^{99}Tc NMR Spectroscopy on Tc Carbonyl Compounds

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During the last ten years there has been a significant increase of activity in technetium chemistry because of the extensive use of ^{99m}Tc complexes in diagnostic medicine [1].

^{99}Tc has a nuclear spin $I = 9/2$. It is obtained in 100% abundance and has a receptivity relative to ^{1}H of 0.275.

Despite this rather high NMR detection receptivity very few reports of ^{99}Tc NMR spectra exist. To our knowledge the NMR data of only six compounds of Tc(VII) [2, 3], one of Tc(V) [3], one of Tc(III) [3], and four of Tc(I) [3–5] have been published.

We report here the first NMR data of three technetium carbonyl compounds of oxidation state 0 and +1. $Tc_2(CO)_{10}$, $Tc(CO)_5Br$ and $TcCl(CO)_3(PPh_3)_2$ were prepared as described previously [6–8]. The measurements were made at room temperature (around 25 °C) with a Bruker-AM-250 Spectrometer with magnetic field strength of 5.87 *T*. We used a broad band probe head and sample tubes of 10 mm diameter. The samples were dissolved in C_6D_6. The resonance frequency of Tc was found at 56.30 MHz. A solution of $NaTcO_4$ in heavy water was used as external frequency standard and was set at 0 ppm. Some difficulties resulted from the wide spectral ranges (up to ~2500 ppm, corresponding to 140 kHz).

Since ^{99}Tc has the spin 9/2 one would expect that the relaxation due to quadrupolar interaction dominates. This means that the relaxation rate should be mainly influenced by the asymmetry of the EFG-tensor at the site of the Tc atom; *i.e.* the lower the symmetry of the electron distribution around ^{99}Tc or – roughly speaking – the lower the symmetry of the first ligand sphere of the technetium atoms the shorter the relaxation times and the broader the absorption lines.

The experimental results confirmed this presumption. The molecule of $Tc_2(CO)_{10}$ possesses D_{4d} symmetry and two chemically identical technetium(0) atoms [9]. One single line was found at –2477 ppm (Fig. 1). Obviously the two Tc atoms are also magnetically equivalent. Relaxation time measurements (at room temperature) yielded the results $T_1 = (0.42 \pm 0.01)$ s (INVERSION RECOVERY) and $T_2 = (0.38 \pm 0.01)$ s (CARR–PURCELL–MEIBOOM–GILL). This shows that the measured halfwidth $\Delta\nu_{1/2} = 1.4$ Hz is not only caused by T_2-relaxation but by magnetic field inhomogeneity, too. In the molecule of the second sample, $Tc(CO)_5$-Br with Tc(I), the symmetry is definitely disturbed by the Br atom. The single resonance line was found at –1630 ppm (Fig. 2). The line is much broader ($\Delta\nu_{1/2} = 186$ Hz) and the relaxation times are much shorter: $T_1 = (2.8 \pm 0.5)$ ms and $T_2 = (1.7 \pm 0.5)$ ms. These values agree with the measured halfwidth of the line. The low molecular symmetry of the third sample, $Tc^{I}Cl(CO)_3(PPh_3)_2$, let us doubt the success of measuring without special pulse sequences (e.g. echo) at our high resolution spectrometer. However, we could detect a very broad line at (-1488 ± 1) ppm with a halfwidth of 5.5 kHz (Fig. 3).

This is the first ^{99}Tc NMR spectrum of a compound with three different ligand atoms around

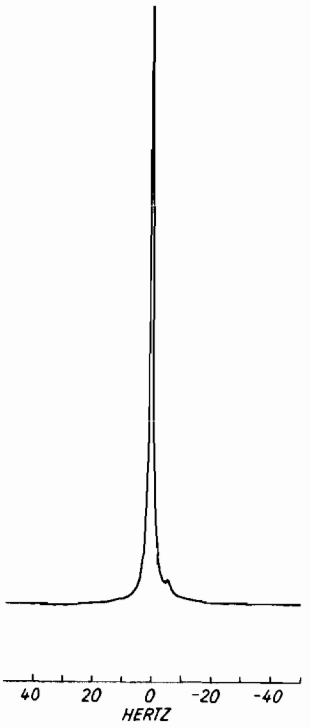

Fig. 1. ^{99}Tc NMR spectrum of $Tc_2(CO)_{10}$ ($\delta = -2477$ ppm *vs.* TcO_4^-). Number of scans 64, Lorentzian folding with 0.1 Hz, 0.12 Hz/point.

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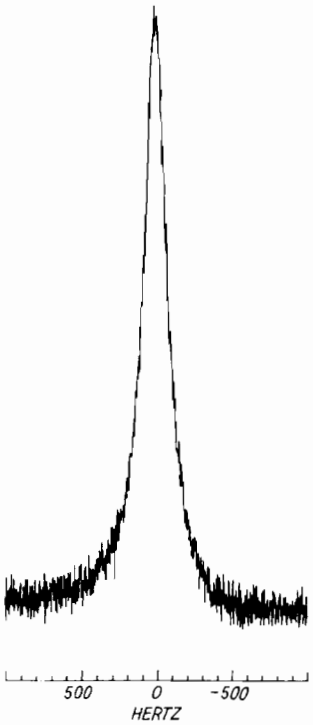

Fig. 2. ^{99}Tc NMR spectrum of $Tc(CO)_5Br$ (δ = −1630 ppm *vs.* TcO_4^-). Number of scans 240. Lorentzian folding with 1 Hz. 1.5 Hz/point.

Fig. 3. ^{99}Tc NMR spectrum of $Tc(CO)_3Cl(PPh_3)_2$ (δ = −1488 ± 1 ppm *vs.* TcO_4^-). Number of scans 324, Lorentzian folding with 100 Hz, 7.6 Hz/point.

the technetium atom. The decay time of the FID of this sample was so short that the dead time of the probe head became a disturbing factor of the measurement. Relaxation time measurements were not made.

Further NMR work on diamagnetic technetium complexes is in progress.

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