$[TcNBr_{4-p}Cl_p]^-$ (p = 1–3) Nitridotechnetate(VI) Mixed-ligand Complexes. An EPR Study

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(Received September 11, 1985)

Abstract

The formation of mixed-ligand complexes of the type $[TcNBr_{4-p}Cl_p]^-$ (p = 1–3) during the reaction between $TcNBr_4^-$ and $TcNCl_4^-$ is reported. Evidence of the individual mixed-ligand compounds is given by their EPR spectral data. In liquid as well as in frozen solution, a strong dependence of the EPR quantities on the composition of the coordination sphere could be detected. This is shown by a nearly linear dependence of g_0, $g_\parallel$, a_0^{Tc} and $A_\parallel^{Tc}$ on the spin–orbit coupling constants of the equatorial donors.

Introduction

During recent years coordination compounds of technetium have attracted a growing interest in view of their relevance to the field of nuclear medicine [1–3]. This is due to the favourable nuclear properties of the isotope ^{99m}Tc (γ-emitter with E_γ = 140 keV, half-life-time $t_{1/2}$ = 6 h) which allow high resolution γ-camera studies.

The ready availability of the nuclide ^{99}Tc (β-energy of about 0.3 MeV, $t_{1/2} = 2.12 \times 10^5$ years) enables conventional chemical studies. However, very little is known about compounds containing Tc in the oxidation state '+6'. The few compounds isolated or at least characterized by spectroscopic methods are listed in the review of Deutsch *et al.* [3]. In addition to these, the nitridotechnetate(VI) complexes $TcNCl_4^-$ and $TcNBr_4^-$ have recently been obtained and characterized by EPR spectroscopy in two different ways: (a) by reduction of TcO_4^- with NaN_3/HCl or NaN_3/HBr [4] and (b) by oxidation of nitridotechnetate(V) complexes of the type $TcN(\widehat{SS})_2$ [5] ($\widehat{SS}$ = dialkyldithiocarbamate, maleonitrile-dithiolate, *O,O'*-dialkyldithiophosphate) with molecular Cl_2 [6, 7] or Br_2 [8]. Furthermore, the formation of $TcOCl_5^-$ in HCl/H_2SO_4 media could be detected by EPR and UV–Vis spectroscopy [9, 10]. However, all previous attempts to obtain oxotechnetate(VI) mixed-ligand complexes have failed.

In this work, we report the first investigation by EPR spectroscopy on the Cl ⟷ Br ligand exchange for the Tc^{6+} state: the reaction between $TcNCl_4^-$ and $TcNBr_4^-$. The chemistry of oxomolybdenum(V) complexes is expected to be close to that of the Tc(VI) compounds because of (a) the similar electronic configurations and (b) the neighbourhood in the periodic table. The formation of $[MoOBr_{4-p}Cl_pX]^{2-}$ (X = Cl, Br in *trans* position to oxygen) mixed-ligand complexes was reported several years ago [11, 12]. As will be seen, nitridotechnetate(VI) halogenides show a behaviour similar to that found for the corresponding oxomolybdenum complexes. Furthermore, a practicable method will be given to detect $[TcNBr_{4-p}Cl_p]^-$ mixed-ligand complexes by means of their EPR parameters. It should be noted that, in contrast to NMR investigations, only very small sample amounts of about 0.1 mg are needed for the EPR studies. This appears to be important considering the radioactivity of technetium.

Experimental

Sample Preparation

Tetraphenylarsonium tetrachloro (and tetrabromo) nitridotechnetate(VI) was obtained according to the method described by Baldas *et al.* [4]. The samples used for the EPR measurements were prepared as follows: $(Ph_4As)TcNCl_4$ and $(Ph_4As)TcNBr_4$ were dissolved in acetonitrile and boiled for 0.5 h (molar ratios used $TcNCl_4^-$:$TcNBr_4^-$ = 1:3, 1:1, 3:1). The solutions obtained were used directly for the EPR studies.

EPR Measurements

EPR spectra were recorded in the X-Band ($\nu \approx$ 9.1 GHz) on an E-112 spectrometer (Varian, U.S.A.) at T = 295 K and 130 K. The EPR parameters were

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obtained by means of the usual second-order expressions [13].

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. EPR spectra were measured in sealed glass tubes to avoid contamination.

^{99}Tc is only a weak β^--emitter (specific activity of 17 μCi/mg) and so no further precautions are necessary provided some elementary ones are taken and no volatile compounds are being produced during the reaction. Normal glassware gives adequate protection against the weak β^--emission. Secondary X-rays (bremsstrahlung) become important when handling ^{99}Tc in a larger scale (>20 mg) only.

Experimental Results

The EPR spectra of the parent complexes $TcNCl_4^-$ and $TcNBr_4^-$ are known [4, 7]. The room temperature spectra consist of ten hyperfine lines due to the interaction of the unpaired electron with the nuclear spin of the technetium isotope ^{99}Tc (nuclear spin $I = 9/2$). In the room temperature spectra of the $TcNCl_4^-/TcNBr_4^-$ mixtures, in addition to the signals of the parent compounds there are several new signals which indicate the formation of mixed-ligand complexes of the type $[TcNBr_{4-p}Cl_p]^-$ with $p = 1$–3. A typical spectrum showing the formation of the Tc(VI)N–mixed-ligand complexes is reproduced in Fig. 1. In the high-field part of the spectrum ($m_I^{Tc} = 7/2, 9/2$), the signals of the three mixed-ligand complexes with $p = 1$–3 are well-resolved: in the low-field part the signals of the individual complexes almost coincide, which complicates the spectral analysis. Therefore, the EPR parameters of the individual spectra were obtained by simulation. They are listed in Table I.

TABLE I. Experimentally obtained[a] and calculated[b] EPR Parameters (g_0, $g_\parallel$, a_0^{Tc} and $A_\parallel^{Tc}$) for $[TcNBr_{4-p}Cl_p]^-$ Mixed-ligand Complexes. Hyperfine couplings are given in 10^{-4} cm^{-1}; solvent: acetonitrile

	g_0		a_0^{Tc}	
	Found	Calculated	Found	Calculated
$TcNBr_4^-$	2.073	2.073	163.0	163.0
$TcNBr_3Cl^-$	2.059	2.056	171.0	169.0
$TcNBr_2Cl_2^-$	2.040	2.038	177.0	175.0
$TcNBrCl_3^-$	2.021	2.021	182.0	181.0
$TcNCl_4^-$	2.003	2.003	187.0	187.0
	$g_\parallel$		$A_\parallel^{Tc}$	
	Found	Calculated	Found	Calculated
$TcNBr_4^-$	2.147	2.147	248.0	248.0
$TcNBr_3Cl^-$	2.115	2.112	258.0	259.5
$TcNBr_2Cl_2^-$	2.076	2.077	268.0	271.0
$TcNBrCl_3^-$	2.046	2.043	280.0	282.0
$TcNCl_4^-$	2.008	2.008	293.0	293.0

[a] Experimental error: g_0, $g_\parallel \pm 0.003$; a_0^{Tc}, $A_\parallel^{Tc} \pm 3.0$.
[b] Using eqns. (3) and (4).

In frozen solutions of $TcNCl_4^-$ and $TcNBr_4^-$ axial-symmetric spectra were observed which can be described by the spin Hamiltonian,

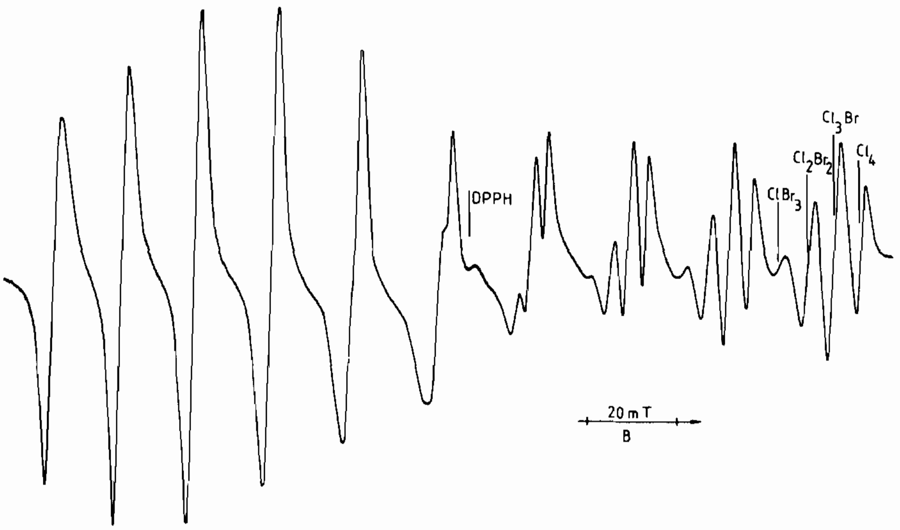

Fig. 1. X-band EPR spectrum showing the formation of $[TcNBr_{4-p}Cl_p]^-$ ($p = 1$–3) mixed-ligand complexes. The well-resolved high-field lines ($m_I^{Tc} = 7/2, 9/2$) show the presence of all three possible mixed-ligand species. $TcNBr_4^-$:$TcNCl_4^-$ = 1:1; solvent = acetonitrile, $T = 295$ K.

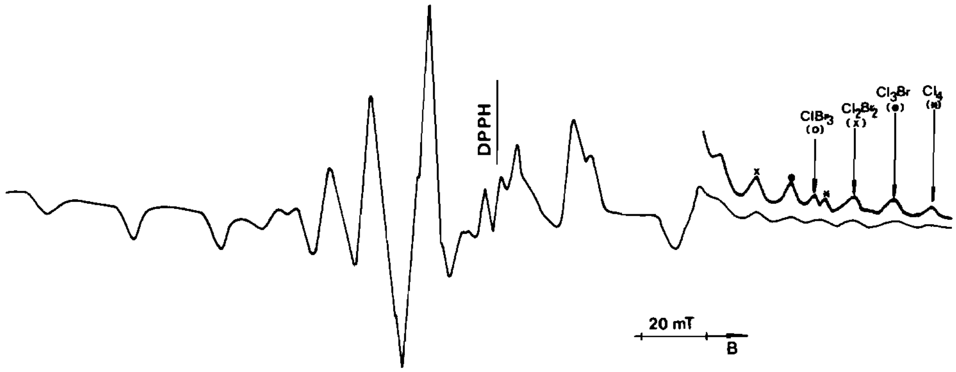

Fig. 2. X-band EPR spectrum of the $TcNBr_4^-/TcNCl_4^-$ reaction products; $T = 130$ K; solvent: acetonitrile. In the high-field region of the parallel part, the lines are attributed to the mixed-ligand complexes as follows: *, $TcNCl_4^-$; ●, $TcNCl_3Br^-$; ×, $TcNCl_2Br_2^-$; o, $TcNClBr_3^-$. In this spectrum $TcNBr_4^-$ could not be detected.

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

where $g_\|$, $g_\perp$, $A_\|^{Tc}$ and $A_\perp^{Tc}$ are the principal values of the $\tilde{g}$ and the ^{99}Tc hyperfine interaction tensor $\tilde{A}^{Tc}$. Quadrupole interactions are small and were neglected.

In the spectra of the $TcNCl_4^-/TcNBr_4^-$ mixtures, in addition to the signals of the parent complexes new signals are to be seen which must be attributed to Tc(VI) mixed-ligand complexes as found in the liquid solution spectra. A typical spectrum is shown in Fig. 2. The perpendicular part of the spectra is very complex due to the many line-overlappings; therefore, no attempts have been made to derive the parameters $g_\perp$ and $A_\perp^{Tc}$. The parameters $g_\|$ and $A_\|^{Tc}$ of the parallel part of the spectra are listed in the second part of Table I. Ligand hyperfine structures due to the interaction of the unpaired electron with the $^{35,37}Cl$ or $^{79,81}Br$ nuclei were not resolved.

Discussion

The investigation of ligand-exchange reactions by means of EPR requires knowledge about the dependence of the EPR parameters on the type (composition, symmetry) of the coordination sphere. Extensive investigations have been made for the d^9 systems Cu^{2+} [14–16], Ag^{2+} [17], and for the d^1 systems CrO^{3+}, MoO^{3+}, WO^{3+} and VO^{2+} [12]. Very recently, Tc(II) nitrosyl complexes were also studied concerning their ligand exchange behaviour [18]. According to this study, a nearly linear dependence of the EPR quantities g_0 and $g_\|$ on the 'heaviness' of the first coordination sphere is expected; this can be defined for the $[TcNBr_{4-p}Cl_p]^-$ complexes under study as given in eqn. (2)

$$g_0,\ g_\| \sim \lambda_L/\lambda_{Tc} = (\tfrac{1}{4})[p\lambda_{Cl} + (4-p)\lambda_{Br}]/\lambda_{Tc} \tag{2}$$

where λ_{Cl}, λ_{Br} and λ_{Tc} are the spin–orbit coupling constants of chlorine, bromine and technetium, respectively.

The proportionality (eqn. (2)) holds true if there are no significant differences concerning the structure and bonding properties of the complexes considered. From eqn. (2) it follows that if the g values of the parent complexes are known, the g_0, $g_\|$ values of the mixed-ligand complexes can be estimated simply using the 'additivity rule' outlined in eqn. (3).

$$g_{0[TcNBr_{4-p}Cl_p]^-} \cong (\tfrac{1}{4})(4-p)g_{0[TcNBr_4]^-} + (\tfrac{1}{4})pg_{0[TcNCl_4]^-} \tag{3a}$$

$$g_{\|[TcNBr_{4-p}Cl_p]^-} \cong (\tfrac{1}{4})(4-p)g_{\|[TcNBr_4]^-} + (\tfrac{1}{4})pg_{\|[TcNCl_4]^-} \tag{3b}$$

In Table I the g_0 and $g_\|$ values estimated for the $[TcNBr_{4-p}Cl_p]^-$ mixed-ligand complexes according to eqn. (3) are compared with the experimentally derived ones. It can be seen that the experimental values are well reproduced by eqn. (3). Similar results have been obtained earlier for oxomolybdenum(V) halide complexes by EPR investigations [11, 12] suggesting some common aspects in the chemistry of Tc^{6+} and Mo^{5+}.

The ^{99}Tc hyperfine coupling parameters a_0^{Tc} and $A_\|^{Tc}$ (Table I) also show a characteristic dependence on the composition of the first coordination sphere. The magnitudes of both a_0^{Tc} and $A_\|^{Tc}$ decrease continuously if going from $TcNCl_4^-$ to $TcNBr_4^-$ and can be described similarly as the magnitudes of the corresponding g values (eqn. (4)).

$$a_0^{Tc}{}_{[TcNBr_{4-p}Cl_p]^-} \cong (\tfrac{1}{4})(4-p)a_0^{Tc}{}_{[TcNBr_4]^-} + (\tfrac{1}{4})pa_0^{Tc}{}_{[TcNCl_4]^-} \tag{4a}$$

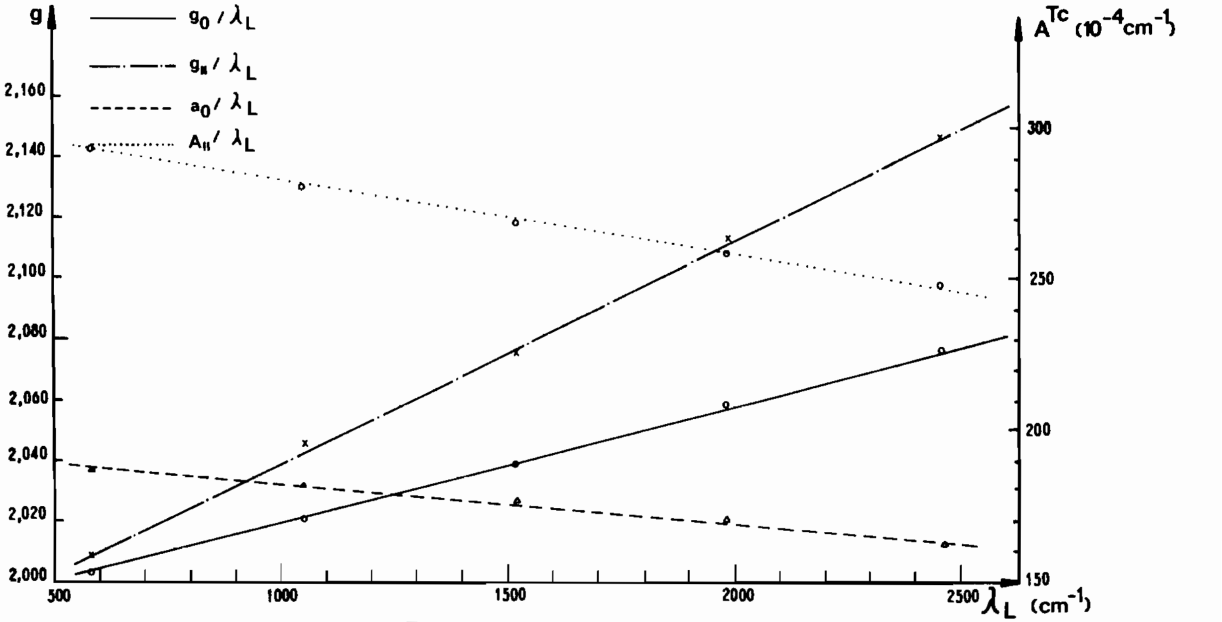

Fig. 3. Dependence of g_0, $g_\parallel$, a_0^{Tc} and $A_\parallel^{Tc}$ of the $[TcNBr_{4-p}Cl_p]^-$ complexes on the effective ligand spin–orbit coupling $\lambda_L = [(4-p)\lambda_{Br} + p\lambda_{Cl}]/4$. $\lambda_{Cl} = 586$ cm^{-1} and $\lambda_{Br} = 2460$ cm^{-1}.

$$A_\parallel^{Tc}{}_{[TcNBr_{4-p}Cl_p]^-} \cong (1/4)(4-p)A_\parallel^{Tc}{}_{[TcNBr_4]^-} + (1/4)pA_\parallel^{Tc}{}_{[TcNCl_4]^-} \qquad (4b)$$

Table I compares the estimated values for the mixed-ligand complexes (obtained using eqn. (4) and the a_0^{Tc} and $A_\parallel^{Tc}$ values of the parent complexes) with the experimentally derived ones. The agreement between those is, surprisingly, as good as that found for the corresponding g values. Figure 3 illustrates the nearly linear dependence of the observed EPR quantities of the $[TcNBr_{4-p}Cl_p]^-$ complexes on the composition of the first coordination sphere.

It should be noted that in solution a sixth ligand (solvent, Cl^-, Br^-) may be coordinated in *trans* position to the nitrogen, leading to species of the formula $[TcNBr_{4-p}Cl_p(\text{solvent})]^-$ or $[TcNBr_{4-p}Cl_pX]^{2-}$ (X = Cl, Br). However, according to several studies made on other d^1 situations [12] there will be no noticeable influence on the EPR quantities under discussion.

Conclusions

The reaction between $TcNBr_4^-$ and $TcNCl_4^-$ leads to the formation of mixed-ligand complexes of the type $[TcNBr_{4-p}Cl_p]^-$ with $p = 1–3$ in which Tc possesses the very uncommon oxidation number '+6'. The composition of the mixed-ligand complexes can easily be determined by means of their EPR parameters, which are found to be dependent in a characteristic manner on the composition of the complexes.

Acknowledgements

The authors wish to thank Prof. Dr. I. N. Marov (Vernadskij-Institute, Academy of Sciences of the U.S.S.R., Moscow) for discussions stimulating this work.

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