

THE STRUCTURE AND PROPERTIES OF PERTECHNETIC ACID IN SOLID STATE AND SOLUTIONS AS PROBED BY NMR

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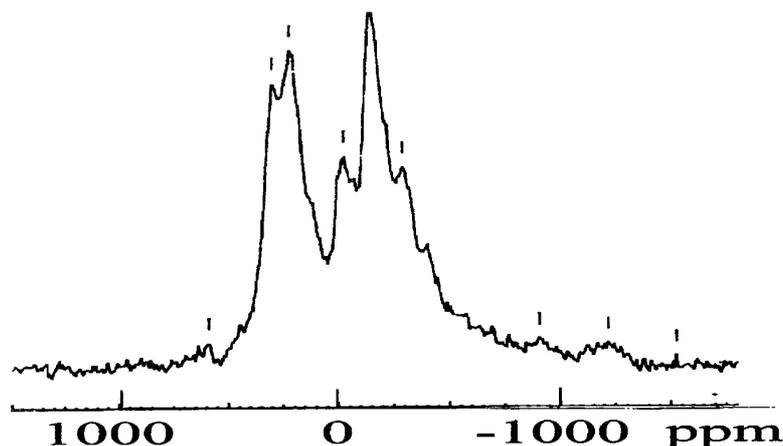
The structure of pertechnetetic acid is still a matter of controversy for researchers engaged in studying basic aspects of technetium chemistry. As early as 1960, Boyd showed based on gravimetry data that this compound either does not contain hydration water so that it should be formulated as HTcO₄ or contains one water molecule per Tc₂O₇ molecule and has the composition Tc₂O₇·H₂O [1].

Major issues that fueled controversy were the red color of this compound and some doubts about its composition. In 1994, the first unit cell parameters of the acid were reported: $a = 11.26(2)$, $b = 12.87(2)$, $c = 14.16(4)$ Å; $\alpha = 71.0(2)^\circ$, $\beta = 69.1(2)^\circ$, $\gamma = 74.1(2)^\circ$; $V = 1783(6)$ Å³ [2]. The unit cell contains at least eight technetium atoms. The crystallographic data for pertechnetetic acid differ dramatically from those for HClO₄·H₂O [3] and anhydrous HIO₄ ($a = 9.3688(5)$, $b = 6.2959(4)$, $c = 4.9530(3)$ Å; $\beta = 94.953(3)^\circ$, space group $C2/c$; or from neutron diffraction data: $a = 9.3660(18)$, $b = 6.2886(13)$, $c = 4.975(3)$ Å; $\beta = 94.953(3)^\circ$, space group $C2/c$) [4]. The IR spectrum of HTcO₄ (846, 901s, 934s cm⁻¹) [5] is similar to that of HReO₄ [6]. The spectral pattern is explained by the lowering of the TcO₄⁻ symmetry from T_d to C_{3v}.

Herein, we present the results of studying the red modification of pertechnetetic acid, both in the solid state and acetonitrile solutions, by ⁹⁹Tc and ¹H NMR in a field of 7.04 T.

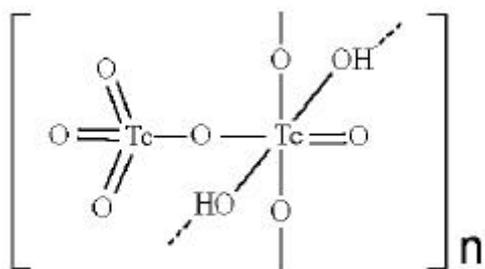
Pertechnetetic acid HTcO₄ and its deuterated analog DTcO₄ were prepared by oxidizing Tc metal in O₂ at 500°C, condensation of solid Tc₂O₇ in quartz receiver, dissolving Tc₂O₇ in H₂O or D₂O, followed by concentration of resulting solutions to complete dryness with P₄O₅ or Mg(ClO₄)₂. No access to air dust was allowed, excluding the possibility of Tc(VII) reduction to Tc(V). The samples were dark red crystalline powders. Elemental analysis gave the ratio H/Tc ≈ 1. The ¹H NMR spectrum of a fresh HTcO₄ powder at 259 K showed two signals: a strong signal at 5.6 ppm with the width at half-maximum of 400 Hz and a weak signal at ~0

ppm (relative to the external H₂O reference). Decreasing temperature to 120 K resulted in the broadening of the spectrum to 4 kHz; however, the expected fine structure of the spectrum (as the Pake doublet) was not observed. This permits a tentative conclusion that the compound under study is not a crystal hydrate and the lattice hydrogen is highly mobile. The most informative are the ⁹⁹Tc NMR spectra of red pertechnetetic acid powders (both freshly prepared and aged for three months):



The ⁹⁹Tc NMR spectrum of an aged fine powder of red pertechnetetic acid (figure) showed two signals at $\delta_1 = +213(5)$ and $\delta_2 = -147(5)$ ppm (referenced to the external standard, a 0.1 M KTcO₄ solution); the integrated intensity ratio was $I_1 : I_2 = 2 : 3$. Each of the signals had a multiplet structure due to first-order quadrupole interactions: the quadrupole coupling constants were $C_Q(1) = \sim 0.25(1)$ and $C_Q(2) = 0.43(1)$ MHz and the asymmetry parameter of the ⁹⁹Tc EFG tensor was $\eta = 0$ in both cases. The spectral pattern for a freshly prepared sample was the same, but the multiplet structure of the downfield signal was observed at considerably lower temperatures. The spectral pattern and resonance parameters indicate that technetium has two states in the structure, *none of them corresponding to the discrete TcO₄⁻ ion*.

Most likely, the pertechnetetic acid structure is represented by a polymeric framework in which Tc(VII) has two types of oxygen surroundings: the signal at 213 ppm corresponds to four-coordinate technetium; the signal at -147 ppm, to six-coordinate technetium. The temperature behavior of the signal at 213 ppm in a freshly prepared sample points to a higher mobility of the four-coordinate T(VII) moiety; hence, this fragment is involved in polymerization to a lesser extent than the six-coordinate Tc(VII) moiety. These observations allow us to suggest the following scheme for the repeat unit in the freshly prepared pertechnetetic acid:



Four-coordinate moieties are involved in polymerization with time and lose their mobility to produce a three-dimensional framework. In our opinion, this scheme is the most probable one, although other schemes cannot be ruled out.

The ^{99}Tc NMR spectrum ($B = 4.7 \text{ T}$) of a freshly prepared acetonitrile solution of the deuterated acid DTcO_4 showed a strong signal at 36 ppm and considerably weaker downfield signals at 100, 105, 266, and 335 ppm. Within 5 days after the preparation of the solution, the spectrum showed only one signal at 12 ppm ($\Delta\nu_{1/2} = 85 \text{ Hz}$). This chemical shift is close to the ^{99}Tc NMR chemical shift of an acetonitrile Bu_4NTcO_4 solution used as the external reference (17.3 ppm). It seems likely that the polymeric structure partially collapses in solution to produce fragments (dimers, trimers, etc.). These fragments are responsible for the signals in the ^{99}Tc NMR spectrum of freshly prepared samples, and a change in their intensities reflects further degradation of the polymeric structure.

Based on these findings, the structures of pertechnetate acid in the solid state and solution are proposed.

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