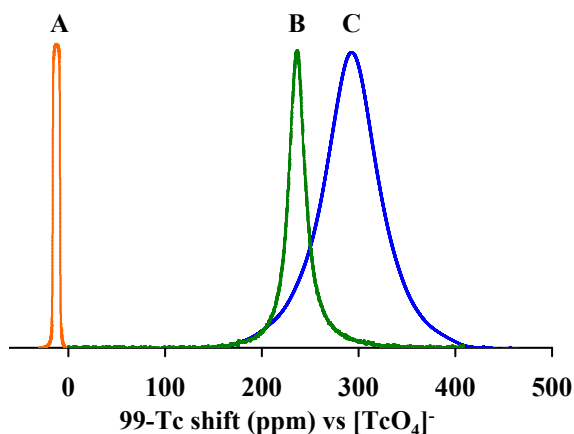


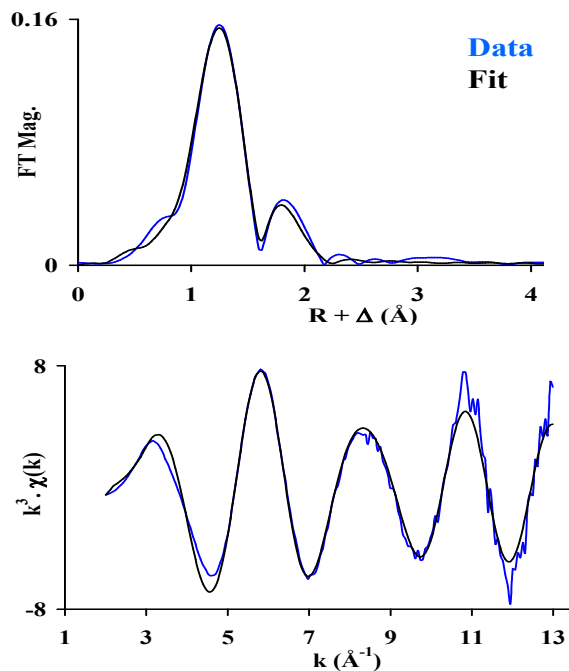
### Supplementary Information



**Figure S1.**  $^{99}\text{Tc}$  NMR spectra obtained after the dissolution of  $\text{NH}_4\text{TcO}_4$  in A) 15.6 M  $\text{HNO}_3$ , B) 13.7 M  $\text{HClO}_4$  and C) 18 M  $\text{H}_2\text{SO}_4$ .

**Table S1.**  $^{99}\text{Tc}$  NMR chemical shift (ppm) vs.  $\text{TcO}_4^-$  as a function of the acid concentration (M) of the solutions obtained after dissolution of  $\text{KTcO}_4$  or  $\text{NH}_4\text{TcO}_4$  in  $\text{HNO}_3$ ,  $\text{HClO}_4$  and in  $\text{H}_2\text{SO}_4$ .

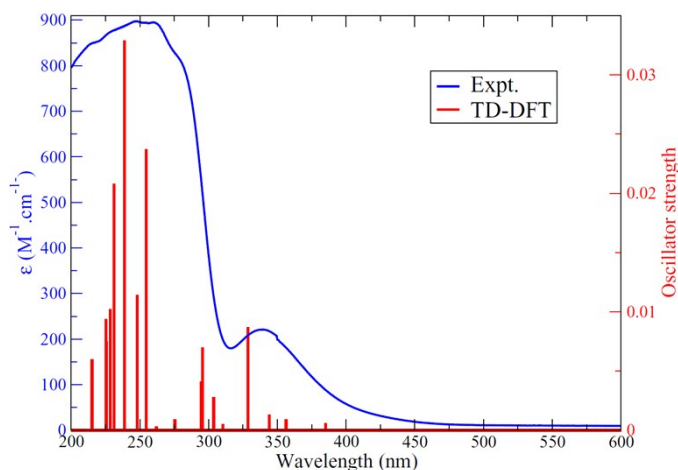
$[\text{H}_2\text{SO}_4]$	Shift (ppm)	$[\text{HClO}_4]$	Shift (ppm)	$[\text{HNO}_3]$	Shift (ppm)
2	-2.47	2	0	2	0
4	-4.32	4	-1.5	4	-1.7
6	-5.05	6	-2	6	-3.5
8	24.5	8	-5	8	-5.2
9	76.3	9.28	12	11.7	-9.5
10	158	10.44	103	15.6	-12.8
11	241.8	11.6	222		
12	290	13.7	235		
13	300				
18	300				



**Figure S2.** Fitted  $k^3$ -EXAFS spectra and Fourier transform of  $k^3$ -EXAFS spectra of the Tc solution obtained after the dissolution of  $\text{KTcO}_4$  in 11.6 M  $\text{HClO}_4$ . Data in blue and fit in black.

**Table S2.** Structural parameters obtained by adjustment of the  $k^3$  -EXAFS spectra of the solution obtained after dissolution of  $\text{KTcO}_4$  in 11.6 M  $\text{HClO}_4$ .  $S_0^2 = 0.9$ .  $\Delta E_0 = 3.42$  eV. Reduced- $\chi^2 = 20.6$ .

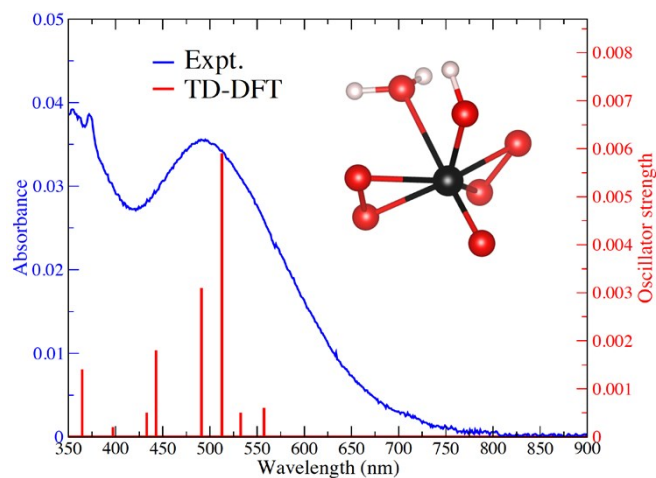
Scattering	C.N	Distance (Å)	$\sigma^2$ (Å <sup>2</sup> )
Tc=O	3.2(6)	1.69(2)	0.0022
Tc-O	2.8(6)	2.23(2)	0.0040



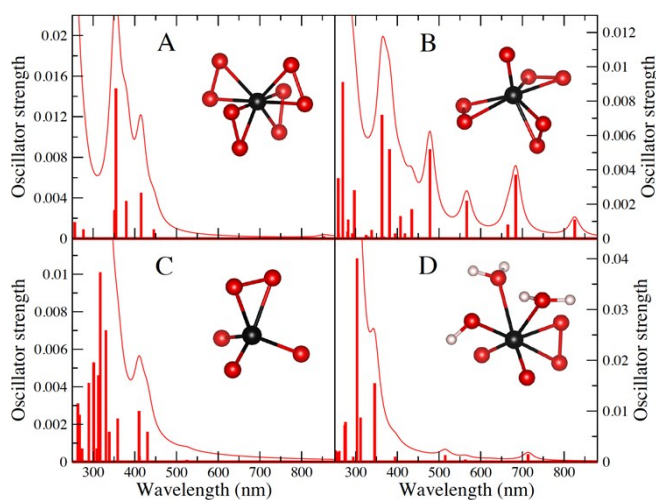
**Figure S3.** Experimental UV-visible spectrum (blue) and TD-DFT calculated oscillator strengths for  $\text{TcO}_3(\text{OH})(\text{H}_2\text{O})_2$  (red).

**Table S3.** Transition energies and oscillator strengths for  $\text{TcO}_3(\text{OH})(\text{H}_2\text{O})_2$  computed using time-dependent density functional theory (TD-DFT) at the B3LYP/SDD level of theory.

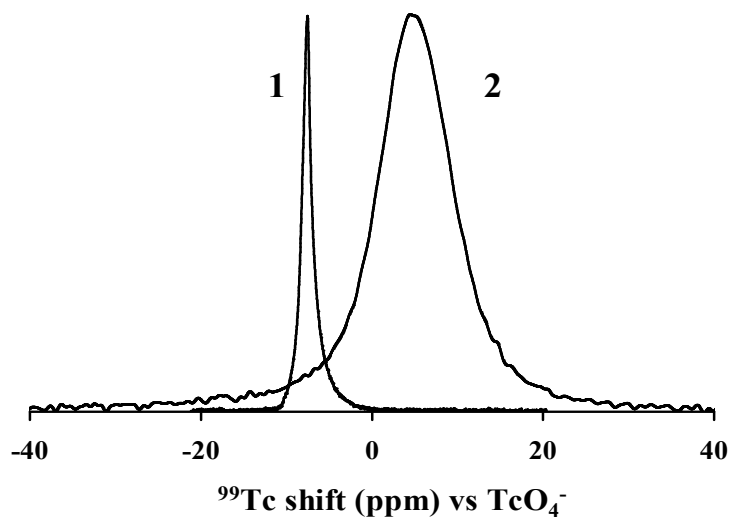
Transition energy (nm)	Composition of major bands	Oscillator strength
385	H-1→LUMO	0.0006
356	H-2→LUMO+1; H-1→LUMO	0.0009
344	H-2→LUMO; HOMO→L+2	0.0013
329	HOMO-1→LUMO+2; HOMO→LUMO+1	0.0087
310	H-2→L+2	0.0005
304	H-3→L+1; H-1→L+2	0.0028
295	H-4→L+1; H-4→LUMO	0.007
275	H-5→LUMO	0.0009
262	H-5→L+1; H-4→L+1	0.0003
255	H-4→L+2	0.0237
248	H-6→LUMO	0.0114
239	H-5→L+2	0.0329
231	H-6→LUMO	0.0208
228	H-7→LUMO; H-5→L+2	0.0102
225	H-8→LUMO; H-6→L+1	0.0094
215	H-8→LUMO	0.006



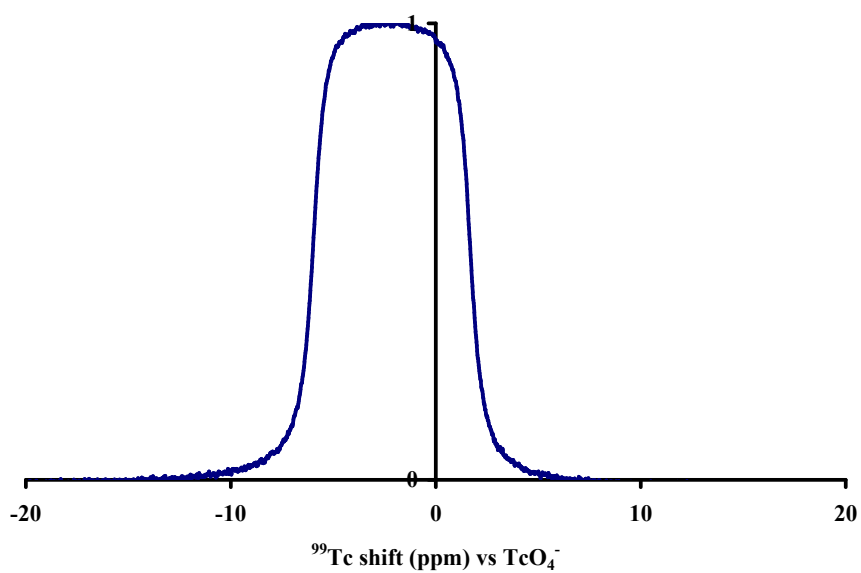
**Figure S4.** Experimental UV-visible spectrum (in blue) of the solution after the reaction of Tc(+7) with  $\text{H}_2\text{O}_2$  in 8 M  $\text{HNO}_3$  and oscillator strengths (in red) of  $\text{TcO}(\text{O}_2)_2(\text{H}_2\text{O})(\text{OH})$  calculated using TD-DFT at the B3LYP/SDD level of theory.



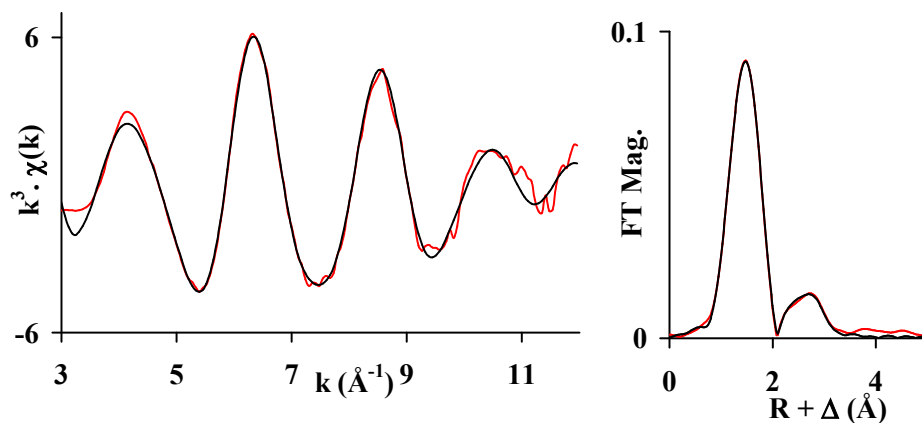
**Figure S5.** Calculated equilibrium structures and oscillator strengths of the transitions: A)  $\text{Tc}(\text{O}_2)_4^-$ ; B)  $\text{TcO}(\text{O}_2)_3^-$ ; C)  $\text{TcO}_3(\text{O}_2)^-$ ; and D)  $\text{TcO}_2(\text{O}_2)(\text{H}_2\text{O})_2(\text{OH})$ . Spectral lines were simulated from the computed oscillator strengths using Lorentzian functions with a full-width-at-half-maximum parameter of 15 nm (solid red lines).



**Figure S6.**  $^{99}\text{Tc}$  NMR spectra of 1) Tc(VII) in 3 M  $\text{H}_2\text{SO}_4$ / 4.9 M  $\text{H}_2\text{O}_2$ ) and 2) Tc(VII) in 6.5 M  $\text{H}_2\text{SO}_4$ / 4.9 M  $\text{H}_2\text{O}_2$ .



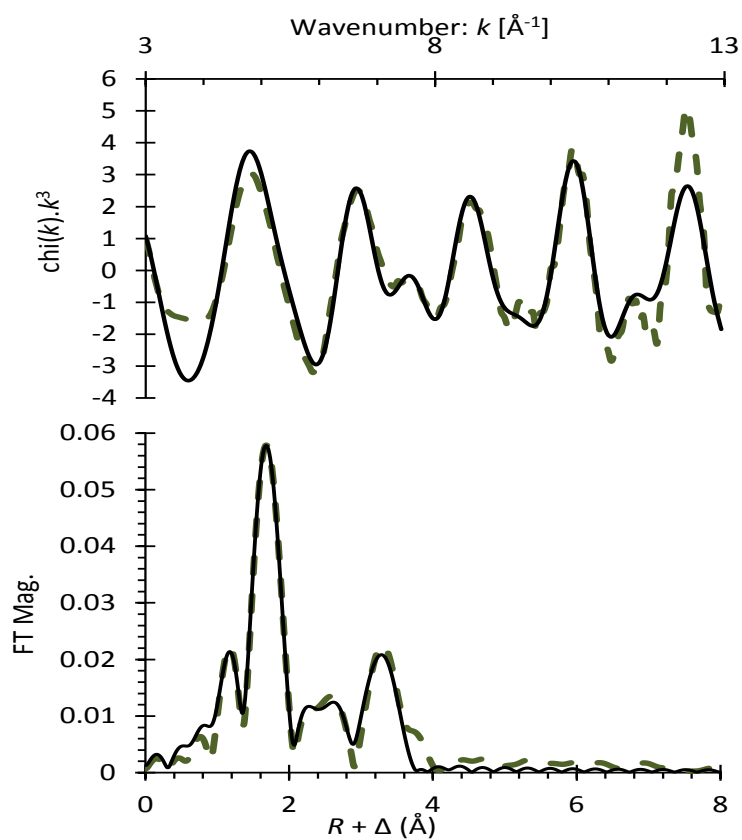
**Figure S7.**  $^{99}\text{Tc}$  NMR spectra of Tc(VII) in 6.5 M  $\text{H}_2\text{SO}_4$



**Figure S8.** Fitted  $k^3$ -EXAFS spectra and Fourier transform of the  $k^3$ -EXAFS spectrum of the solution obtained after the reaction of Tc(VII) with MeOH in 13 M  $H_2SO_4$ . Experimental Data in red and Fit in black.

**Table S4.** EXAFS fit parameters obtained for the solution obtained after the reaction of Tc(VII) with MeOH in 13 M  $H_2SO_4$ .  $\Delta E_0 = 6.5$  eV.  $S_0^2 = 0.9$ . Reduced- $\chi^2 = 8.52$

Atoms	C. N	Distance (Å)	$\sigma^2$ (Å <sup>2</sup> )
O	1.0(2)	1.65(2)	0.0022
O	4.4(9)	2.07(2)	0.004
$S_{bid}$	0.5(1)	2.89(3)	0.006
$S_{mono}$	1.9(4)	3.30(3)	0.009



**Figure S9.** Fitted  $k^3$ -EXAFS spectra (top) and Fourier Transform of  $k^3$ -EXAFS spectra (bottom) for the brown supernate in 12 M  $\text{H}_2\text{SO}_4$ . Fits are in black and experimental data are dashed green lines.

**Table S5.** EXAFS structural parameters obtained for the brown supernate in 12 M  $\text{H}_2\text{SO}_4$ .  $\Delta E_0$  [eV] = -3.62. Reduced- $\chi^2 = 736$ . Residual [%] = 13.51.

Scattering Path	CN	R [Å]	$\sigma^2$ [Å <sup>2</sup> ]
Tc – O(-Tc)	1.3 $\pm$ 0.3	1.81(2)	0.002
Tc – O	3.8 $\pm$ 0.8	2.03(2)	0.004
Tc – S <sub>bid</sub>	0.7 $\pm$ 0.1	2.84(3)	0.006
Tc – S <sub>mono</sub>	1.1 $\pm$ 0.2	3.16(3)	0.009
Tc $\rightleftharpoons$ O $\rightleftharpoons$ Tc	0.7 $\pm$ 0.3	3.62(4)	0.008

## Experimental Section

## I. Chemical

*Caution.* Technetium-99 is a weak beta emitter ( $E_{\text{max}} = 292 \text{ keV}$ ), the dose rate calculated in a typical experiment is 3.54 millirad/hours. All manipulations were performed in radiochemistry laboratory designed for chemical synthesis using efficient HEPA-filtered fume hoods, and following locally approved radioisotope handling and monitoring procedures. The starting material  $\text{NH}_4\text{TcO}_4$  was obtained from stocks at the Los Alamos National Laboratory originally purchased from the Oak Ridge Isotope Office.<sup>1</sup> The chemicals (solvents, Hydrogen peroxide potassium hydroxide, hydrogen sulfide (lecture bottle) were purchases from Sigma-Aldrich and used as received. Water was purified to  $> 18 \text{ M}\Omega \text{ cm}$  by a Milli-Q system.  $\text{KTcO}_4$  was obtained after dissolution of  $\text{NH}_4\text{TcO}_4$  in water, treatment with  $\text{H}_2\text{O}_2$ , and precipitation with an aqueous KOH solution.

## II. XAFS spectroscopy

XAFS measurements were carried out at the Advanced Photon Source (APS) at the BESSRC-CAT 12 BM station in Argonne National Laboratory. XAFS spectra were recorded at the Tc-K edge (21,044 eV) in fluorescence mode at room temperature using a 13 elements germanium detector. A double crystal of Si [1 1 1] was used as a monochromator. The energy was calibrated using a molybdenum foil (Mo-K edge = 20,000 eV). Several spectra were recorded in the  $k$  range  $[0 - 14] \text{ \AA}^{-1}$  and averaged. Background contribution was removed using the Athena<sup>2</sup> software and data analysis was performed using WINXAS.<sup>3</sup> For the fitting procedure, amplitude and phase shift function were calculated by FEFF8.2 software.<sup>4</sup> Input files were generated by Atoms<sup>5</sup> using the crystallographic structure of  $\text{Re}_2\text{O}_7(\text{H}_2\text{O})_2$ .<sup>6</sup>  $\text{K}_4\text{MoO}_2(\text{SO}_4)_3$ .<sup>7</sup> For the study in  $\text{H}_2\text{SO}_4/\text{H}_2\text{S}$  media, the putative  $[\text{Tc}_2\text{O}(\text{HSO}_4)_4(\text{H}_2\text{O})_2(\text{OH}^-)_2]$  complex was used; this complex was derived from  $[\text{Cl}_5\text{-Ru-O-Ru-Cl}_5]^{4-}$ <sup>8</sup> by replacing the Cl by O atoms and by adding monodentate and bidentate sulfate ligands. Adjustments of the  $k^3$ -weighted EXAFS spectra were performed under the constraints  $S_0^2 = 0.9$ . A single value of energy shift ( $\Delta E_0$ ) was used for all scattering.

### II. 1. Preparation of samples for XAFS

**Study in 12 M  $\text{H}_2\text{SO}_4$ .** Potassium pertechnetate (23 mg) was dissolved in 5 ml of 12 M  $\text{H}_2\text{SO}_4$ , after the dissolution 100  $\mu\text{L}$  of the yellow solution were taken and placed in Teflon sample holder of local design.

**Study in  $\text{HClO}_4$ .** Potassium pertechnetate (21 mg) was dissolved in 5 mL of 11.6 M  $\text{HClO}_4$ , after the dissolution 100  $\mu\text{L}$  of the yellow solution were taken and placed in Teflon sample holder.

**Study in  $\text{H}_2\text{SO}_4/\text{MeOH}$ .** Potassium pertechnetate (23 mg, 0.114 mmol) was dissolved in 5 ml of 13 M  $\text{H}_2\text{SO}_4$ , then 1 ml was taken and 20  $\mu\text{L}$  of MeOH (0.5 mmol) were added to the solution. After the reaction, 100  $\mu\text{L}$  of the green solution were taken and placed in a Teflon sample holder

**Study in  $\text{H}_2\text{SO}_4/\text{H}_2\text{S}$ .** Potassium pertechnetate (120 mg) was placed in a glass vial and 10 mL of 12 M sulfuric acid was added. After dissolution, a yellow color was observed.  $\text{H}_2\text{S}_{(\text{g})}$  was bubbled through the solution which immediately turned green and within a minute turned black-brown. After 20 minutes of reaction the tube was closed, centrifuged and 100  $\mu\text{L}$  of the brown supernate were taken and placed in Teflon sample holder.



### III. 99-Tc NMR spectroscopy

**Study in H<sub>2</sub>SO<sub>4</sub>.** The 99-Tc NMR spectra of solutions were recorded on a Bruker Avance 300 spectrometer at a frequency of 67.58 MHz and on a Varian 400 NMR spectrometer at a frequency of 89.575 MHz. Chemical shifts ( $\delta$ ) were measured from a 0.05 M K<sub>2</sub>TcO<sub>4</sub> solution in D<sub>2</sub>O as the external reference ( $\delta = 0$ ). Solutions (in 5 mm NMR glass tube) were prepared by dissolving K<sub>2</sub>TcO<sub>4</sub> in 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13 and 18 M sulfuric acid, the TcO<sub>4</sub><sup>-</sup> concentration in the entire series was 10<sup>-3</sup> M. Measurements were performed at 298 K.

**Study in HNO<sub>3</sub> and HClO<sub>4</sub>.** Ammonium pertechnetate (~ 20 mg) was placed in glass vials and 1 mL of perchloric (2, 4, 6, 8, 9.3, 10.4, 11.6 and 13.7 M) and nitric (2, 3.9, 7.8, 11.7, 15.6 M) acid was added. The 99-Tc NMR (90.074 MHz) spectra of the solutions were collected on a BRUKER Avance-400 spectrometer with 5 mm tubes fitted with Teflon inserts that were purchased from Wilmad Glass. Chemical shifts ( $\delta$ ) were measured relative to a standardized 0.2 M [NH<sub>4</sub>]<sub>2</sub>TcO<sub>4</sub> solution in D<sub>2</sub>O by the substitution method ( $\delta = 0$ ). Measurements were performed at 298 K.

**Study in H<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O<sub>2</sub>.** The 99-Tc NMR spectra of solutions were collected on a JEOL GX-400 spectrometer with 5 mm NMR tubes fitted with Teflon inserts that were purchased from Wilmad Glass. Chemical shifts ( $\delta$ ) were measured from a 0.2 M NH<sub>4</sub>TcO<sub>4</sub> solution in D<sub>2</sub>O as the external reference. The Technetium stock solution ([Tc] = 0.1 M) used to prepare the samples was prepared by dissolution of NH<sub>4</sub>TcO<sub>4</sub> in 6 M and 13 M H<sub>2</sub>SO<sub>4</sub>. Measurements were performed at 298 K.

### IV. UV-visible spectroscopy

UV-visible spectra were recorded at room temperature in a quartz cell (1 cm) on a Cary 6000i double beam spectrometer. The UV-visible spectra of the solutions were recorded between 200 nm and 800 nm. Solutions of HClO<sub>4</sub>, H<sub>2</sub>SO<sub>4</sub>, H<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O<sub>2</sub> and HNO<sub>3</sub> / H<sub>2</sub>O<sub>2</sub> were used as the reference. All measurements were performed at room temperature except for the study in HNO<sub>3</sub> / H<sub>2</sub>O<sub>2</sub> media where the solutions were pre-cooled to 4 °C and immediately transferred to the spectrophotometer for measurement. The molar absorptivities were calculated using the Beer-Lambert law. The concentrations used in the calculations were derived from the mass of pertechnetate salt used or from the concentration of the stock solution used to prepare the samples.

#### IV.1. Cerium titration

**Study in H<sub>2</sub>SO<sub>4</sub>/MeOH.** A volume of 0.9 mL (V1) of the green solution (C1, Tc = 0.01412 M) containing the Tc complex was placed in a 1 cm quartz cell. Aliquot of a 0.25 M Cerium (+4) solution in 3-4 M H<sub>2</sub>SO<sub>4</sub> (C2) were added with a micropipette to the quartz cell. After each addition, the UV-visible spectrum of the solution was recorded and the concentration of the Tc species was monitored using the band at 695 nm. The representation of the absorbance at 695 nm, as a function of the volume of the cerium solution was used to determine the equivalent point. A volume of 105(5)  $\mu$ L of the cerium solution was estimated at the equivalence point.

For the reaction: Tc(+x) + (7-x).Ce(+4)  $\rightleftharpoons$  Tc(+7) + (7-x).Ce(+3), the oxidation state x of the is determined at the equivalence using the equation: C2·V2 = C1 ·V1· (7-x)

C1 = 0.01412 M, V1 = 0.9 mL; C2 = 0.25 M, V2 = 105(5)  $\mu$ L. Calculation indicates x = 4.93(10)

## IV. 2 Formic acid titration

**Study in H<sub>2</sub>SO<sub>4</sub>/MeOH.** The titration of formic acid was performed using the method reported in the literature.<sup>9</sup> A solution of Tc(VII) (0.02 M, 1 mL) in 13 M H<sub>2</sub>SO<sub>4</sub> was reacted with MeOH (20 μl). After the reaction 10 μl of the green solution were diluted 1 mL of water. After the dilution, 10 μL of a mercury acetate solution in acetic acid (12 mg of mercuric acetate by mL) were added to the solution. The UV-visible spectrum was recorded as a function of the time. The spectrum after 1 hour of reaction exhibits the peak at 236 nm which indicate the presence of acetic acid in solution.

## V. Computational method

The optimization of the molecular structure of the Tc complexes was carried out using the density functional theory (DFT) implemented in the Gaussian 09 software<sup>10</sup>. Structural relaxation was performed without symmetry constraints using the generalized gradient approximation (GGA) and the Becke 3-parameter, Lee, Yang and Parr<sup>11</sup>(B3LYP) hybrid functional. The Dunning-Huzinaga valence double- $\zeta$  basis set<sup>12</sup> (D95V) was used for H, S and O atoms in combination with the Stuttgart/Dresden effective core potentials<sup>13</sup> (SDD ECPs) for the Tc metal atom. Transition energies and oscillator strengths were computed using the time-dependent density functional theory (TD-DFT) implemented in Gaussian 09 at the B3LYP/SDD level of theory.

---

## V. References

- <sup>1</sup> <http://www.ornl.gov/sci/isotopes/catalog.html>
- <sup>2</sup> B. Ravel and M. Newville *J. Synchrotron Rad.* 2005, **12**, 537.
- <sup>3</sup> T. Ressler, *J. Synchrotron Rad.*, 1998, **5**, 118.
- <sup>4</sup> J.J. Rehr, R.C. Albers. *Rev. Mod. Phys.*, 2000, **72**, 621.
- <sup>5</sup> B. Ravel., *J. Synchrotron Rad.*, 2001, **8**, 314.
- <sup>6</sup> H. Beyer, O. Glemser, B. Krebs *Angew. Chem. Ind. Ed.* 1968, **7**, 295.
- <sup>7</sup> S. J. Cline Schaffer and R. W. Berg. *Acta Cryst.*, 2008, **E64**, i20.
- <sup>8</sup> J. P. Deloume, R. Faure, G. Thomas-David, *Acta Crystallogr. B*, 1979, **35**, 558-561.
- <sup>9</sup> Y. G. Khabarov and M. S. Yakovlev, *Rus. J. Appl. Chem.*, 2007, **80**, 1481.
- <sup>10</sup> Gaussian 09, Revision A.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V.

---

Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, **2009**.

- <sup>11</sup> A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648; C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* 1988, **37**, 785; [3] S.H. Vosko, L. Wilk, M. Nusair, *Can. J. Phys.*, 1980, **58**, 1200; P. J. Stephens, F.J. Devlin, C.F. Chabalowski, M.J. Frisch, *J. Phys. Chem.*, 1994, **98**, 11623.
- <sup>12</sup> T. H. Dunning Jr. and P. J. Hay, in *Modern Theoretical Chemistry*, Ed. H. F. Schaefer III, Vol. 3 (Plenum, New York, 1976) 1-28.
- <sup>13</sup> D. Andrae, U. Haeussermann, M. Dolg, H. Stoll, and H. Preuss, *Theor. Chem. Acc.*, 1990, **77**, 123.