<u>Supporting Information</u>

Recent Developments in the Synthetic Chemistry of Technetium Disulfide

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1. Preparation of precursors

Caution. Techetium-99 is a weak beta emitter (Emax = 292 keV). All manipulations were performed in a radiochemistry laboratory at UNLV designed for chemical synthesis with radionuclides using efficient HEPA-filtered fume hoods and following locally approved radioisotope handling and monitoring procedures. The starting compound NH_4TcO_4 was purchased from Oak Ridge National Laboratory.

Starting compounds were prepared according to literature: Tc_2S_7 [1], Tc metal [2], $KTcO_4$ [3], $Tc_2(O_2CCH_3)_5$ [4] and K_2TcCl_6 [5]. A lecture bottle of H_2S gas was obtained from Sigma-Aldrich all the other chemicals were used as received.

As the synthesis of ditechnetium penta-acetate has not been published yet, a brief description of the experimental is given:
In a glass vial was added $KTcO_4$ (50 mg, 0.25 mmol) and 7 mL of acetic acid, which was placed inside a 23 mL Teflon Parr Instruments 4749 autoclave. Sodium borohydride (250 mg, 6.6 mmol) was added external to the small glass vial with 200 µL of deionized water. The autoclave was sealed and heated in an oven at 210 °C for 72 hrs. $H_{2(g)}$ was produced in the reaction resulting in approximately 60 atm pressure in the autoclave. The reaction vessel was cooled to room temperature and opened revealing large purple crystals of $Tc_2(\mu\text{-}O_2CCH_3)_4(\eta\text{-}O_2CCH_3)$. The air stable product was rinsed 2 times with each of the following solvents: acetic acid, isopropanol and diethyl ether. The solid was dried in air and weighed (43.9 mg, yield = 72%).

2. EXAFS Spectroscopy

Measurements were performed at the Argonne National Laboratory Advanced Photon Source at the BESSRC-CAT 12 BM-B station. The solids were diluted (2 %) in mass in boron nitride (BN). The samples were placed in an aluminum sample holder equipped with Kapton windows. For the sample C the EXAFS spectra were recorded at the Tc-K edge (21, 044 eV) in fluorescence mode at room temperature using a 13-element germanium detector. For TcS_2, sample A and B, the EXAFS spectra were recorded in transmission mode. A double crystal of Si [1 1 1] was used as a monochromator. Rejections of harmonics were performed using rhodium mirrors. The energy was calibrated using a molybdenum foil. Fifteen scans were recorded in the k range [0 - 15] Å^{-1} and averaged. The EXAFS spectra were extracted using the Athena software [6] and data analysis was performed using Winxas.[7] For the fitting procedure, amplitude and phase shift functions were calculated by FEFF 8.2.[8] Input files were generated by Atoms.[9] The adjustments of the k^3-weighted EXAFS spectra were under the constraints $S_0^2 = 0.9$.

3. Other techniques

Energy Dispersive X-ray (EDX) spectroscopy measurements were performed on a TECNAI-G2-F30 Supertwin transmission electron microscope with a 300 keV field emission gun; the samples were prepared by grinding the compound with hexane in an agate mortar, taking one drop of the solution and placing it onto a 3 mm diameter carbon film supported on a copper grid.

For ^{99}Tc elemental analyses, weighed amounts of the compounds (ca. 5 mg) were suspended in concentrated $HClO_4$ (5 mL) for several days. After complete dissolution, the solutions were diluted by 1000 with DI H_2O. ^{99}Tc concentrations were determined by liquid scintillation counting using a Packard 2500 scintillation analyzer. The scintillation cocktail was ULTIMA GOLD ABTM (Packard). The concentration of the solutions was determined using a calibration curve performed in solution with composition similar to the experimental parameters.

The powder X-ray Diffraction patterns were obtained using a Bruker D8 Advance diffractometer employing Cu Kα_1 X-rays from 10 to 120° (2θ) with a step size of 0.008° (2θ) and 0.65 s/step. The samples (ca. 10-20 mg) were ground in an agate mortar, dispersed on a low-background silicon disk sample holder, covered with a radiological containment dome, and placed in the instrument for measurement.

4. Decomposition of Tc_2S_7 under flowing argon

An initial attempt to prepare TcS_2 from the thermal decomposition of Tc_2S_7 was performed in a flowing gas system under argon. A quartz boat containing Tc_2S_7 (105 mg) was place in a 50 cm quartz tube and heated at 1000 °C for an hour in a clamshell furnace. During the reaction, a yellow powder (sulfur) sublimed to the cold end of the tube. The black powder was weighted (53 mg) and analyzed by EXAFS spectroscopy. The spectrum was fitted using Tc-S and Tc-Tc scattering calculated in TcS_2 and Tc metal.

The XAFS analysis was compared to other solids: TcS_2 the reference compound used in the paper (thermal decomposition of Tc_2S_7 in a sealed tube with excess sulfur) and Tc_2S_7 (starting compound).

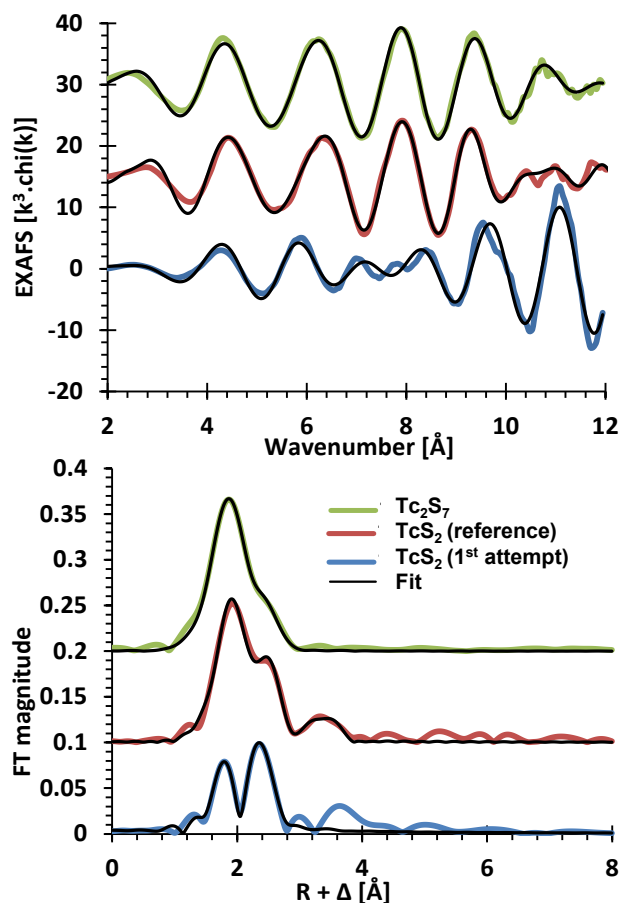Results (Fig. S1) showed the solid to be a mixture of Tc metal and TcS_2 and different from the starting compound.

Fig. S1 Fitted k^3-EXAFS spectra (top) and Fourier Transform of k^3-EXAFS spectra (bottom) for the solids: TcS_2 1st attempt (blue) compared to TcS_2 (red) and Tc_2S_7 (green). Fits are in black. Adjustment performed in the k-range [2; 12] Å^{-1}.

5. LSC

Table S1 LSC result and analysis

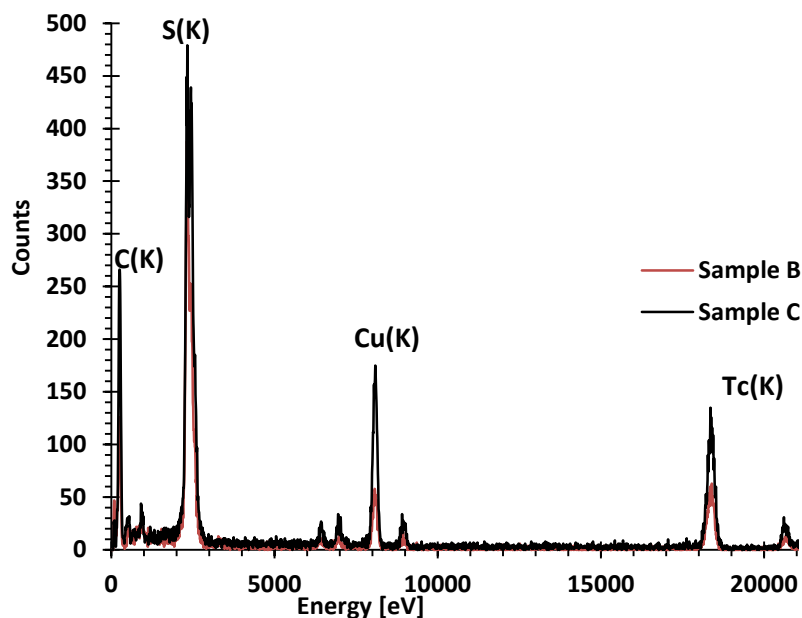|	TcS_2	Sample A	Sample B	Sample C
Mass compound analyzed [g]	0.0045	0.0042	0.0051	0.0044
Counts [CPM]	2055	1955	2308	1986
Concentration ^{99}Tc before dilution [mol/L]	0.0054	0.0051	0.0061	0.0052
Mass Tc deducted [g]	0.0027	0.0025	0.0030	0.0026
% Tc in sample	0.5958	0.6066	0.5920	0.5885
Stoichiometry TcS_x, x =	2.09(6)	2.01(6)	2.13(6)	2.16(6)

6. EDX

Fig. S2 EDX spectra for Sample B (red) and Sample C (black). C and Cu peaks from the sample holder.

Table S2 Values of the EDX analyses of Sample B and Sample C shown in Fig. S2.

	Elements	Weight%	Atomic%	Stoichiometry
Sample B	S (K)	40.864	67.869	$TcS_{2.11}$
	Tc (K)	59.136	32.130	
Sample C	S (K)	43.425	70.116	$TcS_{2.34}$
	Tc (K)	56.574	29.883	

7. EXAFS adjustments

Table S3 Results for the adjustments for the scattering path Tc-Tc for samples B and C at fixed Tc-S scattering C.N. = 6 and $S_0^2 = 0.9$.

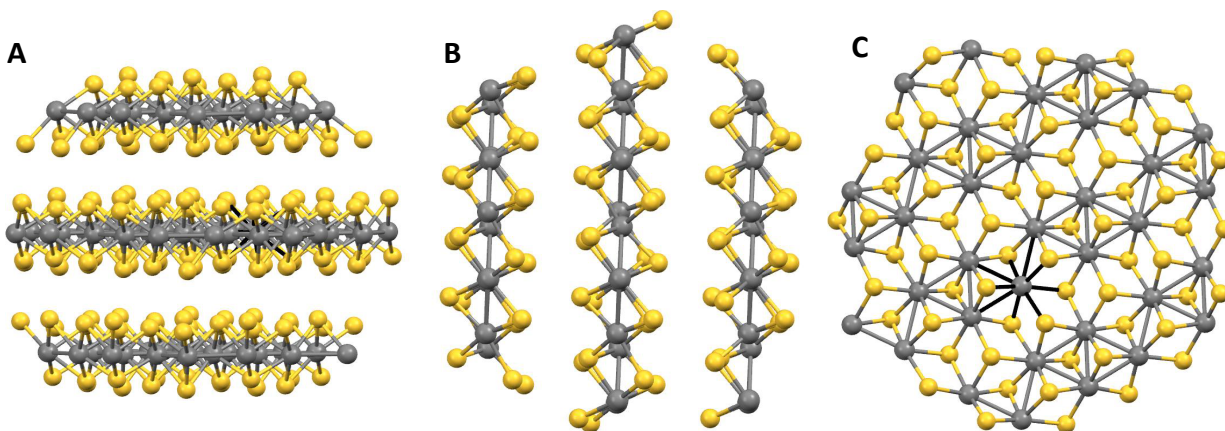|	Scattering path	C.N.	R [Å]	σ^2 [Å^2]	ΔE_0 [eV]	Reduced chi^2
Sample B	Tc-Tc	3	2.79	0.0086	0.96	72.05
		2	2.79	0.0059	0.79	63.24
Sample C	Tc-Tc	3	2.75	0.0087	5.56	118.97
		2	2.75	0.0065	5.28	76.21

8. XRD structure of TcS$_2$

Fig. S3 Ball and stick representation of TcS$_2$: view along a-axis (A), along the b-axis (B), along the c-axis (C).

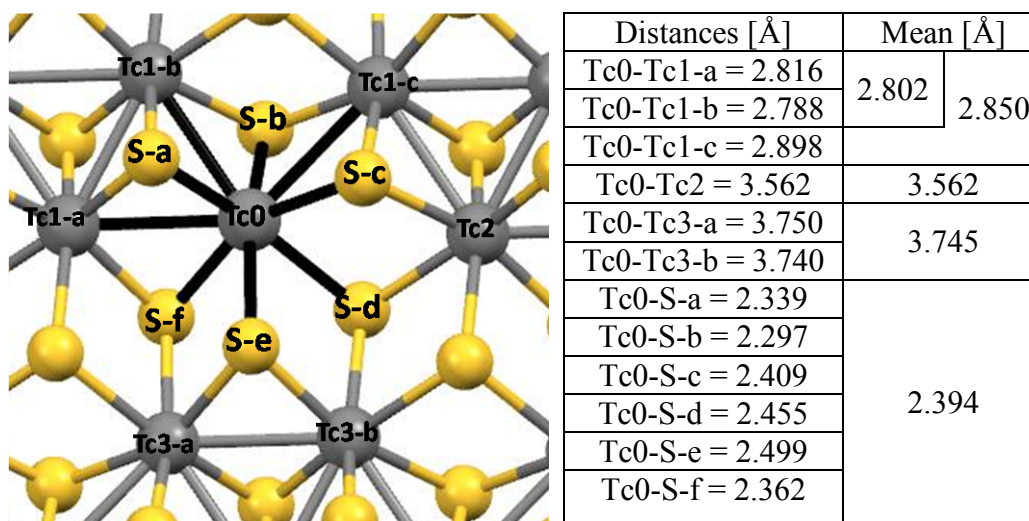| Distances [Å]	Mean [Å]	
Tc0-Tc1-a = 2.816	2.802	2.850
Tc0-Tc1-b = 2.788		
Tc0-Tc1-c = 2.898		
Tc0-Tc2 = 3.562	3.562	
Tc0-Tc3-a = 3.750	3.745	
Tc0-Tc3-b = 3.740		
Tc0-S-a = 2.339	2.394	
Tc0-S-b = 2.297		
Tc0-S-c = 2.409		
Tc0-S-d = 2.455		
Tc0-S-e = 2.499		
Tc0-S-f = 2.362		

Fig. S4 Interatomic distances [Å] in TcS$_2$ determined by XRD. Tc0 represents the absorbing atom.

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