## **Supporting information**

*Caution.* 99- Techetium 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.<sup>1</sup>

## I. Cerium titration.

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 cuvette. Aliquot of a 0.25 M Cerium (+4) solution in 3-4 M H<sub>2</sub>SO<sub>4</sub> (C2, Sigma-Aldrich) were added with a micropipette to the quartz cuvette. 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 is presented in Figure S1\_titration. Using Figure S1\_titration, a volume of 105(5)  $\mu$ L of the cerium solution was estimated at the equivalence point.

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

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



**Figure S1\_titration.** Variation of the absorbance at 695 nm of a solution (Tc = 0.01412 M, V= 0.9 mL) containing the green complexes Tc(+x) as a function of the volume of a Ce(IV) solution (0.25 M in 3-4 M H<sub>2</sub>SO<sub>4</sub>) added. At equivalence, the volume needed to oxidize Tc(+x) to Tc(+7) is 105(5)  $\mu$ L (i.e., x = 4.93(10))

**II. NMR spectroscopy.** The <sup>99</sup>Tc NMR spectra of solutions were collected on a JEOL GX-400 spectrometer with 5 mm 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 ( $\delta$  = 0). Measurements were performed at 298 K.



**Figure S1\_NMR.** 99-Tc NMR spectra of the solution obtained 1 hour after the reaction of: A)  $TcO_4^-$  with MeOH in 6 M H<sub>2</sub>SO<sub>4</sub> and B) HTcO<sub>4</sub> with MeOH in 13 M H<sub>2</sub>SO<sub>4</sub>.

# **III. EPR spectroscopy**



**Figure S1\_EPR.** EPR spectrum of the frozen (77 K) solution obtained after the reaction of  $HTcO_4$  with MeOH in 13 M H<sub>2</sub>SO<sub>4</sub>.

**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.



**Figure S1\_UV.** Reaction between HTcO4 (0.97 mM, 1 mL) and Methanol (20  $\mu$ L) in 13 M H<sub>2</sub>SO<sub>4</sub>. UV-visible spectra before (black) and after: 5 minutes (red), 30 minutes (blue) and 1 hour of reaction (green). A solution of 13 M H<sub>2</sub>SO<sub>4</sub> (1 mL) / MeOH (20  $\mu$ L) was used as the reference.



**Figure S2\_UV:** UV-visible spectrum of a solution of 0.01 M KMnO<sub>4</sub> in 13 M H<sub>2</sub>SO<sub>4</sub> A) before the reaction. B) 2 minutes after the reaction of 1 mL of the solution with MeOH (20  $\mu$ L).



**Figure S3\_UV.** UV-visible spectrum of a solution of 0.01 M KReO<sub>4</sub> in 13 M H<sub>2</sub>SO<sub>4</sub>. Blue: before reaction. Red : 48 hours after the reaction of 1 mL the solution with MeOH (20  $\mu$ L).



**Figure S4\_UV.** Reaction between HTcO<sub>4</sub> (0.97 mM, 1 mL) and MeOH (20  $\mu$ l) in 13 M H<sub>2</sub>SO<sub>4</sub>. Concentration (Moles.L<sup>-1</sup>) of the green Tc(+5) species in solution as function of the reaction time (minutes). Concentration of the Tc green species was determined using the absorbance at 695 nm. The initial reaction rate (2.9.10<sup>-5</sup> Moles. L<sup>-1</sup>.min<sup>-1</sup>) is also represented.



**Figure S5\_UV.** Reaction between HTcO<sub>4</sub> (0.97 mM, 1 mL) and formaldehyde (20  $\mu$ l) in 13 M H<sub>2</sub>SO<sub>4</sub>. A) UV-visible spectra before the reaction. B) UV-visible spectra after 2 minutes of reaction (HTcO<sub>4</sub> has been entirely converted to the Tc(+5) species). A solution of 13 M H<sub>2</sub>SO<sub>4</sub> (1 mL) / formaldehyde (20  $\mu$ L) was used as the reference.



**Figure S6\_UV**. Reaction between HTcO<sub>4</sub> (0.97 mM, 1 mL) and formic acid (20  $\mu$ L) in 13 M H<sub>2</sub>SO<sub>4</sub>. UV-visible spectra before (black) and after 1 hour of reaction (red). A solution of 13 M H<sub>2</sub>SO<sub>4</sub> (1 mL) / formic acid (20  $\mu$ L) was used as the reference.



**Figure S7\_UV.** UV-visible spectrum of the brown solution 3 months after the reaction of a  $[TcO_4]^-$  (Tc = 0.017 M) solution (1 mL) in 6 M H<sub>2</sub>SO<sub>4</sub> solution with MeOH (20 µl). Top: Spectra of the brown solution without dilution. Bottom: Spectra of the brown solution after dilution (1:100) in 6 M H<sub>2</sub>SO<sub>4</sub>.

### V. Formic acid titration.

The titration of formic acid was performed using the method reported in the literature.<sup>2</sup> A solution of  $HTcO_4$  (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 (Figure S1\_Formic).

It is noted that in the same condition, the reaction of mercury acetate with sulfuric acid /MeOH solution (10  $\mu$ L) do not produce the peak at 236 nm (Figure S2\_Formic).



**Figure S1\_Formic.** UV-visible spectra after 1 hour of the solution (10  $\mu$ L mercuric acetate solution + 1 mL H<sub>2</sub>O + 10  $\mu$ L Tc green solution). A solution (10  $\mu$ L Tc green solution + 1 mL H<sub>2</sub>O) was used as a blank. The Tc green solution was prepared after the reaction of HTcO<sub>4</sub> (0.02 M, 1 mL) in 13 M H<sub>2</sub>SO<sub>4</sub> with MeOH (20  $\mu$ L).



**Figure S2\_Formic.** UV-visible spectra after 1 hour of the solution (10  $\mu$ L mercuric acetate solution + 1 mL H<sub>2</sub>O+ 10  $\mu$ l H<sub>2</sub>SO<sub>4</sub>/MeOH solution). A solution (10  $\mu$ L H<sub>2</sub>SO<sub>4</sub>/MeOH + 1 mL H<sub>2</sub>O) was used as a blank. The H<sub>2</sub>SO<sub>4</sub>/MeOH solution was prepared by dilution of MeOH (20  $\mu$ L) in 13 M H<sub>2</sub>SO<sub>4</sub> (1 mL).

#### VI. XAFS spectroscopy.

XAFS measurements were carried out at the Advanced Photon Source (APS) at the BESSRC-CAT 12 BM station in Argonne National Laboratory. Potassium pertechnetate (23 mg, 0.114 mmol) was dissolved in 5 ml of 13 M H<sub>2</sub>SO<sub>4</sub>, then 1 ml was taken and 20 µl of MeOH (0.5 mmol) were added to the solution. After the reaction, 100 µl of the green solution were taken and placed in a 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). Fourteen spectra were recorded in the k range [0 - 14] Å<sup>-1</sup> and averaged. Background contribution was removed using the Athena<sup>3</sup> software and data analysis was performed using WINXAS.<sup>4</sup> For the fitting procedure, amplitude and phase shift function were calculated in the putative [TcO(SO<sub>4</sub>)<sub>3</sub>]<sup>-</sup> specie by FEFF8.2 software.<sup>5</sup> Input files were generated by Atoms<sup>6</sup> using the crystallographic structure of  $K_4MoO_2(SO_4)_3$ .<sup>7</sup> Adjustments of the k<sup>3</sup> -weighted EXAFS spectra were performed under the constraints  $S_0^2 = 0.9$ . A single value of energy shift ( $\Delta E0$ ) was used for all scattering.

In order to determinate the structure of the complexes, various adjustments considering: (1) Tc-O, (2) Tc=O, Tc-O, (3) Tc=O, Tc-O, Tc-S<sub>mono</sub> and (4) Tc=O, Tc-O, Tc-S<sub>bid</sub> scatterings. Results are presented in Table S1 and Table S2.

**Table S1**. Result for the adjustments (1) and 2) considering: (1) Tc-O and (2) Tc=O, Tc-O scatterings. Adjustments performed for R= [0.8; 2.5] Å.  $\Delta E_0$  (eV) = -4.21 for (1), -3.11 for (1a), 6.26 for (2), 8.73 for (2a) and 6.22 for (2b). <sup>a</sup> fixed

Adjustment	Scattering	C.N	R (Å)	$\sigma^2$ (Å <sup>2</sup> )	Reduced chi <sup>2</sup>
1	Tc-O	5.72	2.02(2)	0.004 <sup>a</sup>	156
1a	Tc-O	6 <sup>a</sup>	2.02(2)	0.0046	131
2	Tc=O	1.03	1.64(2)	0.0022 <sup>a</sup>	13.12
	Tc-O	4.42	2.06(2)	0.004 <sup>a</sup>	
2a	Tc=O	2 <sup>a</sup>	1.66(2)	0.0070	102
	Tc-O	4 <sup>a</sup>	2.06	0.0036	
2b	Tc=O	1 <sup>a</sup>	1.65(2)	0.0019	9
	Tc-O	5 <sup>a</sup>	2.06(2)	0.0051	

**Table S2**. Result for the adjustments (3) and (4) considering: (3) Tc=O, Tc-O, Tc-S<sub>mono</sub> and (4) Tc=O, Tc-O, Tc-S<sub>mono</sub> and Tc-S<sub>bid</sub> scatterings. Adjustments performed for R= [0.8; 4] Å.  $\Delta E_0$  (eV) = -2.94 for (3, 2.98 for (4), 6.5 for (4a) and 5.63 for (4b). <sup>a</sup> fixed

Adjustment	Scattering	C.N	R (Å)	$\sigma^2$ (Å <sup>2</sup> )	Reduced chi <sup>2</sup>
3	Tc=O	0.9	1.64(2)	0.0022 <sup>a</sup>	46.75
	Tc-O	4.7	2.05(2)	$0.004^{a}$	
	Tc-S <sub>mono</sub>	2.7	3.27(3)	0.009 <sup>a</sup>	
4	Tc=O	1 <sup>a</sup>	1.64(2)	0.0030	46.7
	Tc-O	5 <sup>a</sup>	2.05(2)	0.0045	
	Tc-S <sub>mono</sub>	2 <sup>a</sup>	3.27(3)	0.0064	
4a	Tc=O	1.0(2)	1.65(2)	0.0022 <sup>a</sup>	8.05
	Tc-O	4.4(9)	2.07(2)	$0.004^{a}$	
	Tc-S <sub>bid</sub>	0.5(1)	2.89(3)	$0.006^{a}$	
	Tc-S <sub>mono</sub>	1.9(4)	3.30(3)	0.009v	
4b	Tc=O	1 <sup>a</sup>	1.65(2)	0.0021	10.5
	Tc-O	$5^{a}$	2.06(2)	0.005	
	Tc-S <sub>bid</sub>	1 <sup>a</sup>	2.88(3)	0.0093	
	Tc-S <sub>mono</sub>	$2^{a}$	3.29(3)	0.0083	



**Figure S1\_XAFS.** XANES spectra of: A) the solution obtained after the reaction of  $HTcO_4$  with MeOH in 13 M H<sub>2</sub>SO<sub>4</sub> and B) the  $[TcCl_6]^{2-}$  anion in  $(Me_4N)_2TcCl_6$ 

**VII. Computational method.** Structural optimization of the molecular complexes proposed in this study was carried out using density functional theory (DFT), as implemented in the Gaussian 09 software.<sup>8</sup> Structural relaxation calculations were performed, without symmetry constraints applied, using the generalized gradient approximation (GGA) and the Becke 3-parameter, Lee, Yang and Parr<sup>9</sup> (B3LYP) hybrid functional. The Dunning-Huzinaga valence double- $\zeta$  basis set<sup>10</sup> (D95V) was used for the H, O and S atoms, in combination with the Stuttgart/Dresden effective core potentials<sup>11</sup> (SDD ECPs) for the Tc metal atom. This computational approach was shown in our previous studies to successfully reproduce experimental structures of molecular complexes containing Tc, O and S.<sup>12</sup>

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