

ESR Studies on Trigonal-Prismatic Technetium and Rhenium Complexes. Tris(*o*-aminobenzenethiolato)-Tc(VI) and -Re(VI)

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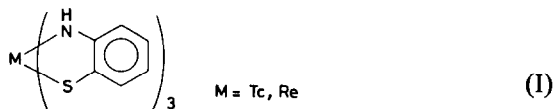
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Unsaturated 1,2-dithiolene ligands have been found to form tris complexes which display interesting chemical, structural and electronic structural properties [1]. Recently, Stiefel *et al.* [2] have shown that aromatic amine thiolate ligands can also be used to synthesize trigonal-prismatic complexes of Mo and Re having properties which are similar to those of the named dithiolene compounds. We extended these studies to complexes of technetium ^{99}Tc , the chemistry of which is much less known than that of the corresponding neighboring elements. Furthermore, coordination compounds of Tc in the higher oxidation states have begun to draw a growing interest in view of the relevance to the field of nuclear medicine [3]. Continuing our work on transition metal dithiolene complexes containing the metal ions in high formal oxidation states [4–8] in this paper we report ESR studies on tris(*o*-aminobenzenethiolato)technetium(VI), $\text{Tc}(\text{abt})_3$ and -rhenium(VI), $\text{Re}(\text{abt})_3$ (I). To our knowledge the only Tc(VI) complex studied up to now by ESR is tris(toluenedithiolato)Tc(VI) [9]. Only the liquid-solution ESR spectrum was reported for this complex. Since $\text{Tc}(\text{abt})_3$ has not yet been reported in the literature, its synthesis will briefly be described.



Experimental

Preparation of Complexes

$\text{Tc}(\text{abt})_3$. 50 μmol NH_4TcO_4 were added to a solution of 30 μl ($\approx 290 \mu\text{mol}$) *o*-aminobenzenethiol in 10 ml 0.1 N hydrochloric acid. The solution turned red-brown with the formation of a brown precipi-

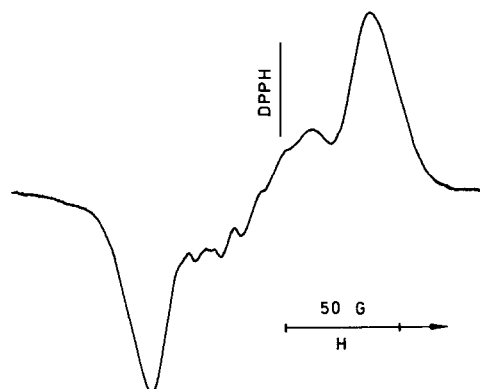


Fig. 1. X band ESR spectrum of $\text{Tc}(\text{abt})_3$ in CHCl_3 at $T = 123 \text{ K}$.

tate which was washed twice with 0.1 N hydrochloric acid. It was dissolved in CH_2Cl_2 and the solution was dried with Na_2SO_4 . After standing overnight the deep green solution was reduced in volume followed by addition of cyclohexane until a dark green powder precipitates. Yield: 40% based on pertechnetate. Elemental analysis: Calculated for $\text{C}_{18}\text{H}_{15}\text{N}_3\text{S}_3\text{Tc}$: C, 46.14%; H, 3.23%; N, 8.97%; S, 20.53%. Found: C, 46.24%; H, 3.63%; N, 8.35%; S, 19.98%. Vis spectrum in ethanol: λ_{max} in nm (ϵ_{max}): 700 (9000) and 420 (12500).

$\text{Re}(\text{abt})_3$ was prepared according to [2].

ESR Measurements

ESR spectra were recorded in the X band ($\nu \approx 9.3 \text{ GHz}$) on an E-112 spectrometer (VARIAN, U.S.A.) at room temperature and at several temperatures down to $T = 123 \text{ K}$. $5 \times 10^{-4} \text{ M}$ solutions of complexes in CH_2Cl_2 and CHCl_3 were used.

Results and Discussion

The room temperature liquid-solution ESR spectra of $\text{Tc}(\text{abt})_3$ and $\text{Re}(\text{abt})_3$ recorded in CH_2Cl_2 or CHCl_3 consist of a single line with a linewidth of $\Delta H_{\text{pp}} \approx 4 \text{ mT}$ ($\text{Tc}(\text{abt})_3$) and 14 mT ($\text{Re}(\text{abt})_3$), respectively. Hyperfine splittings due to the nuclei ^{99}Tc , $^{185,187}\text{Re}$, ^{14}N and ^1H (protons belonging to the coordinated NH groups of the abt ligands) are not resolved. In frozen solutions the ESR spectra of both complexes are more complex indicating a rhombic-symmetrical g tensor and in the case of $\text{Tc}(\text{abt})_3$ partially resolved hyperfine splittings of the peak assigned to g_2 (see Fig. 1). This splitting cannot be interpreted unambiguously, since the hyperfine splittings due to interaction of the unpaired electron with the ^{99}Tc , ^{14}N and ^1H nuclei are expected to be in the same order of magnitude. This is suggested by the isotropic ^{99}Tc hyperfine coupling constant

TABLE I. ESR Parameters of $\text{Tc}(\text{abt})_3$, $\text{Re}(\text{abt})_3$ and Related Compounds. Hyperfine splittings are given in 10^{-4} cm^{-1} .

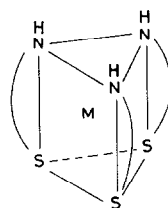
Compound	solvent	g_0	a_0	g_1	g_2	g_3	A_1	A_2	A_3
$\text{Tc}(\text{abt})_3$	CHCl_3	2.008	$-^e$	1.981	2.009	2.041	4	10	4
$\text{Re}(\text{abt})_3$	CHCl_3	2.013	$-^e$	1.981	2.012	2.051	5	5	5
$\text{V}(\text{mnt})_3^{2- a}$	$-^d$	1.980	-57.7	1.974	1.974	2.000	-91	-91	9.2
$\text{Nb}(\text{mnt})_3^{2- b}$	$\text{CH}_3\text{OH}/\text{HCl}$	1.988	94.4		1.988 ^f			127.2 ^f	
$\text{Mo}(\text{S}_2\text{C}_2(\text{C}_6\text{H}_5)_2)_3^{c}$	THF	2.011	10.7		2.010 ^f			$-^g$	
$\text{W}(\text{S}_2\text{C}_2(\text{C}_6\text{H}_5)_2)_3^{c}$	THF	1.992	$-^e$	1.993	1.993	1.987		$-^g$	

^aData taken from [10]. ^bData taken from [11]. ^cData taken from [12]. ^dSingle-crystal study, host complex = $[(\text{C}_6\text{H}_5)_4\text{-As}][\text{Mo}(\text{mnt})_3]$. ^eNot resolved. ^fNearly 'isotropic' tensor. ^gNot reported.

derived from the liquid-solution spectrum by line-width considerations — $a_0^{\text{Tc}} \leq 0.4 \text{ mT}$ — and by the isotropic ^{14}N and ^1H coupling constants obtained for the corresponding molybdenum(V) complex $\text{Mo}(\text{abt})_3$ the values of which are $a_0^{\text{N}} = 0.21 \text{ mT}$ and $a_0^{\text{H}} = 0.63 \text{ mT}$ [2]. The tensor parameters derived from the spectra are listed in Table I together with those of some tris-dithiolene d^1 complexes having trigonal-prismatic coordination also.

The small anisotropy of the g tensor, the closeness of g_0 to the free electron g value as well as the vanishingly small metal hyperfine splitting strongly support a trigonal-prismatic coordination geometry of the chelates studied. For coordination geometries more common for Tc and Re complexes in high oxidation states (C_{2v} , C_{4v}) metal hyperfine splittings are expected which are larger by approximately two orders of magnitude according to the large nuclear magnetic moments of ^{99}Tc and $^{185,187}\text{Re}$ than those actually observed in this work. Reduction of the metal hyperfine splitting is also apparent for trigonal-prismatic d^1 complexes of the vanadium group, e.g. $\text{V}(\text{mnt})_3^{2-}$ [10] and $\text{Nb}(\text{mnt})_3^{2-}$ [11] ($\text{mnt} = 1,2\text{-dicyanoethylene-1,2-dithiolate}$), as well as for $\text{Mo}(\text{abt})_3$ [2]. However, this reduction is much less significant than that found for the corresponding Tc and Re chelates. This result is in agreement with the general observation that the tendency to adopt trigonal-prismatic coordination decreases as one moves from right to left in the periodic table. Also, changes in the ground-state configuration must be taken into account. For $\text{V}(\text{mnt})_3^{2-}$ and $\text{Nb}(\text{mnt})_3^{2-}$ the ground state was determined unambiguously to be 2A_1 (D_3 symmetry assumed). From solution and/or frozen glass ESR [12–14] and theoretical [12, 15] studies made on the isoelectronic $\text{Mo}(\text{V})$, $\text{W}(\text{V})$ and $\text{Re}(\text{VI})$ dithiolene complexes of the type $[\text{M}(\text{S}_2\text{C}_2(\text{C}_6\text{H}_5)_2)_3]^n$ ($n = -1, 0$) different kinds of ground states were discussed, namely 2A_1 , $^2E'$ or $^2A_2'$ (D_3 symmetry). The last one contains ligand orbitals only.

The very small hyperfine coupling constants found for $\text{Tc}(\text{abt})_3$ and $\text{Re}(\text{abt})_3$ suggest that the unpaired electron is placed in a molecular orbital which is mainly ligand in character. This is also supported by the small g tensor anisotropy which can be compared to that observed for sulphur-containing organic radicals [16]. Nevertheless, we do not agree with the formulation of a pure ligand molecular orbital for the unpaired electron suggested by Al-Mowali and Porte [14]. Single-crystal ESR studies on planar $\text{Ni}(\text{III})$, $\text{Pd}(\text{III})$ and $\text{Pt}(\text{III})$ dithiolene chelates [8], ESR studies on $\text{Pt}(\text{V})$ and $\text{Pd}(\text{V})$ [4] as well as on $\text{Ni}(\text{I})$ and $\text{Pd}(\text{I})$ dithiolates [17] show that for the higher oxidized metals most of the unpaired spin density will be found in the ligand orbitals. The same trend is expected for the high oxidation numbers $\text{Tc}(\text{IV})$ and $\text{Re}(\text{VI})$. An $^2A_2'$ ground state (D_3 symmetry) can be easily ruled out by further consideration of d - p mixing and second-order spin-orbit contributions, especially for $\text{Re}(\text{abt})_3$. Therefore, the ESR spectra of the $\text{M}(\text{abt})_3$ complexes can be explained by assuming a 2A ground state based on the formulation of a *cis*-arrangement of the *abt* ligands (II) (C_3 symmetry). *Cis*-coordination has been found by X-ray structure determination for $\text{Mo}(\text{abt})_3$ [18].



(II)

The EHT-MO calculations published by Schrauzer and Mayweg [15] and Stiefel *et al.* [12] for trigonal-prismatic dithiolene complexes cannot be used for calculating the tensor parameters of the spin-Hamiltonian. The differences obtained between the calcu-

lated and the experimental values are too large to allow conclusive statements concerning the foregoing considerations. Obviously, such calculations are successful only for complexes of the 3d transition metals and not for heavier ones [19]. Single-crystal ESR studies would help to clarify these questions. However, we did not succeed in obtaining suitable crystals to do such experiments.

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