^{99}Tc NMR Spectroscopy on Neutral and Cationic Tc(I) Carbonyl Complexes

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The NMR investigation of ^{99}Tc is still in the beginning stages. The interest in this method is caused by the rapid development of technetium complex chemistry because of the widespread application of ^{99m}Tc complexes for diagnostic purposes. The diamagnetic Tc(I) compounds with d^6 configuration are promising candidates for structural investigations by NMR. In a previous publication [1] we reported the first NMR spectra of technetium carbonyl compounds and found increasing line broadening due to the high nuclear spin of 9/2 of ^{99}Tc with increasing unsymmetry of the electron distribution around ^{99}Tc. To obtain further information about this effect we have investigated other neutral and cationic complexes of Tc(I) with different ligand atoms around Tc.

In Table I the compounds **1–10** measured by us (solvent CD_2Cl_2), their chemical shifts in ppm against a solution of $NaTcO_4$ in D_2O as external standard, the half-width $\Delta\nu_{1/2}$ of the ^{99}Tc signal in Hz and coupling constants J(Tc–P) (if measurable) are given.

Compounds **1–2** were prepared according to Mazzi *et al.* [2], compounds **4–7** analogous to a procedure of Hieber *et al.* [3]. The preparation of the new cationic complexes **8–10** is described in ref. 4. For comparison also the NMR data of the four cationic Tc(I) complexes published so far are included in Table I. Compound **11** was synthesized by Wester *et al.* [5] and measured in $CDCl_3$.

For the cations **12** [6], **13** and **14** [7] the anions and solvents are not clearly mentioned. The neutral complexes **1–7** all contain the structure element $Tc(CO)_3$ and have an octahedral arrangement of ligands around ^{99}Tc. The chemical shifts are found at $\delta \approx (-1650 \pm 200)$ ppm. Minor structural and electronic changes, e.g. *trans* to *cis* (*cf.* **2** *versus* **3** and **4** *versus* **5**), give rise to differences of δ values, so that high sensitivity of ^{99}Tc NMR to such changes is documented. The ^{99}Tc line of compound **1** was shifted slightly from −1481 to −1488 ppm when replacing the solvent CD_2Cl_2 with C_6D_6 (for comparison: $Tc(CO)_5Br$ from −1802 to −1830 ppm).

In the cationic $Tc(CO)_3$ complexes **8–10** the chemical shifts are found at a distinctly higher field around −3000 ppm. However, the very large differences of δ within that series of octahedral cationic Tc(I) complexes **8–14** is only caused by different ligand atoms (**8**: TcC_3N_3; **9** + **10**: TcC_3NP_2; **11** + **12**: TcP_6; **13** + **14**; TcC_6) and were unexpected. This counts particularly for the phosphite complex **11** and the phosphine complex **12** with 6 identical phosphorus ligands.

The δ values of **13** and **14** are close to those of **8–10** confirming the well known similarity of carbonyl and isonitrile groups as ligands. Compounds **5** and **9** give a signal with a triplet structure as expected for coupling of Tc with two identical phosphorus

TABLE I. ^{99}Tc Data of Tc(I) Complexes

Compound	δ (ppm)	$\Delta\nu_{1/2}$ (Hz)	J(Tc–P) (Hz)
1 *trans*-$TcCl(CO)_3(PPh_3)_2$	−1481	3300	
2 *trans*-$TcCl(CO)_3(PMe_2Ph)_2$	−1623	1600	
3 *cis*-$TcCl(CO)_3(PMe_2Ph)_2$	−1603	1300	
4 *trans*-$TcBr(CO)_3(PPh_3)_2$	−1555	2800	
5 *cis*-$TcBr(CO)_3(PPh_3)_2$	−1460	500 (triplet)	400
6 *cis*-$TcBr(CO)_3(PMe_2Ph)_2$	−1655	1530	
7 $TcBr(CO)_3$diphos	−1816	2160	
8 $[Tc(CO)_3(CH_3CN)_3]^+PF_6^-$	−2853	48	
9 $[Tc(CO)_3(CH_3CN)(PPh_3)_2]^+PF_6^-$	−3213	395 (triplet)	440
10 $[Tc(CO)_3(CH_3CN)\text{diphos}]^+PF_6^-$	−3517	2000	
11 $[Tc(P(OCH_3)_3]^+(BPh_4)^-$ [5]	−422	(septet)	909
12 $[Tc(DMPE)_3]^+$ [6]	−13	70 (septet)	574
13 $[Tc(CH_3NC)_6]^+$ [7]	−1908	74	
14 $[Tc(\text{tert.}BuNC)_6]^+$ [7]	−1908	74	

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atoms. The coupling constant J(Tc–P) is 440 Hz, less than the published values of 909 Hz for **11** [5] and 574 Hz for **12** [6]. From our other compounds we obtained only one broad ^{99}Tc line. Corresponding to our preliminary results [1] line broadening was less in **8** with only two different ligand atoms ($\Delta\nu_{1/2} = 48$ Hz) compared with the other compounds (**1**–**7**; **9**, **10**) having three different ligand atoms ($\Delta\nu_{1/2} = 400$–3000 Hz). The line broadening is due to strong quadrupole relaxation caused by asymmetry in the tensor of the electric field gradient at the site of the technetium atom.

In our compounds **1** and **2** we cannot quite exclude the presence of small amounts of paramagnetic impurities, which are formed during the syntheses, particularly in the synthesis of **1**. But in general narrow lines ($\Delta\nu_{1/2} = 3$ Hz) in ^{99}Tc NMR have been obtained only from high symmetrical compounds such as TcO_4^- [7] and $Tc_2(CO)_{10}$ [1]. Rather narrow lines were found also for complexes with high symmetry such as **8** and **12**–**14**.

References

1 M. Findeisen, L. Kaden, B. Lorenz, S. Rummel and M. Wahren, *Inorg. Chim. Acta, 128,* L15 (1987).
2 U. Mazzi, A. Bismondo, N. Kotsev and D. A. Clemente, *J. Organomet. Chem., 135,* 177 (1977).
3 W. Hieber, F. Lux and C. Herget, *Z. Naturforsch., Teil B, 20,* 1159 (1965).
4 L. Kaden, B. Lorenz, S. Rummel, K. Schmidt and M. Wahren, *Inorg. Chim. Acta, 142,* 000 (1988).
5 D. W. Wester, D. H. White, F. W. Miller and R. T. Dean, *Inorg. Chem., 23,* 1501 (1984).
6 J. L. Vanderheyden, A. R. Ketring, K. Libson, M. J. Heeg, L. Roecker, P. Motz, R. Whittle, R. C. Elder and E. Deutsch, *Inorg. Chem., 23,* 3184 (1984).
7 K. J. Franklin, C. J. L. Lock, B. G. Sayer and G. J. Schrobilgen, *J. Am. Chem. Soc., 104,* 5303 (1982).