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The ^{99}Tc and ^{17}O Nuclear Magnetic Spectra of TcO_4^- – the First Detailed Report of a ^{99}Tc Resonance

MALCOLM J. BUCKINGHAM, GEOFFREY E. HAWKES

Department of Chemistry, Queen Mary College, Mile End Road, London, E1 4NS

and JOHN R. THORNBACK*

Department of Chemistry, Chelsea College, Manresa Road, London SW3, U.K.

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Technetium chemistry is currently of considerable interest because of the utility of ^{99m}Tc complexes in diagnostic medicine [1]. Because of the potentially high sensitivity of ^{99}Tc magnetic resonance and the lack of published data on ^{99}Tc NMR, we have undertaken a preliminary NMR study of this nucleus.

Technetium does not occur in nature, but is produced by either neutron bombardment of molybdenum followed by decay, or fission of ^{235}U or ^{239}Pu. The isotope produced in the greates quantities is ^{99}Tc ($t_{1/2}$ = 2.1 × 10^5 y), which has nuclear spin I = 9/2, a high NMR detection receptivity relative to natural abundance ^{13}C of 2134 and a quadrupole moment [2] of 0.34 ± 0.17 × 10^{-28} m^2. These properties are comparable with those of ^{59}Co on which many studies have been carried out [3]. While there have been no published reports of a nuclear magnetic resonance signal from this isotope, Kidd [3] briefly mentions that the half-height line-width ($\Delta\nu_{1/2}$) for ^{99}Tc in aqueous TcO_4^- was 29 Hz. Figgis *et al.* [4] have reported a single ^{17}O NMR signal from aqueous ^{17}O-enriched TcO_4^- with $\delta(H_2O)$ 749 p.p.m. and $\Delta\nu_{1/2}$ *ca.* 1150 Hz.

We report here the first detailed characterisation of the TcO_4^- ion by ^{99}Tc and ^{17}O NMR spectroscopy. A sample of 0.55 mCi of NH_4 $^{99}TcO_4$ dissolved in 2 ml of D_2O gave a single resonance at 90.06 MHz at 9.4 T with $\Delta\nu_{1/2}$ = 3.0 Hz (Ξ *ca.* 22, 508, 304). A single transient gave an excellent signal to noise ratio, (see Fig. 1). The relaxation parameters T_1 and T_2 were measured by the inversion-recovery and CPMG methods respectively and yielded T_1 = 0.13 s, T_2 = 0.10 s. The similarity in these values is expected for quadrupolar relaxation of ^{99}Tc and are in excellent agreement with the value for T_2 (0.11 s) estimated from $\Delta\nu_{1/2}$.

The 54.2 MHz natural abundance ^{17}O NMR spectrum of this sample gave the expected 10 line spectrum (see Fig. 1) by scalar coupling to ^{99}Tc with ^1J = 131.6 Hz. That the outer lines of this ^{17}O multiplet are sharper than the inner is expected from the finite relaxation rate of ^{99}Tc. The reduced coupling constant K (eqn. 1) fits a previously established [5] correlation with atomic number of metal in the tetrahedral oxoanions MO_4^{x-} (see Table I).

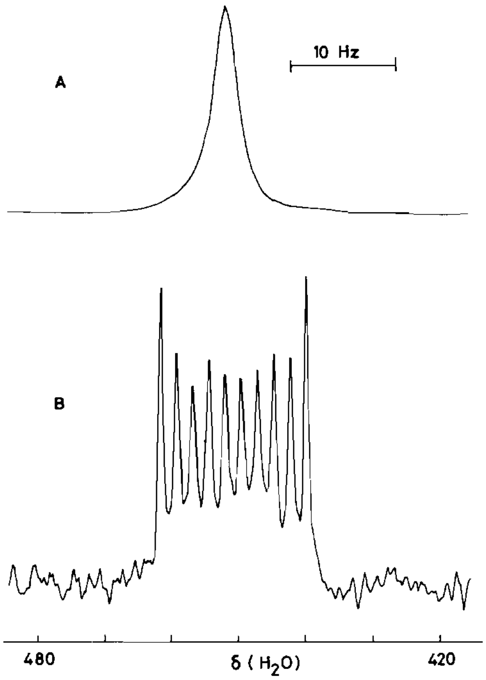

Fig. 1. NMR spectra of $^{99}TcO_4^-$; (A) 90.06 MHz ^{99}Tc spectrum, single transient; (B) 54.24 MHz natural abundance ^{17}O spectrum, 750,000 transients in 34 h. Spectra from the ULIRS WH-400 NMR Service at Queen Mary College.

$$K_{M^{17}O} = \frac{J_{M^{17}O} 4\pi^2}{h\gamma_M \gamma_{^{17}O}} \qquad (1)$$

where γ is the magnetogyric ratio of the nucleus. The inverse relationship between K and atomic number across the periodic table ($^{51}V \rightarrow {}^{53}Cr \rightarrow {}^{55}Mn$) is reproduced for ^{95}Mo and ^{99}Tc and the increase in K with atomic number down the periodic table $^{53}Cr \rightarrow {}^{95}Mo$ is reproduced for ^{55}Mn and ^{99}Tc. No accurate coupling constants are available for ReO_4^- or WO_4^{2-} but Bank and Schwenk [6] have suggested that $K(^{183}W^{17}O)$ in WO_4^{2-} may contradict this trend.

In one highly symmetric environment ^{99}Tc therefore gives a very sharp signal but in non symmetrical environments this will be probably be broadened 1 (*cf.* ^{59}Co).

The last of well-characterized diamagnetic complexes of technetium, hinders, at present, applications of this technique but with the current interest in this element it seems likely that ^{99}Tc NMR will be utilised extensively in the future.

*Author to whom correspondence should be addressed.

TABLE I. Correlation between K ($M-^{17}O$) and Atomic Number of Oxoanions.

Oxoanion	At. No.	$K/10^{-18}NA^{-2}m^{-2}$
$^{51}VO_4^{3-}$	23	14.4[a]
$^{53}CrO_4^{2-}$	24	~10.9[a]
$^{55}MnO_4^-$	25	~7.35[a]
$^{95}MoO_4^{2-}$	42	38.2[a]
$^{99}TcO_4^-$	43	35.9

[a]From reference 5.

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