to observe by EPR because of symmetry reasons. This has been shown for a number of d^1 complexes [24], but was recently also proved for nitrosyl complexes of Tc(II) [13]. These spectroscopic results together with the elemental analysis of the isolated intermediate (C, 35.2; H, 3.7; N, 2.3; Tc, 17.5%) suggests this compound to be $Tc(NO)Cl_2Br(Me_2PhP)_2$ (the elemental analysis of which requires C, 34.5; H, 4.0; N, 2.5; Tc, 17.8%) with a ligand arrangement as given in **Ia** or (possibly) **Ib**.



Ia



Ib

EPR Spectra

The EPR spectra observed agree with those expected for Tc(II) complexes with the corresponding $d^5(t_{2g}{}^5)$–'low-spin' configuration. This configuration can be regarded as a d^1 one via the hole formalism. The EPR theory for such systems is given by Stevens [25] and Bleaney [26]. Caused by the combination of the low symmetric ligand field with the spin-orbit interaction of the technetium a splitting of the sixfold degenerated $^2T_2$ ground state into three well separated Kramer's doublets is given [27].

Assuming tetragonal quantization as suggested by the EPR spectra of the studied complexes these states can be written as follows:

$$-|1\rangle = 1/\sqrt{2}(d_{xz} + id_{yz}) \quad (2a)$$

$$|-1\rangle = 1/\sqrt{2}(d_{xz} - id_{yz}) \quad (2b)$$

$$\xi_1 = id_{xy} = 1/\sqrt{2}(|2\rangle - |-2\rangle) \quad (2c)$$

Two possibilities are given for the description of the ground state of the unpaired electron: (i) the ground state is mainly determined by ξ_1 (2c), the other orbit states lie much higher concerning their energies ($\geqslant 10^{-4}$ cm^{-1}) and (ii) the unpaired electron occupies the states $-|1\rangle$ or $|-1\rangle$ ((2a) or (2b)) at axial symmetry only separated by spin orbit interactions. The splitting of (2a) and (2b), however, should be small due to the small spin-orbit coupling constant λ for Tc^{2+} ($\lambda(Tc^{2+}) = 850$ cm^{-1} [28], which would result in short spin-lattice relaxation times not allowing well-resolved room-temperature EPR spectra. According to the experimental results for the complexes under study the ground state of the unpaired electron should be given by (2c) which also agrees with the ^{99}Tc hfs observed reflecting a 'd_{xy}' ground state.

The evidence of resolved ligand hyperfine interactions due to ^{31}P and, partially, to ^{35,37}Cl nuclei proves a marked delocalization of spin-density into ligand orbitals. So, a consideration of the bonding situation in the complexes under study in terms of molecular orbitals (MO) seems to be reasonable. In accordance with the results obtained earlier for nitrosyl complexes of technetium(II) [13–17] the EPR spectra of the $Tc(NX)Y_3(Me_2PhP)_2$ complexes suggest an 'in-plane-π-type' for the MO of the unpaired electron as can be described by eqn. (3)

$$\psi_{MO}(B_2) = \beta_2|d_{xy}\rangle - \beta'_2|\Phi_L\rangle \quad (3)$$

where $|\Phi_L\rangle$ represents a linear combination of ligand orbitals of the equatorial ligands and β and β' are measures of covalency of the equatorial Tc–ligand bonds.

^{99}*Tc hfs*

Applying the formalism given by McGarvey (eqn. (4)) [29] the ^{99}Tc hfs observed can be used to estimate the degree of covalency of the equatorial Tc–ligand bonds

$$A_{\parallel}^{Tc} = -K - (4/7)\beta^2 P + (g_{\parallel} - g_e)P + (3/7)(g_{\perp} - g_e)P \quad (4a)$$

$$A_{\perp}^{Tc} = -K + (2/7)\beta^2 P + (11/14)(g_{\perp} - g_e)P \quad (4b)$$

$$a_0^{Tc} = -K + (g_0 - g_e)P \quad (4c)$$

Hereby, K is a measure of the Fermi contact interaction; P has been estimated to be 200×10^{-4} cm^{-1} [29]. Table III contains the values of the covalency parameters β^2 and K derived for the nitrosyl and thionitrosyl complexes under study.

TABLE III. Bonding Parameters for the Complexes Under Study Derived from the EPR Parameters (L = Me_2PhP)

	$Tc(NO)Cl_3L_2$	$Tc(NO)Br_3L_2$	$Tc(NS)Cl_3L_2$	$Tc(NS)Br_3L_2$
K^a	139.0	134.8	156.3	147.8
β^2	0.75	0.71	0.77	0.73

^{a}In 10^{-4} cm^{-1}.

For the nitrosyl as well as for the thionitrosyl moieties the bromo complexes show a larger extend of covalency of the Tc–ligand bonds as their chloro analogues. This is not unexpected and comes close to the results obtained for Tc(II) complexes of the

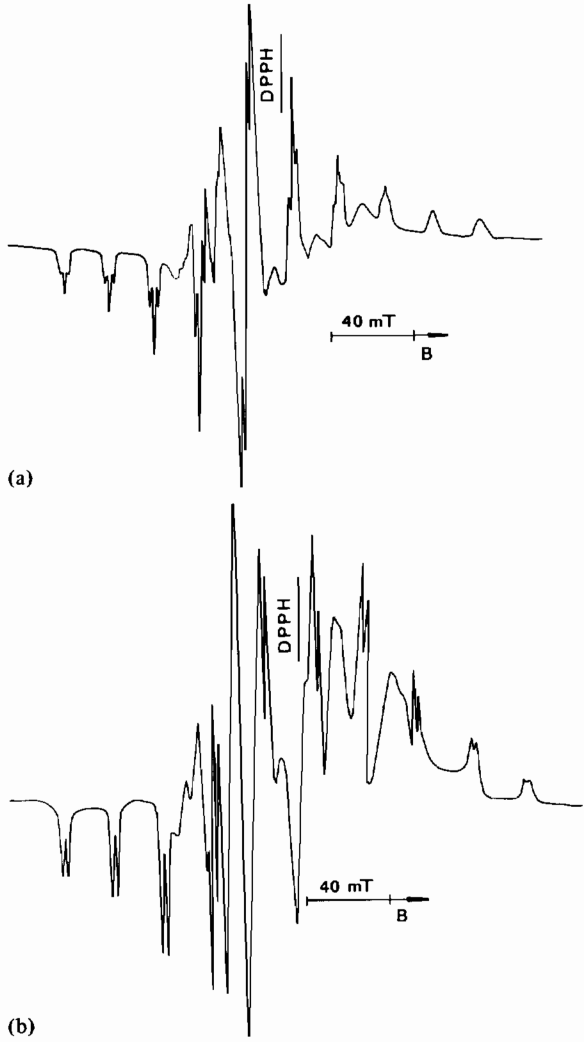


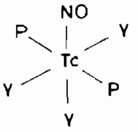
Fig. 3. Frozen solution EPR spectra of (a) $Tc(NO)Cl_3(Me_2PhP)_2$ and (b) $Tc(NS)Cl_3(Me_2PhP)_2$ with well resolved ^{31}P splittings at the parallel part lines.

type $[Tc(NO)X_{4(5)}]^{(2)-}$ (X = Cl, Br, I) [13] and should only be caused by the influence of the bromo ligands.

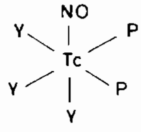
A comparison between the nitrosyl and thionitrosyl complexes is a little bit more complicated due to their different ligand arrangements (**II** and **III**) which should be discussed below. In general, a more covalent character of the Tc–(equatorial) ligand bonds in the nitrosyl complexes must be stated (but most probably determined by the presence of two of the strong π-acceptor ligands Me_2PhP in the equatorial coordination sphere). Thus, from the ^{99}Tc hfs the influence of the sulphur atom in the NX group cannot be derived unambiguously.

Ligand shfs

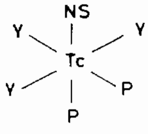
More insight in the bonding situation can be obtained by using ligand hyperfine interactions. Figure 3 shows the frozen solution spectra of $Tc(NO)Cl_3(Me_2PhP)_2$ and $Tc(NS)Cl_3(Me_2PhP)_2$, respectively. In the parallel parts of the spectra a well resolved shfs due to the ^{31}P nuclei of the phosphine ligands can be observed. From the multiplicity of these splittings conclusion can be drawn on the ligand arrangement in the complexes studied. Whereas the ^{31}P triplet (intensity ratio 1:2:1) in the spectrum of the nitrosyl complex suggests both phosphine ligands to be in equatorial position, in the thionitrosyl compound only one Me_2PhP ligand is coordinated equatorially (^{31}P shfs: doublet with intensity ratio 1:1). From this, structures for the complexes under study can be assumed corresponding to **II** for the nitrosyls and **III** for the thionitrosyl compounds.



IIa



IIb



III

The stated structures are not unexpected taking into account the structures of the starting materials used for their preparation: *mer*-$TcCl_3(Me_2PhP)_3$ [23, 30] and *mer*-$TcNCl_2(Me_2PhP)_3$ [20], no ligand rearrangement provided. The meridional ligand arrangement in $TcCl_3(Me_3PhP)_3$ makes two structures possible for the resulting nitrosyl complex, depending on the phosphine ligand substituted by NO, which cannot be distinguished in the frozen solution EPR spectra.

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