# Speciation of heptavalent technetium in sulfuric acid: structural and spectroscopic studies†

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**The speciation of Tc(VII) was studied in 12 M H₂SO₄ by NMR, UV-visible and XAFS spectroscopy. Experimental results and density functional calculations show the formation of $TcO_3(OH)(H_2O)_2$.**

Heptavalent transition metal complexes of group VII with the $d^0$ electronic configuration are often used in catalysis and biomedical applications.[1] For manganese, the high electron affinity and oxidation potential of its heptavalent complexes make these species the catalysts of choice for the oxidation of organic compounds.[2] 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.[1c] 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.[3] 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.[4] In concentrated acid, permetallates are generally unstable and reduction, dimerisation, dehydration or complexation can occur.[5] The reaction of pertechnetate in water with strong acid leads to dehydration and various complexes with $TcO_3^+$ core have been synthesized.[6] In these synthetic reactions, it is assumed that the anhydrous $Tc_2O_7$ is formed as an intermediate product.[6] Sulfuric acid is widely used in industrial applications. It is also a solvent of choice for the dehydration process.[7] Speciation of Mn(VII) in $H_2SO_4$ has been documented; $Mn_2O_7$ is formed after dissolution of $KMnO_4$ and the $MnO_3^+$ cation has been reported.[8] For technetium and rhenium, speciation data are still sparse, the $HReO_2(SO_4)_2 \cdot 3H_2O$ complex has been mentioned while $Tc_2O_7$ has been proposed, but no structural nor speciation data were provided.[9] In the present work, the speciation of technetium complexes after dissolution of $KTcO_4$ in sulfuric acid has been examined. The molecular structure and spectroscopic properties of the complexes were studied by UV-visible, X-ray absorption fine structure and NMR spectroscopy and density functional theory techniques.

Potassium pertechnetate (~ 30 mg) was placed in glass vials, and 1 M, 6 M, 12 M, 18 M sulfuric acid (5 mL) was added with a glass pipette. After dissolution of the salt, a yellow color is observed in 12 M and 18 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 $TcO_4^-$ (bands at 244 nm and 288 nm)[9b] while in 12 M and 18 M, the spectrum of the yellow solution differs from that of the pertechnetate (*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*. $TcO_4^-$ (Fig. 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 $H_3O^+$.[10] Therefore, it is likely that an acid–base phenomenon is responsible for the formation of the yellow species.
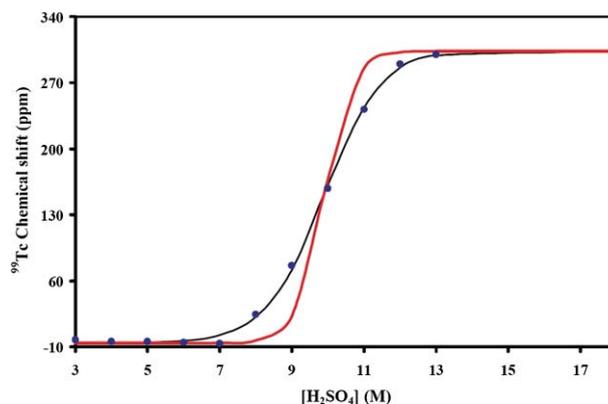


**Fig. 1** 99Tc NMR shift *vs*. $TcO_4^-$ of $KTcO_4$ dissolved in 3 M, 4 M, 5 M, 6 M, 7 M, 8 M, 9 M, 10 M, 11 M, 12 M, 13 M and 18 M $H_2SO_4$. Experimental data are indicated by points; the black line is the chemical shift fit using eqn (1) and the red line using eqn (2).

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.[11] 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 on the core structure. For complexes with the $TcO_3^+$ core, the shift varies between 43.7 and 375 ppm, for compounds with the $TcO_2^{3+}$ core, shifts between 140 and 393 ppm have been reported. The chemical shift of $Tc_2O_7 \cdot H_2O$ has been reported to be ~10 ppm.[12] The chemical

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† Electronic supplementary information (ESI) available: Additional details on XAFS experiment and computational method. XANES spectra of the yellow solution, simulated EXAFS spectra of $Tc_2O_7$ and $TcO_2(SO_4)_3^{3-}$. Transition energies and oscillator strengths for $TcO_3(OH)(H_2O)_2$ computed using TD-DFT. See DOI: 10.1039/c0dt00695e

shift of the yellow Tc species, 300 ppm, is most similar to those of $\{CpCo[PO(OEt)_2)]_3\}TcO_3$ and $(tacn)TcO_3Cl$.[13] 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 simple equilibrium formulae, given by eqn (1) and eqn (2), and the Hammett acidity, $H_0$, of sulfuric acid.[14]

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

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

The $^{99}Tc$ NMR data were fit by allowing the $pK_a$s and the chemical shifts of the unprotonated and protonated species to vary. The best fit was provided by eq. 1 with $\delta = -5.8$ ppm for $TcO_4^-$, $\delta = 303$ 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 Fig. 1, eqn (1) fits the data while eqn (2) does not. The value of $pK_{HTcO4}$ is different from those determined by solvent extraction and ion exchange[15] but consistent with spectroscopic studies that report no appreciable formation of $HTcO_4$ when $[H^+]$ is less than 7 M.[9b,16]

To better understand the molecular structure of the yellow species, X-ray absorption fine structure (XAFS) measurements were performed. A solution of $KTcO_4$ in 12 M $H_2SO_4$ was prepared and shipped to the Advanced Photon Source.[17] The X-ray absorption near edge spectrum (XANES) is given in the supplemental information. The energy of the absorption edge (21058.2 eV) is consistent with Tc(VII) and spectra exhibit a pre-edge feature which corresponds to the 1 s → 4d electronic transition. This transition is forbidden in complexes 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 $k^3$-weighted, and Fourier transform (FT) was 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 that 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 transforms of $Tc_2O_7$ and $TcO_2(SO_4)_3^{3-}$ complexes (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 Fig. 2. 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.[18] 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 are very similar to the model complex. It should be noted

**Table 1**  EXAFS fit parameters for $KTcO_4$ in 12 M $H_2SO_4^a$

| Neighbor | # of Neighbors | Distance/Å | σ²/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), $\Delta E_0 = -1(3)$ 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.
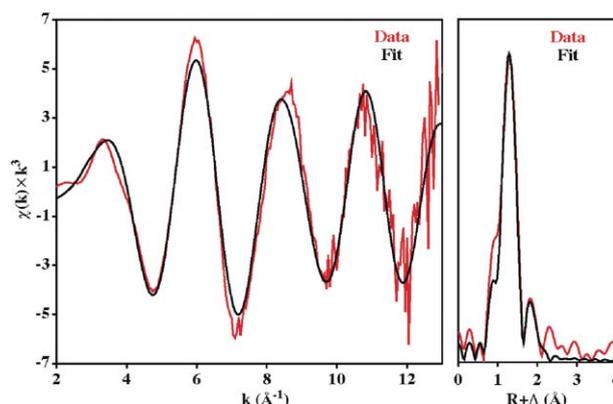


**Fig. 2**  Fitted $k^3$ EXAFS spectra and Fourier transform of $k^3$ EXAFS spectra of $KTcO_4$ in 12 M $H_2SO_4$. Data in red and fit in black.

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.

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–(H₂O) 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 $H_2O$ molecules. This proposed 6-coordinate structure is quite similar to 6-coordinate $TcO_3^+$ complexes 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.[13,19]

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 (details in supplemental information). The computed equilibrium geometry of the $TcO_3(OH)(H_2O)_2$ complex with $C_s$ symmetry depicted in Fig. 3 closely matches structural parameters 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–OH₂ bonds of 2.31 Å and one Tc–OH bond of 2.02 Å). 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,
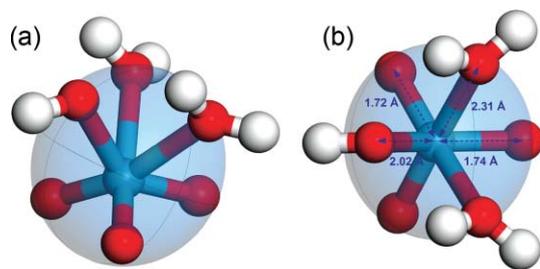
**Fig. 3** Calculated equilibrium structure of the $TcO_3(OH)(H_2O)_2$. Side view (a), top view (b). Color legend: Tc, cyan; O, red; H, white.

slightly smaller than the one of $TcO_4^-$ (5.16 eV) but significantly larger than the gap of 6-coordinate Tc complexes.[20]

The highest-occupied MOs ranging from the HOMO to the HOMO-7 are ligand-localized (Fig. 4), and are mainly formed 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 → Tc 4d transitions.
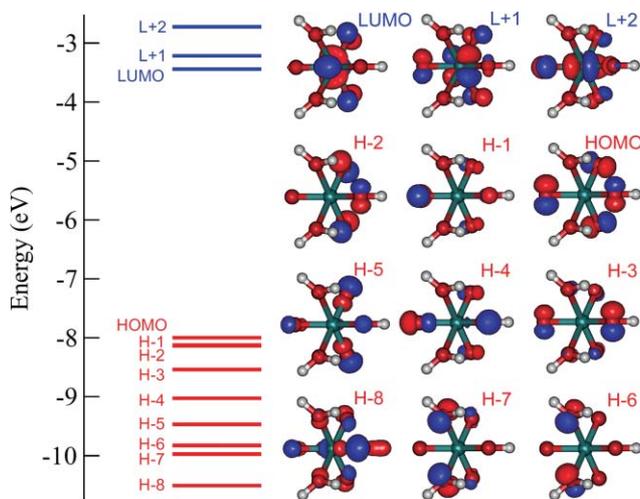


**Fig. 4** Energy diagram of the highest-lying molecular orbitals of the $C_s$-symmetry $TcO_3(OH)(H_2O)_2$ complex.

The spectroscopic properties of the yellow species were analyzed in 12 M $H_2SO_4$.[21] Its electronic spectrum (Fig. 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. 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 Fig. 5 along with the experimental spectrum (*cf.* Table S2 for numerical values). The major bands for the lowest-lying excited states of $TcO_3(OH)(H_2O)_2$ are computed to be at
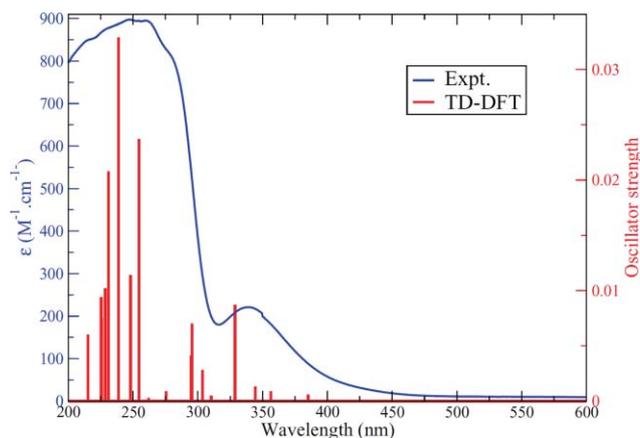


**Fig. 5** Experimental UV-visible spectrum of $KTcO_4$ in 12 M $H_2SO_4$ (blue) and calculated oscillator strengths for $TcO_3(OH)(H_2O)_2$ (red).

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 dissolution of $KTcO_4$ in 12 M $H_2SO_4$.

In summary, the speciation of heptavalent 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 XAFS 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 in accordance with those found by XAFS spectroscopy. The experimental electronic spectra exhibit ligand-to-metal charge transfer transitions that have been assigned using TD-DFT methods. Calculations show 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 work focuses on the speciation of these species.

## Acknowledgements

## Notes and references

1 (*a*) C. T. Bui, K. Rees and R. G. H. Cotton, *Nucleosides, Nucleotides Nucleic Acids*, 2003, **22**, 1835; (*b*) K. Schwochau, *Technetium: Chemistry and Radiopharmaceutical Applications*, Wiley-VCH: Weinheim, Germany, 2000; (*c*) C. C. Romao, F. E. Kuehn and W. A. Herrmann, *Chem. Rev.*, 1997, **97**, 3197.

2 E. S. Rudakov and V. L. Lobachev, *Russ. Chem. Bull.*, 2000, **49**, 761.

3 Y. Tooyama, H. Braband, B. Spingler, U. Abram and R. Alberto, *Inorg. Chem.*, 2008, **47**, 257.

4 N. de Zoubov and M. Pourbaix, CEBELCOR, Rappt. 1957, **No. 51**, 1.

5 (*a*) A. Engelbrecht and A. V. Grosse, *J. Am. Chem. Soc.*, 1954, **76**, 2042; (*b*) T. S. Briggs, *J. Inorg. Nucl. Chem.*, 1968, **30**, 2866; (*c*) R. W. Thomas, M. J. Heeg, R. C. Elder and E. Deutsch, *Inorg. Chem.*, 1985, **24**, 1472; (*d*) D. E. Grove, N. Johnson and W. G. Peter, *Inorg. Chem.*, 1969, **8**, 1196.

6 R. Alberto, Technetium. In *Comprehensive Coordination Chemistry. II*J. A. McCleverty, T. J. Mayer, ed.; Elsevier: Amsterdam, The Netherlands, 2003; Vol. 5, p 136.

7 J. B. Senderens, *Compt. rend.*, 1923, **176**, 813.

8 (*a*) D. J. Royer, *J. Inorg. Nucl. Chem.*, 1961, **17**, 159; (*b*) R. J. Gillespie and R. Kapoor, *Can. J. Chem.*, 1987, **65**, 2665; (*c*) A. Simon, R. Dronskowski, B. Krebs and B. Hettich, *Angew. Chem.*, 1987, **99**, 160.

9 (*a*) V. A. Bardin, K. I. Petrov and K. A. Bol'shakov, *Zh. Neorg. Khim.*, 1966, **11**, 2101; (*b*) C. L. Rulfs, R. A. Pacer and R. F. Hirsch, *J. Inorg. Nucl. Chem.*, 1967, **29**, 681.

10 G. E. Walrafen, W. H. Yang, Y. C. Chu and M. S. Hokmabadi, *J. Solution Chem.*, 2000, **29**, 905.

11 (*a*) V. A. Mikhalev, *Radiokhimiya*, 2005, **47**, 319; (*b*) H. Braband, Y. Tooyama, T. Fox and R. Alberto, *Chem.–Eur. J.*, 2009, **15**, 633; (*c*) K. J. Franklin, C. J. L. Lock, B. G. Sayer and G. J. Schrobilgen, *J. Am. Chem. Soc.*, 1982, **104**, 5303; (*d*) J. A. Thomas and A. Davison, *Inorg. Chim. Acta*, 1989, **161**, 39.

12 V. I. Spitsyn, V. P. Tarasov, K. E. Guerman, S. A. Petruchin, A. F. Kuzina and S. V. Kryutchkov, *Dolk. Akak. Nauk. SSSR.*, 1986, **290**, 1411.

13 (*a*) J. A. Thomas and A. Davison, *Inorg. Chem.*, 1992, **31**, 1976; (*b*) H. Braband and U. Abram, *Inorg. Chem.*, 2006, **45**, 6589.

14 (*a*) M. A. Paul and F. A. Long, *Chem. Rev.*, 1957, **57**, 1; (*b*) M. J. Jorgensen and D. R. Hartter, *J. Am. Chem. Soc.*, 1963, **85**, 878.

15 J. A. Rard, M. H. Rand, G. Anderegg and H. Wanner, *Chemical Thermodynamics of Technetium*, MCA Sandino E Östhols, ed.; Elsevier: Amsterdam, 1999.

16 G. E. Boyd, *Inorg. Chem.*, 1978, **17**, 1808.

17 XAFS experiment in 18 M $H_2SO_4$ shown the solution to be sensitive to the X-ray beam and measurement was stopped.

18 H. Beyer, O. Glemser and B. Krebs, *Angew. Chem., Int. Ed. Engl.*, 1968, **7**, 295.

19 J. Supel, A. Hagenbach, U. Abram and K. Seppelt, *Z. Anorg. Allg. Chem.*, 2008, **634**, 646.

20 P. F. Weck, E. Kim and K. R. Czerwinski, *Chem. Phys. Lett.*, 2010, **487**, 190.

21 UV-visible measurements were performed in 18 M $H_2SO_4$ and shown the spectra to be identical to the one in 12 M $H_2SO_4$ (Fig. S4†).