Speciation of Heptavalent Technetium in Sulfuric Acid: Structural and Spectroscopic Studies.

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Summary. The speciation of Tc(VII) in 12 M sulfuric acid was studied by NMR, UV-visible and XAFS spectroscopy, experimental results were supported by DFT calculation and were in agreement with the formation of $TcO_3OH(H_2O)_2$.

Heptavalent transition metal complexes of group VII with the d^0 electronic configuration are often used in catalysis and biomedical applications. [1, 2, 3] For manganese, the high electron affinity and oxidation potential of its heptavalent complexes make these species the catalysts of choice for oxidation of organic compounds.[4] The chemistry of Re(VII) complexes has been extensively studied, and species with the ReO_3^+ core (e.g., CH_3ReO_3) have been reported to be efficient catalysts.[3] Concerning technetium, its coordination chemistry has mainly been driven by radiopharmaceutical applications. Pentavalent and trivalent Tc complexes have been the most studied while heptavalent coordination complexes are still rare.[5] Permetallates with the tetrahedral geometry are the most common heptavalent species and are stable in aqueous media over a large range of pH and electrochemical potential.[6] In concentrated acid, permetallates are generally unstable and reduction, dimerisation, dehydration or complexation can occur.[7, 8, 9,10] The reaction of pertechnetate in water with strong acid leads to dehydration and various complexes with TcO_3^+ core have been synthesized.[11] In theses synthetic reactions, it is assumed that the anhydrous Tc_2O_7 is formed as an intermediate product.[11]

Sulfuric acid is widely used in industrial applications; it is also a solvent of choice for dehydration process. [12-13] Speciation of Mn(VII) in H_2SO_4 has been documented; manganese heptoxide is formed after dissolution of $KMnO_4$ and the MnO_3^+ cation has been reported. [14,15,16]. For technetium and rhenium, speciation data are still sparse, the $HReO_2(SO_4)_2.3H_2O$ complex has been mentioned while technetium heptoxide has been proposed but no structural nor speciation data were provided. [17-18] In the present work, the speciation of technetium complexes after dissolution of $KTcO_4$ in sulfuric acid has been performed. The molecular structure and spectroscopic properties of the complexes were studied by UV-visible, X-ray absorption fine structure (XAFS) and NMR spectroscopy and density functional theory (DFT) techniques.

Potassium pertechnetate (~ 30 mg) was placed in glass vials, and 1 M, 6 M, 12 M sulfuric acid (5 mL) was added with a glass pipette. After dissolution of the salt, a yellow color is observed in 12 M while for 1 M and 6 M, the solution remains clear. UV-visible spectroscopy measurements in 1 M and 6 M show the presence of TcO_4^- while in 12 M, the spectrum of the yellow solution differs from that of the pertechenate (*vide supra*). The conditions of formation of the yellow species were investigated by NMR spectroscopy. Technetium samples were prepared in H_2SO_4 (from 3 M to 18 M) and ^{99}Tc NMR spectra

were recorded. The representation of the ^{99}Tc chemical shift vs TcO_4^- (Figure 1) indicates that the formation of the new species is noticeable at 8 M and is complete at ~12 M H_2SO_4. In this domain of concentration, the dissociation of sulfuric acid produces mainly HSO_4^- and H_3O^+.[19] Therefore, it is likely that an acid-base phenomenon is responsible for the formation of the yellow species.
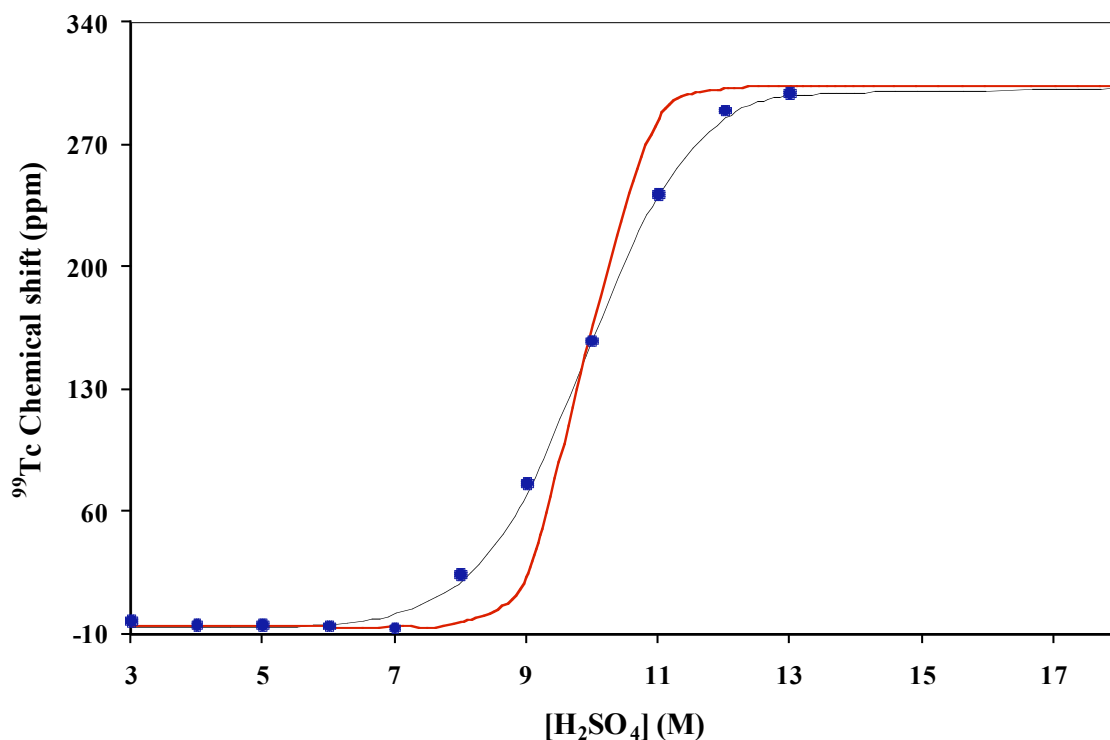

Figure 1. [99]Tc NMR shift vs TcO_4^- of $KTcO_4$ dissolvd in 3 M and 18 M H_2SO_4. Data are externally referenced to 0.05 M $KTcO_4$ in water. Experimental data are indicated by points, black line is the chemical shift fit using eq 1, and the red line chemical shift fit using eq 2.

The chemical shift of the protonated species is a function of the coordination environment of Tc. Previous ^{99}Tc NMR studies have shown that the shift of Tc(VII) complexes varies between 0 and 430 ppm. [20, 21, 22a-d] In the present experiment, the shift measured in 12 M (300 ppm) is consistent with the presence of a heptavalent species. The value of the shift depends of the core structure. For complexes with the TcO_3^+ core, the shift varies between 43.7 ppm and 375 ppm, for compounds with the TcO_2^{3+} core, a shift between 140 ppm and 393 ppm has been reported. The chemical shift of $Tc_2O_7 \cdot H_2O$ has been reported to be ~10 ppm.[23] The chemical shift of the yellow Tc species, 300 ppm, is most similar to those of $\{CpCo[PO(OEt_2)]_3\}TcO_3$ and $(tacn)TcO_3Cl$. [24a- 24b] This similarity suggests that the yellow Tc complex may possess the TcO_3^+ core structure resulting from single protonation ("$HTcO_4$") or double protonation ("$TcO_3(H_2O)^+$") of TcO_4^-.

To determine the stoichiometry of the reaction, the chemical shift of the Tc species was modeled using a simple equilibria, give by eq 1 and 2, and the Hammett acidity, H_0, of sulfuric acid.[25]

$$\log([HTcO_4]/[TcO_4^-]) = pK_{HTcO4} - H_0 \qquad\qquad eq\ 1.$$

$$\log([TcO_3(H_2O)^+]/[TcO_4^-]) = pK_{TcO3(H2O)+} - 2H_0 \qquad\qquad eq\ 2.$$

The ^{99}Tc NMR data were fit by allowing the pK_as and the chemical shifts of the unprotonated and protonated species to vary. The best fit was provided by eq with δ = -5.8 ppm for TcO_4^-, δ = 303 ppm for "$HTcO_4$", and pK_{HTcO4} = -4.9 (the chemical shift of TcO_4^- differs from 0 because the spectra were externally referenced)..As shown in Figure 1, eq 1 fits the data while eq 2 does not.. The value of pK_{HTcO4} is different with values of pK_{HTcO4} determined by solvent extraction and ion exchange.[26] However, this value for pK_{HTcO4} is consistent with previous spectroscopic studies that report no appreciable formation of $HTcO_4$ when $[H^+]$ is less than 7 M. [18, 27]

To better understand the molecular structure of the yellow species, X-ray absorption fine structure measurements were performed. A solution of $KTcO_4$ (0.01 M) in 12 M H_2SO_4 was prepared and shipped to the Advanced Photon Source for XAFS measurement. (Details about measurement are provided in supporting information) The x-ray absorption near edge spectrum (XANES) is given in the supplemental information (Figure S1). The energy of the absorption edge (21058.2 eV) is consistent with Tc(VII) and spectra exhibits a pre-edge feature which correspond to the 1s → 4d electronic transition. This transition is forbidden in complex with inversion symmetry and indicates that the species under investigation does not exhibit an inversion center.

The extended x-ray absorption fine structure (EXAFS) spectrum was k^3-weighed and Fourier transform (FT) done in the k range [2-12] Å^{-1}. The FT shows one peak centered at R + Δ ~1.4 Å, which is at the same position as in TcO_4^- and indicates the yellow species possesses Tc=O bonds. Further analysis of the FT indicates the absence of significant peaks above 2.5 Å, thus eliminating the possibility of Tc_2O_7 and Tc sulfato-complexes. Simulated Fourier transform of Tc_2O_7 and $TcO_2(SO_4)_3{}^{3-}$ complexes (Figure S2 and S3 in supporting information) exhibit respectively a significant peak around 3.2 Å due to Tc⇆Tc scattering and around 2.8 Å due to Tc⇆S scattering.

To determinate the geometry of the complex, various models with short oxygen and long oxygen distances were tested (supplemental information). The best models all have three short Tc terminal oxo bonds. The parameters for the best fit are given in Table 1, and the EXAFS spectrum and fit are shown in Figure 2.
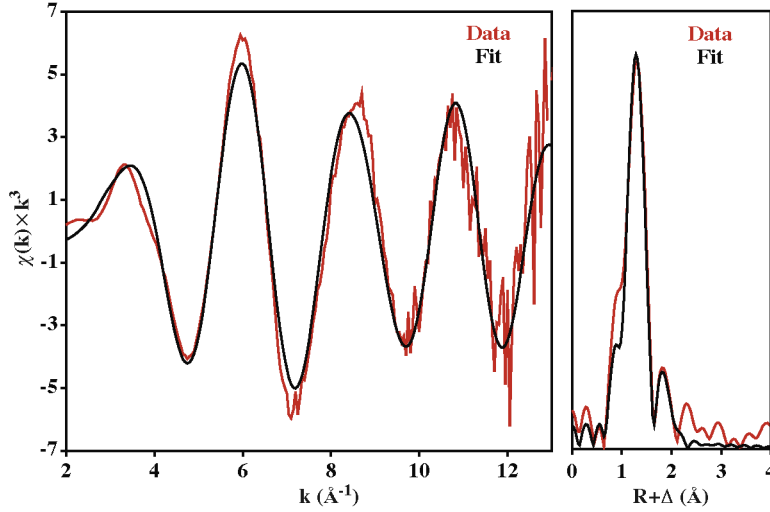
Figure 2. Fitted k^3 EXAFS spectra and Fourier transform of k^3 EXAFS spectra of $KTcO_4$ in 12 M H_2SO_4. Data is show in red and the fit is shown in black

Table 1: EXAFS fit parameters for $KTcO_4$ in 12 M H_2SO_4[a]

Neighbor	# of Neighbors	Distance (Å)	σ^2 (Å2)	$p(F)$[b]
O	3	1.702(8)	0.0022(4)	<0.001
O	1	2.07(4)	0.004(4)	0.14
O	2	2.23(3)	0.004(4)[c]	0.048

a) $2<k<12$, $0.8<R<3$, r=0.009, $\chi_v^2 = 24$, S_0^2=0.9 (fixed), ΔE_0 =-1(3) eV
b) Probability that improvement in fit due to adding this shell is due to random error.
c) Debye-Waller parameter was constrained to equal that of the previous shell

The model used to fit the EXAFS spectrum is based on the structure of perrhenic acid, $Re_2O_7(H_2O)_2$, which is an asymmetric dimer consisting of a tetrahedral Re with three terminal oxo ligands joined by a bridging oxo to a distorted octahedral Re with three terminal oxo ligands and two water ligands. [28] The six coordinate Re center was used as the model complex by replacing the tetrahedral Re moiety by a proton. The parameters for the best fit, given in Table 1, are very similar to the model complex. It should be noted that although the Tc-O interaction at 2.07 Å improves the fit, its p(F) is 0.14, and this interaction cannot rigorously be considered observed in the EXAFS experiment (there is a 14% chance that the improvement due to including this scattering shell is due to random error). In contrast, the other Tc-O interactions have p(F) < 0.05 and can be considered to be observed in the EXAFS experiment. The EXAFS fit shows 3 Tc=O groups at 1.70 Å, in good agreement with the three Re=O groups at 1.74 Å; one Tc-O at 2.07 Å, which is similar to the Re-bringing oxide distance of 2.10 Å. Finally the longest Tc-O distance of 2.23 Å is similar to the Re-(H_2O) distance, 2.18 Å. Moreover, the ligand most likely responsible for this Tc-O interaction is water since a coordinated sulfate ligand should have a scattering contribution at longer distances as described above.

Overall, the EXAFS spectrum of the yellow species is consistent with $TcO_3(OH)(H_2O)_2$, which can also be described as $HTcO_4$ coordinated by two H_2O molecule. This proposed 6-coordinate structure is quite similar the previously mentioned 6-coordinate TcO_3^+ complexes as well as $[TcO_3][SO_3F]$ where the Tc terminal oxo bond distances vary from 1.68 Å to 1.72 Å and the distance to the longer nitrogen or oxygen ligands varies from 2.15 Å to 2.24 Å. [29]

To better define the identity of "$HTcO_4$" in 12 M H_2SO_4, a search for the possible structures was carried out using DFT calculations within the generalized gradient approximation (GGA) and with the Becke 3-parameter, Lee, Yang and Parr (B3LYP) hybrid functional (details in supplemental information). The computed equilibrium geometry of the $TcO_3(OH)(H_2O)_2$ complex with C_s symmetry depicted in Figure 3 closely matches structural parameters previously found by XAFS spectroscopy. This complex possesses three short Tc=O bonds (two Tc=O bonds of 1.72 Å and one Tc=O bond of 1.74 Å), and three Tc-O bonds (two $Tc-OH_2$ bonds of 2.31 Å and one Tc-OH bond of 2.02 Å).
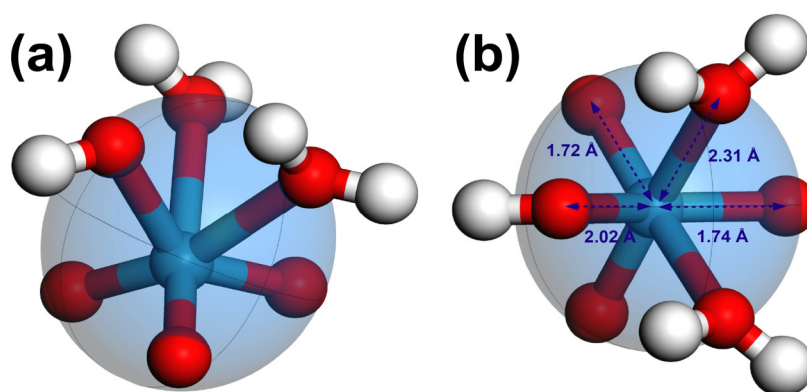

Figure 3. Equilibrium structure of the $TcO_3(OH)(H_2O)_2$ complex with C_s symmetry calculated using DFT at the B3LYP/SSD level of theory. (a) Side view, (b) top view. Color legend: Tc, cyan; O, red; H, white.

The electronic structure of $TcO_3(OH)(H_2O)_2$ reflects the C_s symmetry of this complex, with non-degenerate MOs belonging either to the A' or A'' representations of this point group. The calculated HOMO-LUMO energy gap is 4.56 eV, slightly smaller than the one of TcO_4^- (5.16 eV) but significantly larger than the gap of 6-coordinate Tc complexes (e.g., ~1.2 eV for TcX_6^{2-} (X= Cl, Br). [30] The highest-occupied MOs ranging from the HOMO to the HOMO-7 are ligand-localized (cf. Figure 4), and are mainly derived from the O $2p$ orbitals of the TcO_3^+ core or OH ligand (HOMO to HOMO-5), and of the H_2O ligands (HOMO-6 and HOMO-7). The lower-lying HOMO-8 orbital shows a significant contribution from the Tc $4d$ orbitals in addition to the O $2p$ orbitals of the core and the OH ligand. The lowest-lying unoccupied MOs of the complex are based almost exclusively on the TcO_3^+ core (LUMO), with the presence of unoccupied O $2p$ and Tc $4d$ orbitals, and some modest O $2p$ contribution from the OH ligand (LUMO+1 and LUMO+2). These low-lying unoccupied d orbitals of the TcO_3^+ ion favor ligand-to-metal charge transfer (LMCT), i.e. O $2p \rightarrow$ Tc $4d$ transitions.
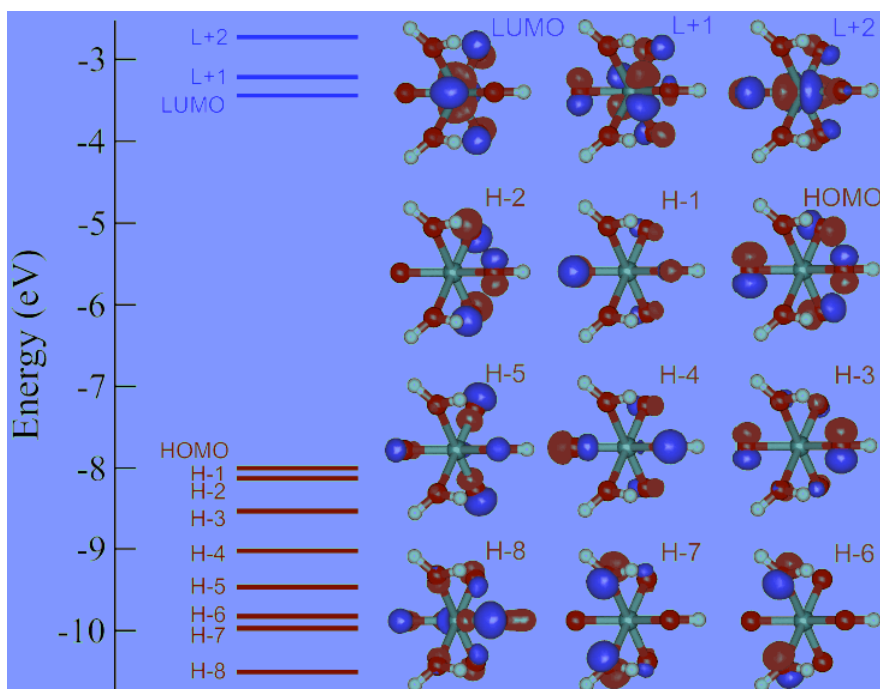
Figure 4. Energy diagram of the highest-lying molecular orbitals (MO) of the C_s-symmetry $TcO_3(OH)(H_2O)_2$ complex computed at the B3LYP/SDD level of theory. Occupied and unoccupied energy levels are represented in red and blue, respectively. The MOs involved in the major LMCT bands are also represented.

The spectroscopic properties of the yellow species were analyzed in 12 M H_2SO_4 by UV-visible spectroscopy. Its electronic spectrum (Figure 5) is different from that of TcO_4^-; it exhibits a distinct band at 335 nm, a shoulder at 270 nm and a series of bands in the vicinity 250 nm- 200 nm. The valence of the complex was further confirmed after dilution of yellow solution with water; the UV-visible spectrumt of the diluted the is identical to that of TcO_4^-. Moreover, the yellow species is unlikely to be be Tc(IV), Tc(V), or Tc(VI), since in water, Tc(IV) complexes exhibit characteristic spectra, and Tc(V) and Tc(VI) species disproportionate to Tc(IV).[31, 26]

Excitation energies and oscillator strengths for the lowest-lying excited states of the $TcO_3(OH)(H_2O)_2$ complex were computed using the time-dependent density functional theory (TD-DFT) at the GGA/B3LYP level of theory. Theoretical results are reported in Figure 5 along with the experimental spectrum (cf. Table S2 for numerical values).
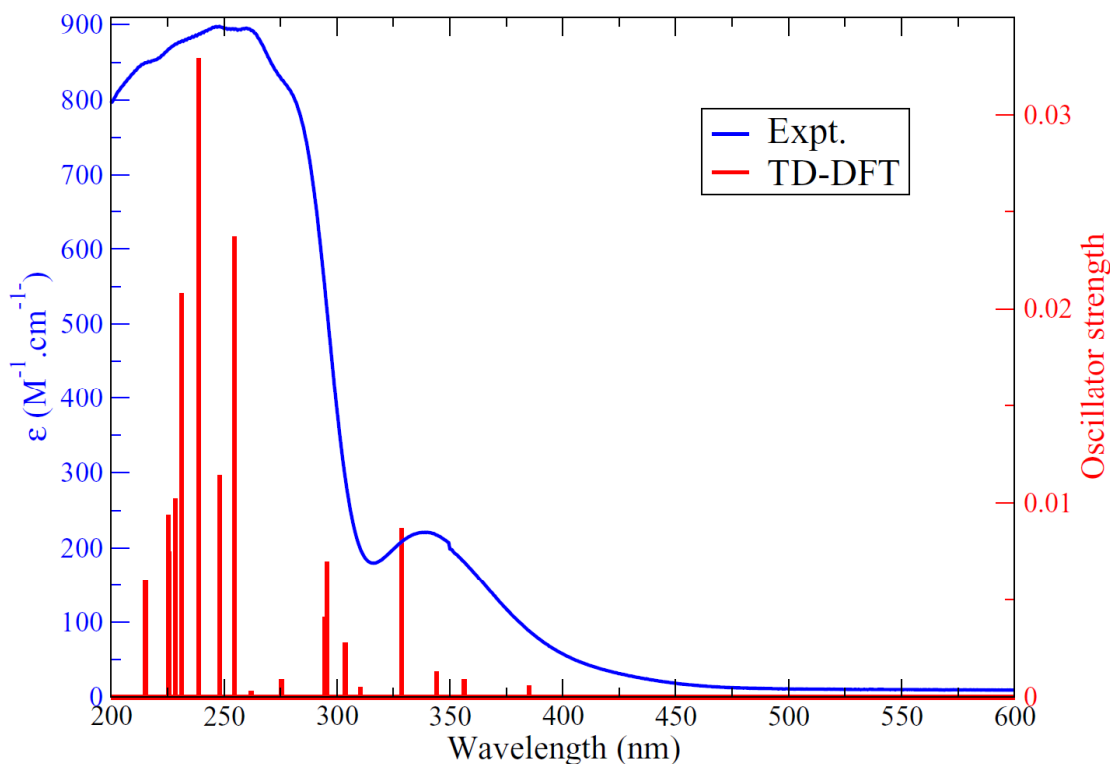
Figure 5. Experimental UV-Visible spectrum of $KTcO_4$ in 12 M H_2SO_4 (blue) and oscillator strengths for the C_s-symmetry $TcO_3(OH)(H_2O)_2$ complex calculated using TD-DFT at the B3LYP/SSD level of theory (red).

The major bands for the lowest-lying excited states of $TcO_3(OH)(H_2O)_2$ are computed to be at 329, 295, 255, 248, 239, 231, 228, 225 and 215 nm. For most of the bands, calculations show a combination of one-electron transitions from occupied O ligand-based MOs into the virtual Tc metal-localized MOs. The first band at 329 nm corresponds to pure HOMO-1→LUMO+2 and HOMO→LUMO+1 transition. The bands at 295 nm and 255 nm correspond to one-electron excitations from HOMO-4 to LUMO/LUMO+1 and LUMO+2. The band predicted at 248 nm and 231 nm stems from the HOMO-6→LUMO transition. The most intense band at 239 nm results from HOMO-5→LUMO+2 excitation. Finally, transitions to the LUMO from the HOMO-7 and HOMO-8 are mostly responsible for the bands at 228 nm and 225 nm and 215 nm, respectively. The overall good agreement between the calculated spectrum of $TcO_3(OH)(H_2O)_2$ and the experimental spectrum confirms that $TcO_3(OH)(H_2O)_2$ is likely the species formed after dilution of $KTcO_4$ in 12 M H_2SO_4.

In summary, the speciation of heptvalent technetium has been investigated in sulfuric acid. In 12 M H_2SO_4, a yellow solution is observed, and its ^{99}Tc NMR spectrum is consistent with a heptavalent complex. The yellow solution was further characterized by EXAFS spectroscopy, and results are consistent with the formation of $TcO_3(OH)(H_2O)_2$. No technetium heptoxide or sulfato- complexes were detected in these conditions. The molecular structure of $TcO_3(OH)(H_2O)_2$ has been optimized by DFT techniques, and the structural parameters are well in accordance with those found by XAFS spectroscopy.

The experimental electronic spectra exhibit ligand-to-metal charge transfer transitions that have been assigned using TDDFT methods. Calculations demonstrate the theoretical electronic spectrum of $TcO_3(OH)(H_2O)_2$ to be in very good agreement with the experimental one. Recent experiments in 12 M H_2SO_4 show the yellow solution to be very reactive in presence of reducing agents presumably forming low valent Tc species. Current spectroscopic works focus on the speciation of these species.

Notes and references.

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† Electronic Supplementary Information (ESI) available: Additional details on XAFS experiment and computational method. XANES spectra of the yellow solution, and simulated EXAFS spectra of Tc_2O_7 and $TcO_2(SO_4)_3$. Transition energies and oscillator strength for $TcO_3(OH)(H_2O)_2$ computed using TD-DFT.

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Table of contents.

The speciation of heptavalent technetium has been performed in sulfuric acid. In 12 M H_2SO_4, EXAFS and NMR results are consistent with the formation of the $TcO_3OH(H_2O)_2$ species. Molecular structure and electronic spectra of $TcO_3OH(H_2O)_2$ were investigated using density functional theory techniques.