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Mixed-ligand complexes of technetium
X. Detection of nitridotechnetate(VI) complexes with coordinated azido ligands, $[TcNX_n(N_3)_{4-n}]^-$ (X = Cl, Br; n = 1–4), by EPR spectroscopy in solution*

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Abstract

Reactions of $(Bu_4N)TcNX_4$ (X = Cl, Br) and $(Bu_4N)TcOCl_4$ with sodium azide in acetonic solutions are studied by EPR. During the reactions mixed-ligand complexes of the type $[TcNX_n(N_3)_{4-n}]^-$ (n = 0–4) are formed which can be characterized by their EPR spectral data. The parameters of the individual species strongly depend on the composition of the equatorial coordination sphere. $[TcN(N_3)_4]^-$ is characterized by a nearly isotropic frozen solution EPR spectrum ($g_\parallel = 1.979$; $g_\perp = 1.982$). By means of an MO model the covalency of the Tc(equatorial)–ligand bond was found to be higher than those in analogous halide complexes.

Introduction

Since the preparation of the first nitridotechnetium complexes in 1981 [2, 3], the chemistry of the $Tc\equiv N$ core was established to become one of the keystones of the coordination chemistry of the metal involving the oxidation states '+5' and '+6'. The azide ion plays an important role in the formation of the technetium–nitrogen triple bond [4–6]. Nevertheless, N_3^- was not used as a ligand in the coordination chemistry of Tc until now.

EPR spectroscopy has been shown to be an excellent method for studying Tc(VI) complexes due to their 4 d^1 configuration [1, 4, 7–14]. Information on the coordination geometry and bonding properties of complex molecules can be derived from the spectra obtained. EPR was used to study the ligand exchange and the mixed-ligand complexes formed during the reactions of $TcNX_4^-$ complexes (X = Cl, Br) with halides and NCS^- [7, 9, 11]. The spectral parameters derived can be used for a structural assignment of the individual species which are formed during the reaction. This is due to a nearly linear dependence of the spectral parameters on the composition of the equatorial coordination sphere. Thus, EPR seems to be a reasonable method for the detection of further ligand exchange reactions by studying the reaction mixtures without isolation of the products.

In this paper, the formation of azido complexes of Tc which occur during the interaction of $TcOCl_4^-$ or $TcNX_4^-$ (X = Cl, Br) with sodium azide are considered.

Experimental

$(Bu_4N)TcOCl_4$, $(Bu_4N)TcNCl_4$ and $(Bu_4N)TcNBr_4$ were prepared by standard methods [3, 14].

Ligand exchange reactions

To 5 mg samples of $(Bu_4N)TcNX_4$ (X = Cl, Br) or $(Bu_4N)TcOCl_4$ in 2 ml acetone, solid sodium azide

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(30 mg) was added. The initial colour changes via several intermediate stages to blue–purple. After 1, 3, 5, 15, 30 min and 1 h samples were taken and studied by EPR spectroscopy.

EPR spectra

EPR spectra were recorded at $T=295$, 130 and 30 K on a Varian E-112 spectrometer (U.S.A.) in the X-band ($\nu \approx 9.5$ GHz).

Results and discussion

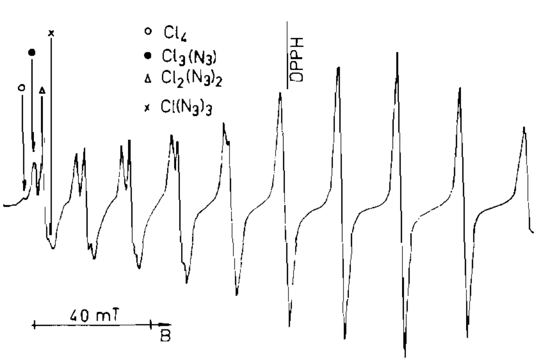
EPR spectra of axially-symmetric $Tc^{VI}NX_4^-$ complexes (X = halides, pseudohalides) consist of well-resolved ten-line ^{99}Tc hyperfine multiplets due to the interaction of the unpaired electron with the nuclear spin of ^{99}Tc ($I=9/2$) [7–12, 15]. In frozen solution, well-resolved decets can be detected in the parallel and perpendicular part. The spectra can be analyzed by an axially-symmetric spin-Hamiltonian (eqn. (1))

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

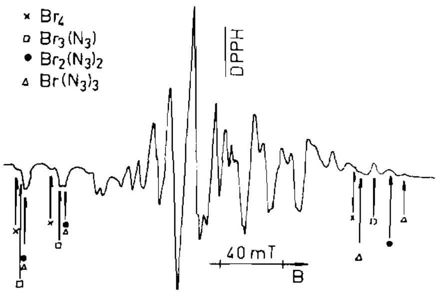
where $g_\parallel$, $g_\perp$, $A_\parallel^{Tc}$ and $A_\perp^{Tc}$ represent the principal values of the $\tilde{g}$ and the ^{99}Tc hyperfine tensor $\tilde{A}^{Tc}$. Contributions due to quadrupole couplings are expected to be small and have been disregarded.

Acetonic solutions of $TcNCl_4^-$ or $TcNBr_4^-$ immediately change their colours if solid sodium azide is added. In the EPR spectra the signals of different Tc(VI) species can be observed. The number and nature of the compounds strongly depend on the reaction time. At short times, the starting materials and species which are characterized by high g_0 and $g_\parallel$ values dominate. The signal intensities of these species decrease during the reaction and signals appear which can be assigned to Tc(VI) complexes with lower g values.

A typical room-temperature spectrum of a $TcNCl_4^-/NaN_3$ reaction mixture is shown in Fig. 1(a). The signals of four species with different intensities are well resolved in the downfield region of the spectrum. Whereas the signal indicated with (o) is identical with that of the well-known starting compound $TcNCl_4^-$ [4, 7, 8, 15], the other signals are strongly suggested to belong to ligand-exchange products with azido ligands. During a reaction time of 1 h all five $[TcNX_n(N_3)_{4-n}]^-$ complexes ($n=0$–4) can be detected. Similar patterns can be observed for the frozen solution spectra where the individual species can clearly be distinguished by their parallel part lines. Figure 1(b) shows the $T=130$ K spectrum of a $TcNBr_4^-/NaN_3$ reaction mixture 5 min after starting the reaction.



(a)



(b)

Fig. 1. (a) Room-temperature EPR spectrum of a typical $TcNCl_4^-/NaN_3$ reaction mixture (30 min after mixing the reactants); (b) frozen solution spectrum of a $TcNBr_4^-/NaN_3$ reaction mixture (5 min after mixing the reactants).

The EPR parameters which have been derived for the complexes by means of usual second order expressions are summarized in Table 1. The g values and ^{99}Tc hyperfine coupling constants (a_0^{Tc}, $A_\parallel^{Tc}$) are correlated with the spin–orbit coupling constants λ_L of the equatorial donor atoms according to eqn. (2). This proportionality holds true if there are no

$$g; A^{Tc} \sim \lambda_L/\lambda_{Tc} \qquad (2)$$

significant differences concerning the structure and bonding properties of the complexes considered. Thus, the g values of the individual mixed-ligand complexes can be calculated from those of $TcNX_4^-$ (X = Cl, Br) and $[TcN(N_3)_4]^-$, respectively, following 'additivity rules' as described in detail in refs. 7 and 16. A nearly linear dependence of the derived parameters of the $[TcNX_n(N_3)_{4-n}]^-$ complexes (X = Cl, Br) on the composition of the equatorial coordination sphere (expressed by the sum of the spin–orbit coupling constants of the equatorial donors) was found, as can be seen from the values of Table 1. It should be mentioned that in solution a sixth ligand

TABLE 1. Experimentally-obtained EPR parameters of the ligand exchange products between $TcNX_4^-$ complexes (X = Cl, Br) and sodium azide (coupling constants in 10^{-4} cm^{-1})

	g_0	a_0^{Tc}	$g_\parallel$	$A_\parallel^{Tc}$
$TcNCl_4^-/N_3^-$ reaction				
$[TcNCl_4]^-$	2.006	184.9	2.007	292.5
$[TcNCl_3(N_3)]^-$	1.997	179.3	1.999	280.2
$[TcNCl_2(N_3)_2]^-$	1.987	175.1	1.994	273.2
$[TcNCl(N_3)_3]^-$	1.980	172.6	1.987	268.5
$[TcN(N_3)_4]^-$	1.974	168.5	1.979	263.0
$TcNBr_4^-/N_3^-$ reaction				
$[TcNBr_4]^-$	2.066	162.5	2.146	248.8
$[TcNBr_3(N_3)]^-$	2.038	164.3	2.082	251.3
$[TcNBr_2(N_3)_2]^-$	2.023	164.9	2.039	256.3
$[TcNBr(N_3)_3]^-$	2.008	166.0	2.007	261.7
$[TcN(N_3)_4]^-$	1.976	168.5	1.979	266.3

Experimental error: $g_0 \pm 0.004$; $g_\parallel \pm 0.003$; a_0^{Tc}, $A_\parallel^{Tc} \pm 3.0$.

(solvent, Cl^-, Br^-, N_3^-) may be coordinated in *trans*-position to the nitrido ligand leading to species of the formula $[TcNX_n(N_3)_{4-n}(\text{solvent})]^-$ or $[TcNX_n(N_3)_{4-n}Y]^-$ (X = Cl, Br; Y = X^-·N_3^-). However, according to several studies made on other d^1 complexes [16] there will be no noticeable influence on the EPR quantities under study.

Despite the behaviour of the g_0 and $g_\parallel$ values of the $[TcNX_n(N_3)_{4-n}]^-$ complexes and the situation at corresponding $[TcNCl_nBr_{4-n}]^-$ compounds [7] an analogous dependence of the ^{99}Tc coupling constants a_0^{Tc} and $A_\parallel^{Tc}$ of the $[TcNX_n(N_3)_{4-n}]^-$ species failed. This is obviously due to the influence of marked π-acceptor properties of the azido ligands. With this, one of the main requirements mentioned above (no significant differences in bonding properties) is not fully accomplished. Hyperfine coupling constants are more sensitive to this kind of deviation than the corresponding g values. The results derived for the TcN halide/azide mixed-ligand complexes, however, come close to the behaviour of nitrosyl–technetium(II) complexes with phosphine and NCS^- ligands which deviate from a linear dependence of the ^{99}Tc coupling constants of $[Tc(NO)X_nY_{4-n}]^-$ (X, Y = Cl, Br, I) [17] and observations on ligand exchange products of other d^1 complexes [16].

EPR spectroscopical monitoring of the reaction of $(Bu_4N)TcOCl_4$ with sodium azide in acetonic solution gives the same spectral pattern as was observed for $TcNCl_4^-$. The result is in correspondence with the formation of $TcNCl_4^-$ from $TcOCl_4^-$ in HCl by the reaction with NaN_3 [6]. In acetonic solution $TcNCl_4^-$ is formed intermediately and undergoes further ligand exchange reactions with excess N_3^-.

The final product of the $TcNX_4^-/NaN_3$ reaction (X = Cl, Br) is formed independently of the halide in the starting complex and should be assigned to $[TcN(N_3)_4]^-$. The EPR spectra of this compound are characterized by a ten-component spectrum with narrow lines at room temperature (Fig. 2(a)) and well-resolved ^{99}Tc multiplets in the parallel and perpendicular parts in the $T = 130$ K spectrum (Fig. 2(b)). The spectral parameters are contained in Table 2.

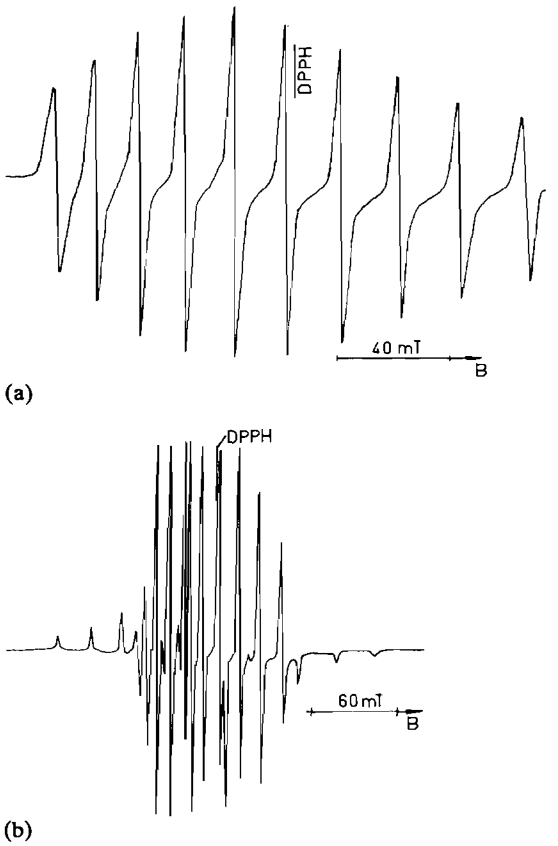


Fig. 2. X-band EPR spectra of $[TcN(N_3)_4]^-$: (a) at room temperature; (b) at $T = 30$ K (liquid He).

TABLE 2. EPR parameters of $[TcN(N_3)_4]^-$ (coupling constants in 10^{-4} cm^{-1})

$\tilde{g}$	$\tilde{A}^{Tc}$
$g_0 = 1.975 \pm 0.005$	$a_0^{Tc} = 168.5 \pm 5$
$g_\parallel = 1.979 \pm 0.003$	$A_\parallel^{Tc} = 264.0 \pm 3$
$g_\perp = 1.982 \pm 0.003$	$A_\perp^{Tc} = 123.0 \pm 3$
$g_{av} = 1.981$	$a_{av}^{Tc} = 170.0$

$g_{av} = (g_\parallel + 2g_\perp)/3$; $a_{av}^{Tc} = (A_\parallel^{Tc} + 2A_\perp^{Tc})/3$.

Ligand hyperfine splittings due to interactions of the unpaired electron with the ^{14}N nuclei of the ligands (^{14}N: $I=3/2$) cannot be observed in the temperature range 300 K > T > 30 K. The same result was obtained for a sample which was prepared with ^{15}N-enriched (enrichment: 95%) sodium azide (^{15}N: $I=1/2$): 0.9 mT were found for the linewidth of the narrowest EPR line of the perpendicular part ($m_z=7/2$) without evidence of any ligand hyperfine splittings. The order of magnitude of the tensor component $A_{\pi}^{Tc}(^{15}N)$ can roughly be estimated from linewidth considerations to be $<9\times10^{-4}$ cm^{-1}.

An 'in-plane-π-type' ground state can be derived for the molecular orbital (MO) of the unpaired electron (eqn. (3)). Applying

$$\Psi_{MO}(B_2)=\beta_2|d_{xy}\rangle-\beta'|\Phi_L\rangle \tag{3}$$

the mechanism of McGarvey [18] some bonding parameters can be derived from the ^{99}Tc couplings. With the constants which were applied for Tc(VI) in former publications [10, 15] a value of $\beta_2=0.72$ is derived. This parameter is a measure of the covalency of the Tc(equatorial)–ligand bonds. The extent of covalency in the complex under study is somewhat larger than found for $TcNCl_4^-$ and $TcNBr_4^-$ [19]. This tendency comes close to the situation in Tc(II) nitrosyl complexes (Tc^{2+}: d^5-low-spin system with one unpaired electron), where the isothiocyanato complex $[Tc(NO)(NCS)_5]^{2-}$ exhibits a larger covalency of the Tc(equatorial)–ligand bonds as was found for the corresponding chloro and bromo complexes [17]. The result can be understood by the marked π-acceptor properties of the coordinated pseudohalide ligands.

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