Supporting information

Caution. Techetium-99 is a weak beta emitter (Emax = 292 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 NH_4TcO_4 was obtained from stocks at the Los Alamos National Laboratory originally purchased from the Oak Ridge Isotope Office.[1]

EXAFS spectroscopy. XAFS measurements were carried out at the Advanced Photon Source (APS) at the BESSRC-CAT 12 BM station at Argonne National Laboratory. Potassium pertechnetate (23 mg) was dissolved in 5 ml of 12 M H_2SO_4, after the dissolution 100 µl of the yellow solution were taken and placed in teflon sample holder of local design. 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). For each sample, four spectra were recorded in the k range [0 - 14] Å-1 and averaged. Background contribution was removed using the Athena [2]software and data analysis was performed using Artemis/Ifeffit.[3] For the fitting procedure, amplitude and phase shift function were calculated by FEFF 7.[4] Input files were generated by Atoms[5] using the crystallographic structure of $Re_2O_7(H_2O)_2$.[6] Adjustments of the k_3 -weighted EXAFS spectra were performed under the constraints S02 = 0.9. A single value of energy shift (ΔE0) was used for all scattering.

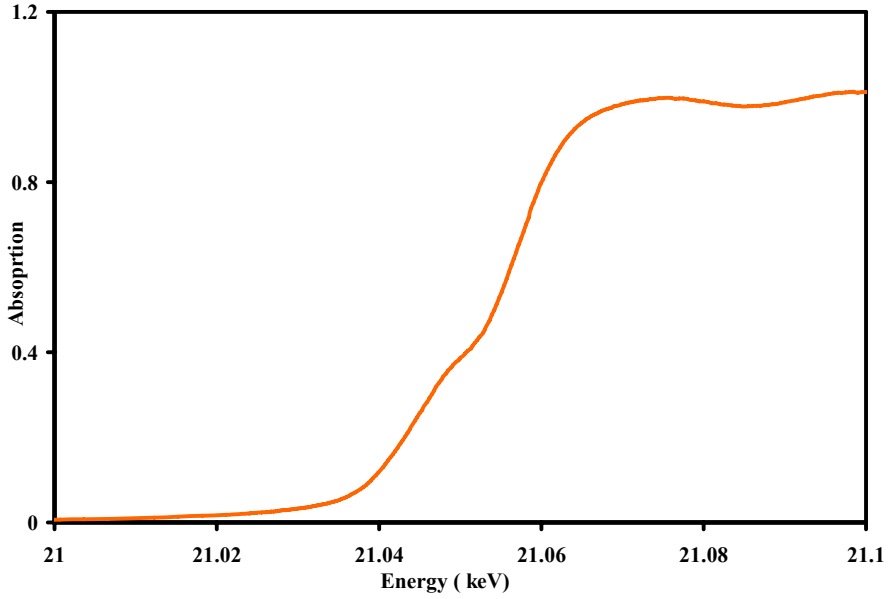

Figure S1. XANES spectra of $KTcO_4$ in 12 M H_2SO_4

In order to determinate the core structure of the yellow complex in 12 M H_2SO_4 complex, various models with short oxygen and long oxygen distances were tested, results are presented in Table S1. In comparison to the other models, the six-coordinate one best fits the data; the 5-coordinate model cannot be ruled out. The 4-coordinate models can be ruled out. Finally, the model with 2 terminal oxo groups and 3 long Tc-O distances is much worse than the best model. Therefore, of these models, the best description of the EXAFS data is obtained with the model with three short Tc-O bonds, one longer Tc-O bond, and two long Tc-O bonds.

Table S1. Comparison of the models used to fit the EXAFS data

# oxo	# long Tc-O bonds	reduced chi squared
4	0	17.2
3	0	15.6
3	1	12.4
3	2	10.6
3	3	9.8
3	1@2.07 Å, 2@2.23 Å	9.5
3	1@2.07 Å, 2@2.23 Å	10.9
3	2@2.07 Å, 2@2.23 Å	10.1
2	1@2.07 Å, 2@2.23 Å	19.2
4	1@2.07 Å, 2@2.23 Å	72

For the spectral simulation studies, the scattering and amplitude function were generated by FEFF 8.2 using the structures of Tc_2O_7 and $K_4MoO_2(SO4)_3$.

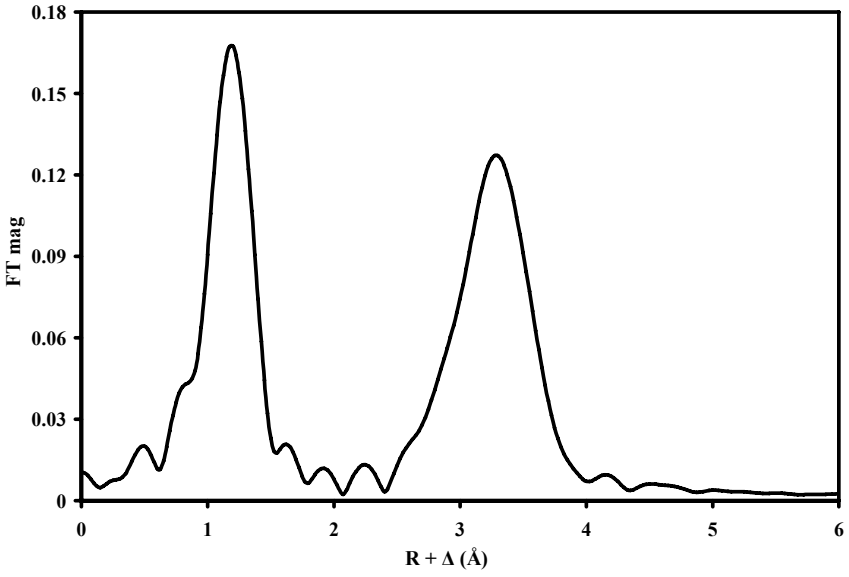

Figure S2. Simulated Fourier transform of the k^3 -EXAFS spectrum of Tc_2O_7. Simulation for k = [2, 12] $Å^{-1}$.

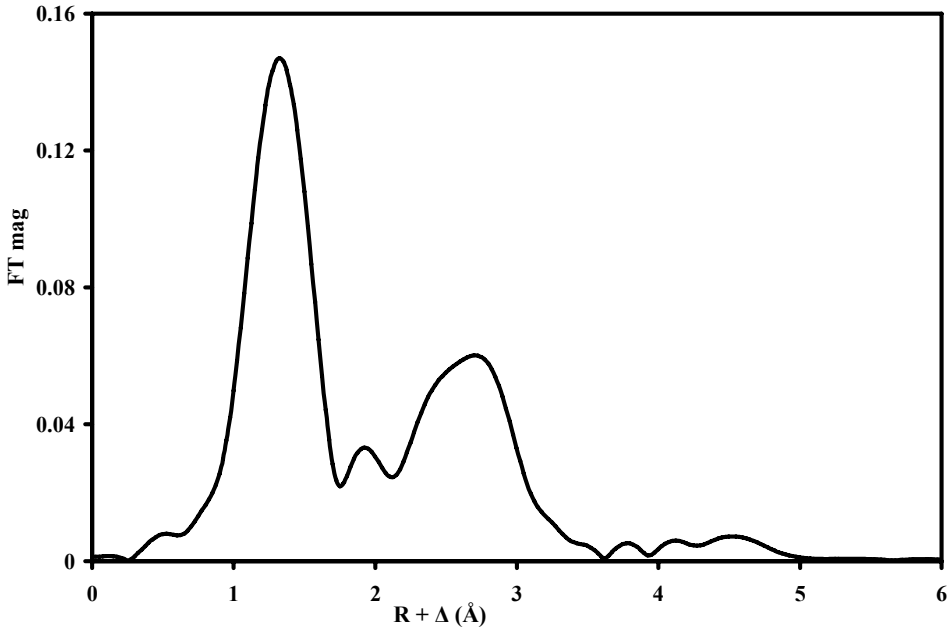

Figure S3. Simulated Fourier transform of k^3-EXAFS spectrum of the $TcO_2(SO_4)_3^{3-}$ anion. Simulation for k = [2, 12] $Å^{-1}$.

Computational method. A search for the possible structures of TcO_3^+ complexes in the presence of H_2O, HSO_4^-, or H_3O^+ was carried out using the density functional theory (DFT) implemented in the Gaussian 09 software [7]. Structural relaxation was performed without symmetry constraints using the generalized gradient approximation (GGA) and the Becke 3-parameter, Lee, Yang and Parr [8] (B3LYP) hybrid functional. The Dunning-Huzinaga valence double-ζ basis set [9] (D95V) was used for H and O atoms in combination with the Stuttgart/Dresden effective core potentials [10] (SDD ECPs) for the Tc metal atom. Transition energies and oscillator strengths were computed at the same level of theory using time-dependent density functional theory (TD-DFT) implemented in the Gaussian 09 software.

Table S2. Transition energies and oscillator strengths for $TcO_3(OH)(H_2O)_2$ computed using time-dependent density functional theory (TD-DFT) at the B3LYP/SDD level of theory. The composition of individual excitations is also reported in terms of major one-electron transitions between the molecular orbital levels represented in Figure 5.

Transition energy		Composition of major bands	Oscillator strength
(nm)	(eV)		
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		H-1→L+2; HOMO→L+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

NMR. 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 (δ) were measured from a 0.05 M $KTcO_4$ solution in D_2O as the external reference (δ = 0). Solutions for NMR measurements (in 5 mm NMR glass tube) were prepared by dissolving $KTcO_4$ 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 sulfuric acid, the TcO_4^- concentration in the entire series was 10^{-3} mol/L. Measurements were taken at 298 K. The following spectral conditions were used: pulse width, 8 μs; acquisition time, 0.16 s; repetition delay, 0.5 s; scan width, 2500 Hz; number of scans, 200.

Other techniques. UV-visible spectra were recorded at room temperature in 12 M H_2SO_4 in a quartz cell (1 cm) on a Cary 6000i double beam spectrometer. 12 M H_2SO_4 was used as the reference. 99Tc concentrations were determined by liquid scintillation counting using a Packard 2500 scintillation analyzer. The scintillation cocktail was ULTIMA GOLD ABTM (Packard).

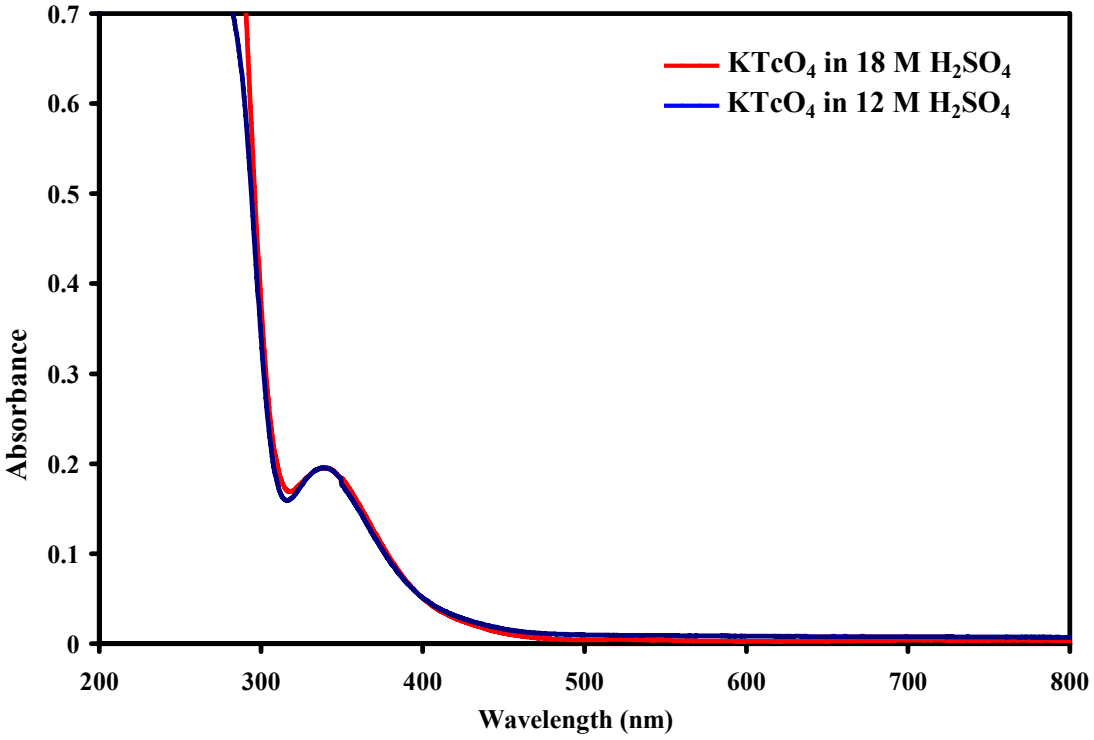

Figure S4. UV-visible spectrum of $KTcO_4$ in 12 M H_2SO_4 (blue) and in 18 M H_2SO_4 (red).

[1] http://www.ornl.gov/sci/isotopes/catalog.html

[2] B. Ravel and M. Newville *J. Synchrotron Rad.* 2005, **12,** 537.

[3] T. Ressler, *J. Synchrotron Rad.,* 1998, **5**, 118.

[4] J.J. Rehr, R.C. Albers. *Rev. Mod. Phys.,* 2000, **72**, 621.

[5] B. Ravel., *J. Synchrotron Rad.,* 2001, **8**, 314.

[6] H. Beyer, O. Glemser, B. Krebs *Angew. Chem. Ind. Ed.* 1968, **7**, 295.

7 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.**

[8] 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.

[9] 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.

[10] D. Andrae, U. Haeussermann, M. Dolg, H. Stoll, and H. Preuss, Theor. Chem. Acc., 1990, **77**, 123.