Supporting information

Multi-configurational Quantum Chemical Studies of the $Tc_2X_8^{n-}$ (X = Cl, Br; n = 2, 3) Anions. Crystallographic Structure of Octabromoditechnetate(3-).

Frederic Poineau, Paul M. Forster, Tanya K. Todorova, Laura Gagliardi, Alfred P. Sattelberger and Kenneth R. Czerwinski

I. Methods and materials

Caution. Techetium-99 is a weak beta emitter (E_{max} = 292 keV). All manipulations were performed in a radiochemistry laboratory at UNLV designed for chemical synthesis using efficient HEPA-filtered fume hoods, Schlenk and glove box techniques, and following locally approved radioisotope handling and monitoring procedures.

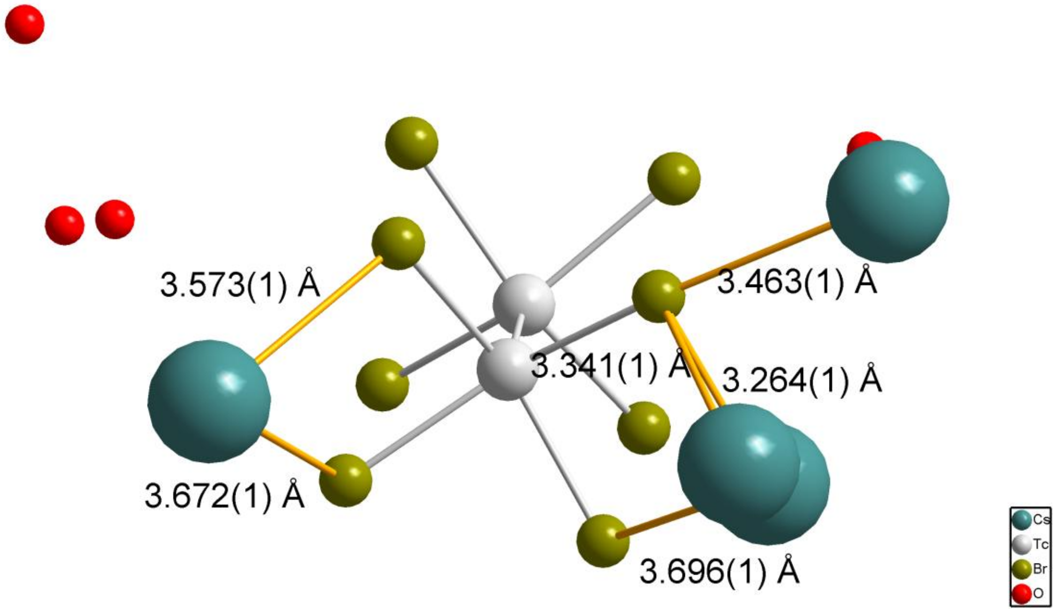
The starting compound NH_4TcO_4 was purchased from Oak Ridge National Laboratory. The compound was purified by treatment with an aqueous ammonia/hydrogen peroxide solution, followed by evaporation to dryness. The compounds $(n\text{-}Bu_4N)_2Tc_2X_8$ (X= Cl, Br) were synthesized and purified according the methods reported in the literature. Single crystals of $(n\text{-}Bu_4N)_2Tc_2Cl_8\cdot 2[(CH_3)_2CO)]$ (**2**) were grown in a freezer at -25 °C from a concentrated acetone solution of the $(n\text{-}Bu_4N)_2Tc_2Cl_8$ salt that was layered with ether (2:1 v:v). ^{99}Tc concentrations were determined by liquid scintillation counting using a Packard 2500 scintillation analyzer. The scintillation cocktail was ULTIMA GOLD ABTM (Packard).

Preparation of 1. The $(n\text{-}Bu_4N)_2Tc_2Br_8$ (60 mg, 0.045 mmol) salt was placed in a 10 mL Schlenk flask, then 4 mL of concentrated aqueous HBr previously purged with argon was added. The flask was connected to a Schlenk line, placed in an oil bath and warmed for 20 minutes at 85°C under an argon atmosphere. After cooling to room temperature, the flask was disconnected and the orange solution transferred into a glass centrifuge tube; then a solution of CsBr (100 mg, 0.47 mmol) in HBr (0.5 mL) was added, resulting in the complete precipitation of Cs_2TcBr_6. After centrifugation, the golden supernatant was transferred in a second tube and a large excess of solid CsBr (300 mg) was added in the tube, resulting in the precipitation of an orange micro crystalline powder (10.2 mg) containing the octabromoditechnetate(-3) cesium salt; yield = 18%. Single crystals of **1** were grown in a freezer at -25°C after dissolution of the orange powder in 3 mL of concentrated HBr.

II. Crystallography

Single crystal X-ray diffraction data on **1** and **2** were collected on a Bruker Apex II system equipped with an Oxford nitrogen cryostream. A crystal was mounted under Paratone on a glass fiber. Data processing was performed using the Apex II suite, and an absorption correction performed with SADABS. Structure solution (Direct Methods) and refinement against F^2 were carried out using SHELX97.[1]

The disorder in this compound is complicated and a number of models were considered. Original attempts to model the species as water molecules resulted in negative displacement parameters, suggesting that there was more electron density present than could be accounted for by water. HBr (from the solvent) was also considered, but rejected from chemical sensibility and charge balance considerations. Close examination of the Fourier peaks indicated that all with negative displacement parameters when refined as oxygen atoms were in reasonable chemical positions to be Cs atoms. Their positions and bond lengths are shown below. One might note chemically unreasonable distances between Cs and O atoms used to model the disordered solvent/cation; these are the result of partial occupancy. In all cases, the model does not have a total occupancy larger than 1 for species too close to be reasonable.



Tables presenting complete crystallographic parameters, bond distances/angles and atomic coordinates on **1** and **2** are presented below:

Table S1. Crystal data and structure refinement for **1**

Empirical formula	Br4 Cs1.11 O1.78 Tc	
Formula weight	593.68	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Trigonal	
Space group	P3(2)21	
Unit cell dimensions	a = 13.571(3) Å	α= 90°.
	b = 13.571(3) Å	β= 90°.
	c = 9.322(2) Å	γ = 120°.
Volume	1486.9(6) $Å^3$	
Z	6	
Density (calculated)	3.978 Mg/m^3	
Absorption coefficient	21.527 mm^{-1}	
F(000)	1550	
Crystal size	? x ? x ? mm^3	
Theta range for data collection	1.73 to 30.62°.	
Index ranges	-19<=h<=19, -19<=k<=19, -13<=l<=13	
Reflections collected	23966	
Independent reflections	3049 [R(int) = 0.0551]	
Completeness to theta = 30.62°	99.6 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3049 / 0 / 87	
Goodness-of-fit on F^2	1.230	
Final R indices [I>2sigma(I)]	R1 = 0.0276, wR2 = 0.0646	
R indices (all data)	R1 = 0.0283, wR2 = 0.0647	
Absolute structure parameter	0.056(10)	
Largest diff. peak and hole	2.406 and -2.740 e.$Å^{-3}$	

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for **1**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Cs(1)	6892(1)	1842(1)	856(1)	11(1)
Tc(1)	9211(1)	5666(1)	2775(1)	4(1)
Br(1)	9423(1)	4564(1)	746(1)	7(1)
Br(2)	7896(1)	6190(1)	4037(1)	11(1)
Br(3)	8026(1)	3753(1)	3962(1)	10(1)
Br(4)	9450(1)	7089(1)	902(1)	9(1)
Cs(2B)	9970(30)	9340(20)	-1320(20)	52(11)
Cs(2A)	6960(20)	6930(20)	200(40)	54(7)
O(1W)	10000	1025(9)	-1667	48(3)
O(2W)	9371(11)	1849(15)	1295(12)	29(4)
O(3W)	10550(20)	9344(15)	-1380(20)	34(7)
O(4W)	9110(20)	1270(30)	1210(20)	33(8)
Cs(2C)	7170(20)	7330(20)	850(30)	40(8)

Representation of $Tc_2Br_8^{3-}$ anion in **1**.

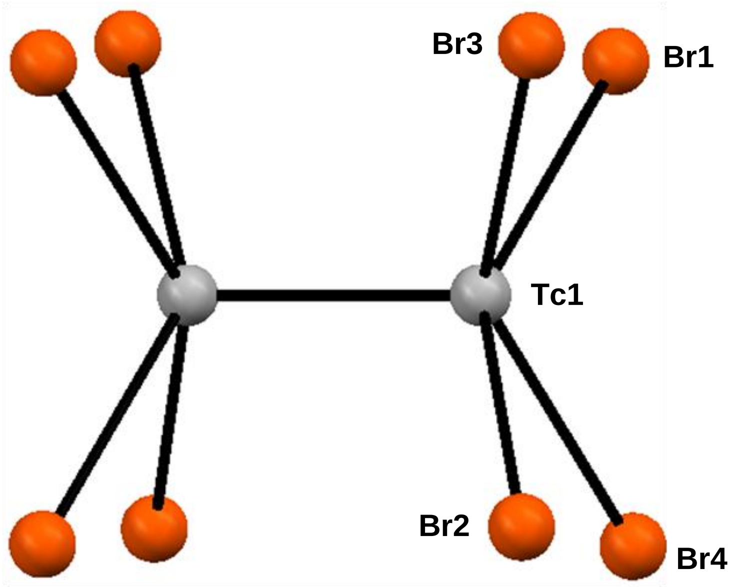


Table S3. Bond lengths [Å] and angles [°] for **1**.

Cs(1)-O(2W)	3.384(12)
Cs(1)-O(4W)	3.49(2)
Cs(1)-Br(1)#1	3.5525(10)
Cs(1)-Br(1)	3.5725(11)
Cs(1)-Br(3)	3.6722(9)
Cs(1)-Br(1)#2	3.6807(10)
Cs(1)-Br(2)#3	3.6911(10)
Cs(1)-Br(3)#3	3.7190(10)
Cs(1)-Br(4)#1	3.7639(10)
Cs(1)-Br(3)#4	3.8186(12)
Cs(1)-Cs(2C)#5	3.89(2)
Cs(1)-Br(4)#2	3.9759(10)
Tc(1)-Tc(1)#6	2.1265(10)
Tc(1)-Br(4)	2.5011(9)
Tc(1)-Br(1)	2.5152(9)
Tc(1)-Br(2)	2.5192(9)
Tc(1)-Br(3)	2.5259(9)
Tc(1)-Cs(2A)#5	4.201(19)
Tc(1)-Cs(2A)#2	4.23(2)

Br(1)-Cs(2C)#5	3.32(2)
Br(1)-Cs(2A)#5	3.38(3)
Br(1)-Cs(1)#7	3.5524(10)
Br(1)-Cs(2A)#2	3.62(3)
Br(1)-Cs(1)#4	3.6807(10)
Br(2)-Cs(1)#8	3.6911(10)
Br(2)-Cs(2C)	3.70(2)
Br(2)-Cs(2A)	4.09(3)
Br(2)-Cs(1)#2	4.0966(12)
Br(3)-Cs(2A)#2	3.25(3)
Br(3)-Cs(2A)#5	3.37(3)
Br(3)-Cs(2C)#2	3.69(3)
Br(3)-Cs(2C)#5	3.71(3)
Br(3)-Cs(1)#8	3.7190(10)
Br(3)-Cs(1)#2	3.8186(12)
Br(4)-Cs(2C)	3.26(2)
Br(4)-Cs(2A)	3.34(3)
Br(4)-Cs(2C)#9	3.36(2)
Br(4)-Cs(2B)	3.46(2)
Br(4)-Cs(2A)#9	3.49(3)
Br(4)-Cs(1)#7	3.7639(11)
Br(4)-Cs(2B)#10	3.90(2)
Br(4)-Cs(1)#4	3.9759(10)
Br(4)-Cs(2B)#9	4.00(3)
Br(4)-Cs(2B)#11	4.18(3)

Tc(1)#6-Tc(1)-Br(4)	104.13(3)
Tc(1)#6-Tc(1)-Br(1)	106.38(3)
Br(4)-Tc(1)-Br(1)	85.72(3)
Tc(1)#6-Tc(1)-Br(2)	107.83(3)
Br(4)-Tc(1)-Br(2)	86.82(3)
Br(1)-Tc(1)-Br(2)	145.79(3)
Tc(1)#6-Tc(1)-Br(3)	105.44(3)
Br(4)-Tc(1)-Br(3)	150.42(3)
Br(1)-Tc(1)-Br(3)	85.49(3)

Br(2)-Tc(1)-Br(3)	84.75(3)
Tc(1)#6-Tc(1)-Cs(2A)#5	76.2(6)
Br(4)-Tc(1)-Cs(2A)#5	135.7(4)
Br(1)-Tc(1)-Cs(2A)#5	53.5(5)
Br(2)-Tc(1)-Cs(2A)#5	136.1(4)
Br(3)-Tc(1)-Cs(2A)#5	53.4(5)
Tc(1)#6-Tc(1)-Cs(2A)#2	74.6(6)
Br(4)-Tc(1)-Cs(2A)#2	140.8(4)
Br(1)-Tc(1)-Cs(2A)#2	58.4(5)
Br(2)-Tc(1)-Cs(2A)#2	131.6(4)
Br(3)-Tc(1)-Cs(2A)#2	50.1(5)
Cs(2A)#5-Tc(1)-Cs(2A)#2	5.1(9)
Tc(1)-Br(1)-Cs(2C)#5	102.1(5)
Tc(1)-Br(1)-Cs(2A)#5	89.7(5)
Cs(2C)#5-Br(1)-Cs(2A)#5	13.2(5)
Tc(1)-Br(1)-Cs(1)#7	96.69(2)
Cs(2C)#5-Br(1)-Cs(1)#7	116.9(4)
Cs(2A)#5-Br(1)-Cs(1)#7	114.6(7)
Tc(1)-Br(1)-Cs(1)	104.88(2)
Cs(2C)#5-Br(1)-Cs(1)	68.6(4)
Cs(2A)#5-Br(1)-Cs(1)	76.0(7)
Cs(1)#7-Br(1)-Cs(1)	156.18(2)
Tc(1)-Br(1)-Cs(2A)#2	85.2(4)

Symmetry transformations used to generate equivalent atoms:

#1 y,x-1,-z #2 -x+y+1,-x+1,z+1/3 #3 -x+y+1,-x+1,z-2/3

#4 -y+1,x-y,z-1/3 #5 x-y+1,-y+1,-z+1/3 #6 -x+2,-x+y+1,-z+2/3

#7 y+1,x,-z #8 -y+1,x-y,z+2/3 #9 y,x,-z #10 -x+2,-x+y+1,-z-1/3

#11 -x+y+1,-x+2,z+1/3 #12 x,y+1,z #13 -x+y+2,-x+2,z+1/3

#14 x-y,-y+1,-z+1/3 #15 x,y-1,z #16 -x+2,-x+y,-z-1/3

#17 -y+2,x-y,z-1/3 #18 x-y+1,-y+1,-z-2/3 #19 -y+2,x-y+1,z-1/3

Table S4. Crystal data and structure refinement for **2**

Empirical formula	C19 H42 Cl4 N O Tc	
Formula weight	540.34	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 10.1601(19) Å	α= 90°.
	b = 14.838(3) Å	β= 91.345(3)°.
	c = 17.398(3) Å	γ = 90°.
Volume	2622.0(8) Å^3	
Z	4	
Density (calculated)	1.369 Mg/m^3	
Absorption coefficient	0.965 mm^{-1}	
F(000)	1128	
Crystal size	0.1 x 0.08 x 0.08 mm^3	
Theta range for data collection	1.80 to 31.31°.	
Index ranges	-14<=h<=14, -21<=k<=21, -25<=l<=25	
Reflections collected	43997	
Independent reflections	8579 [R(int) = 0.0265]	
Completeness to theta = 31.31°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7462 and 0.6384	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8579 / 0 / 242	
Goodness-of-fit on F^2	1.024	
Final R indices [I>2sigma(I)]	R1 = 0.0206, wR2 = 0.0504	
R indices (all data)	R1 = 0.0259, wR2 = 0.0526	
Largest diff. peak and hole	1.408 and -0.282 e.Å^{-3}	

Representation of $Tc_2Cl_8^{2-}$ anion in **2**.

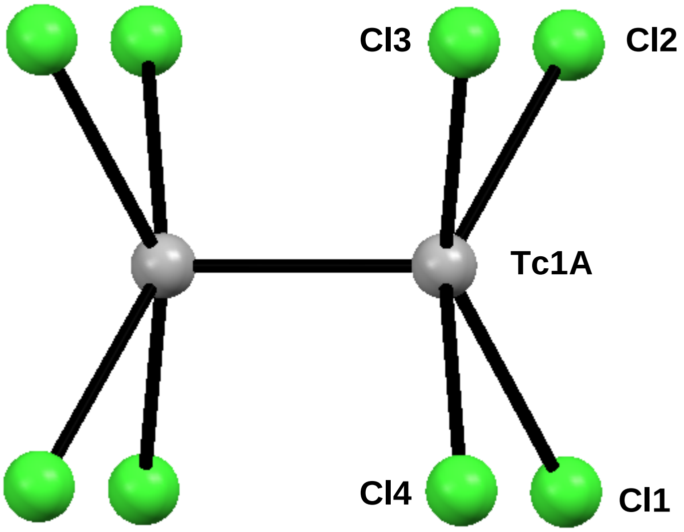


Table S5. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3)for **2**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Tc(1A)	420(1)	5395(1)	465(1)	12(1)
Tc(1B)	931(6)	4976(4)	-256(4)	31(2)
Cl(1)	2378(1)	4659(1)	765(1)	21(1)
Cl(2)	-414(1)	4719(1)	1560(1)	20(1)
Cl(3)	-1112(1)	6536(1)	647(1)	20(1)
Cl(4)	1685(1)	6470(1)	-137(1)	20(1)
O(1)	-4615(1)	5544(1)	2338(1)	32(1)
C(21)	-4606(2)	5935(1)	1019(1)	35(1)
C(22)	-4520(1)	5290(1)	1678(1)	25(1)
C(23)	-4290(2)	4319(1)	1488(1)	43(1)
N(1)	1749(1)	1873(1)	1720(1)	18(1)
C(1)	2494(1)	2159(1)	1015(1)	21(1)

C(2)	3862(1)	1752(1)	936(1)	28(1)
C(3)	4530(2)	2147(1)	242(1)	30(1)
C(4)	5787(2)	1664(1)	36(1)	40(1)
C(5)	348(1)	2217(1)	1616(1)	21(1)
C(6)	-545(1)	2019(1)	2283(1)	25(1)
C(7)	-1936(1)	2339(1)	2111(1)	33(1)
C(8)	-2857(2)	2138(1)	2766(1)	35(1)
C(9)	1772(1)	852(1)	1811(1)	19(1)
C(10)	1160(1)	324(1)	1148(1)	22(1)
C(11)	1332(1)	-686(1)	1289(1)	26(1)
C(12)	720(2)	-1248(1)	640(1)	32(1)
C(13)	2400(1)	2250(1)	2450(1)	19(1)
C(14)	2363(1)	3270(1)	2533(1)	25(1)
C(15)	2957(1)	3542(1)	3310(1)	27(1)
C(16)	2881(2)	4555(1)	3454(1)	35(1)

Table S6. Bond lengths [Å] and angles [°] for **2**.

Tc(1A)-Cl(4)	2.3140(4)
Tc(1A)-Cl(1)	2.3184(4)
Tc(1A)-Cl(3)	2.3260(4)
Tc(1A)-Cl(2)	2.3310(4)
Tc(1B)-Tc(1B)#1	2.111(13)
Tc(1B)-Cl(1)	2.327(6)
Tc(1B)-Cl(4)	2.353(7)
Tc(1B)-Cl(3)#1	2.353(7)
Tc(1B)-Cl(2)#1	2.360(6)
Cl(2)-Tc(1B)#1	2.360(6)
Cl(3)-Tc(1B)#1	2.353(7)
O(1)-C(22)	1.2137(17)
C(21)-C(22)	1.494(2)
C(22)-C(23)	1.498(2)
N(1)-C(1)	1.5176(15)
N(1)-C(5)	1.5192(16)
N(1)-C(9)	1.5225(14)
N(1)-C(13)	1.5241(15)
C(1)-C(2)	1.5247(19)
C(2)-C(3)	1.5173(17)
C(3)-C(4)	1.515(2)
C(5)-C(6)	1.5181(18)
C(6)-C(7)	1.5147(19)
C(7)-C(8)	1.521(2)
C(9)-C(10)	1.5162(17)
C(10)-C(11)	1.5278(17)
C(11)-C(12)	1.5235(19)
C(13)-C(14)	1.5220(17)
C(14)-C(15)	1.5218(17)
C(15)-C(16)	1.5268(19)
Tc(1A)#1-Tc(1A)-Cl(4)	104.458(15)
Tc(1A)#1-Tc(1A)-Cl(1)	103.583(13)
Cl(4)-Tc(1A)-Cl(1)	86.756(16)

Tc(1A)#1-Tc(1A)-Cl(3)	104.120(13)
Cl(4)-Tc(1A)-Cl(3)	86.610(17)
Cl(1)-Tc(1A)-Cl(3)	152.297(11)
Tc(1A)#1-Tc(1A)-Cl(2)	103.520(15)
Cl(4)-Tc(1A)-Cl(2)	152.021(11)
Cl(1)-Tc(1A)-Cl(2)	86.544(14)
Cl(3)-Tc(1A)-Cl(2)	86.818(14)
Cl(1)-Tc(1B)-Cl(4)	85.7(2)
Tc(1B)#1-Tc(1B)-Cl(3)#1	103.4(4)
Cl(1)-Tc(1B)-Cl(3)#1	88.6(2)
Cl(4)-Tc(1B)-Cl(3)#1	153.7(3)
Tc(1B)#1-Tc(1B)-Cl(2)#1	102.6(4)
Cl(1)-Tc(1B)-Cl(2)#1	153.4(3)
Cl(4)-Tc(1B)-Cl(2)#1	88.2(2)
Cl(3)#1-Tc(1B)-Cl(2)#1	85.5(2)
O(1)-C(22)-C(21)	121.45(13)
O(1)-C(22)-C(23)	121.57(14)
C(21)-C(22)-C(23)	116.98(13)
C(1)-N(1)-C(5)	107.04(9)
C(1)-N(1)-C(9)	110.77(9)
C(5)-N(1)-C(9)	111.02(9)
C(1)-N(1)-C(13)	110.86(9)
C(5)-N(1)-C(13)	111.33(9)
C(9)-N(1)-C(13)	105.89(8)
N(1)-C(1)-C(2)	115.80(9)
C(3)-C(2)-C(1)	110.11(11)
C(4)-C(3)-C(2)	113.62(12)
C(6)-C(5)-N(1)	114.72(9)
C(7)-C(6)-C(5)	111.11(11)
C(6)-C(7)-C(8)	112.21(12)
C(10)-C(9)-N(1)	115.53(9)

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y+1,-z

III. XANES spectroscopy. Measurements were done at the Advanced Photon Source (APS) at the BESSRC-CAT 12 BM station. Compound **1** was diluted (~1% Tc in mass) in boron nitride, ground in a mortar, and placed in an aluminium sample holder equipped with Kapton windows. Spectra were recorded at the Tc-K edge (21,044 eV) in fluorescence mode at room temperature using a 13-element 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). The XANES spectra of **1** (Figure S1) was recorded, normalised and background subtracted. The energy of the absorption edge was determined using the first derivative method.

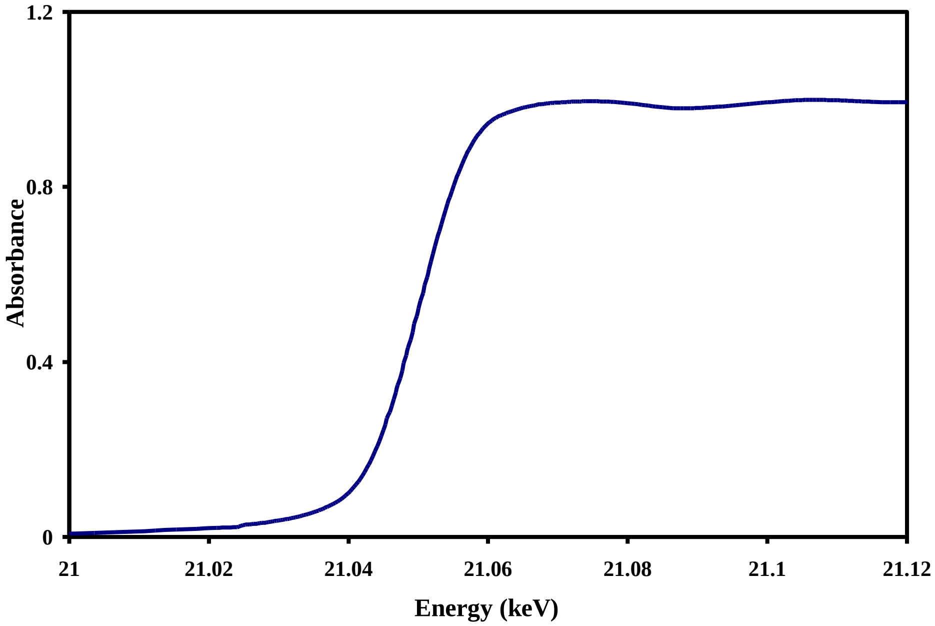


Figure S1. XANES spectrum of **1**.

IV. UV-visible spectroscopy

UV-visible spectra of **1** in concentrated HBr (Figure S2) was recorded at room temperature in a quartz cell (1 cm) on a Cary 6000i double beam spectrometer. HBr was used as the reference.

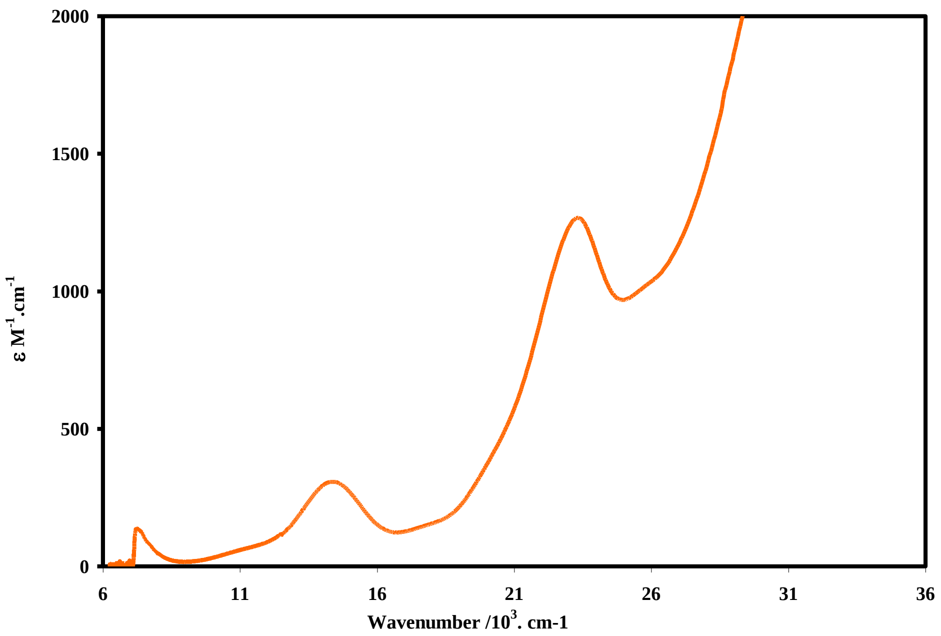


Figure S2. UV-visible spectra of **1** in concentrated HBr

V. Computational methods.

Quantum chemical calculations were performed using the multi-configurational Complete Active Space SCF (CASSCF) method,[2] followed by second-order perturbation theory (CASPT2).[3] Relativistic all electron ANO-RCC basis sets of triple-zeta quality (VTZP) were employed on all atoms with the following contractions: 7s6p4d2f1g for Tc, 5s4p2d1f for Cl, and 6s5p3d1f for Br.[4] Scalar relativistic effects were included using the Douglas-Kroll-Hess Hamiltonian.[5] In the CASSCF calculations, the complete active space contains twelve electrons in twelve active orbitals (12/12) for $Tc_2X_8^{2-}$ and thirteen electrons in twelve active orbitals (13/12) for $Tc_2X_8^{3-}$. This space comprises one 4dσ, two 4dπ and one 4dδ Tc–Tc bonding orbitals and the corresponding antibonding orbitals, two Tc-X σ bonding and the corresponding antibonding orbitals. In the subsequent CASPT2 calculations, orbitals up to and including the 3d for Tc, 2p for Cl, 3p for Br were kept frozen. This approach has proven to be very successfully in the studies of metal-metal bonded compounds.[6-9] A numerical CASPT2 optimization of the Tc–Tc and Tc–X bond distances was performed for the ground states of the $Tc_2X_8^{2-}$ and $Tc_2X_8^{3-}$ species imposing D_{2h} symmetry. The computational costs arising from the two-electron integrals were drastically reduced by employing the Cholesky decomposition (CD) technique in all CASSCF/CASPT2 calculations[10-12] combined with the Local Exchange (LK) screening.[13] All calculations were performed with the MOLCAS 7.4 package.[14]

Table S7. Excitation energies and intensities for $[Tc_2Cl_8]^{3-}$ at the CASPT2(13/12)/ANO-RCC-VTZP level.

Excitations	TZVP	Intensity
$\delta\rightarrow\delta^*$	6132	0.91×10^{-2}
$\delta^*\rightarrow$Tc-Clσ^*	9622	0.13×10^{-5}
$\delta^*\rightarrow\pi^*$	11322	0.15×10^{-4}
$\delta^*\rightarrow\sigma^*$	13341	$< 1.0 \times 10^{-8}$
$\delta\rightarrow\pi^*$	17777	$< 1.0 \times 10^{-8}$
$\delta\rightarrow$Tc-Clσ^*	21688	0.17×10^{-6}
$\pi\rightarrow\delta^*$	23803	$< 1.0 \times 10^{-8}$
$\pi\rightarrow\pi^*$	30009	0.53×10^{-4}

Table S8. Excitation energies and intensities for $[Tc_2Br_8]^{3-}$ at the CASPT2(13/12)/ANO-RCC-VTZP level.

Excitations	TZVP	Intensity
$\delta\rightarrow\delta^*$	6344	0.13×10^{-1}
$\delta^*\rightarrow$Tc-Brσ^*	9546	0.12×10^{-5}
$\delta^*\rightarrow\pi^*$	11942	0.17×10^{-4}
$\delta^*\rightarrow\sigma^*$	13654	$< 1.0 \times 10^{-8}$
$\delta\rightarrow\pi^*$	18492	$< 1.0 \times 10^{-8}$
$\delta\rightarrow$Tc-Brσ^*	21133	0.13×10^{-5}
$\pi\rightarrow\delta^*$	23374	$< 1.0 \times 10^{-8}$
$\pi\rightarrow\pi^*$	30652	0.76×10^{-4}

---

[1] G. M. Sheldrick, *Acta Cryst. A*, 2008, **64**, 112-122.

[2] B. O. Roos, P. R. Taylor and P. E. M. Siegbahn, *Chem. Phys.,* 1980, **48,** 157-173.

[3] Andersson, K.; Malmqvist, P. A.; Roos, B. O. *J. Chem. Phys.*, 1992, **96**, 1218-1226.

[4] B. O. Roos, R. Lindh, P.-Å. Malmqvist, V. Veryazov and P.-O. Widmark, . *J. Phys. Chem. A,* 2005, **109**, 6575-6579.

[5] B. A. Hess, *Phys. Rev. A*, 1986, **33**, 3742-3748.

[6] F. Ferrante, L. Gagliardi, B. E. Bursten and A. P. Sattelberger, *Inorg. Chem.*, 2005, **44**, 8476-8480.

[7] L. Gagliardi and B. O. Roos, *Inorg. Chem*., 2003**, 42**, 1599-1603.

[8] B. O. Roos, A. Borin and L. Gagliardi, *Angew. Chem. Int. Ed.*, 2007, **46**, 1469-1472.

[9] M. Brynda, L. Gagliardi and B. O. Roos, *Chem. Phys. Lett.*, 2009, **471**, 1 -10.

[10] F. Aquilante, P. A. Malmqvist, T. B. Pedersen, A. Ghosh and B. O. Roos, *J. Chem. Theory Comput.*, 2008, **4**, 694-702.

[11] F. Aquilante, T. B. Pedersen, R. Lindh, B. O. Roos, A. S. De Meras and H. Koch, *J. Chem. Phys.*, 2008, **129**, 024113.

[12] F. Aquilante, T. B. Pedersen, L. Gagliardi and R. Lindh, *J. Chem. Phys.*, 2009, **130**, 154107.

[13] F. Aquilante, T. B. Pedersen and R. Lindh, *J. Chem. Phys*., 2007, **126**, 194106.

[14] G. Karlström, R. Lindh, P.-Å. Malmqvist, B. O. Roos, U. Ryde, V. Veryazov, P.-O Widmark, M. Cossi, B. Schimmelpfennig, P. Neogrady and L. Seijo, *Comput. Mat. Sci.*, 2003, **287**, 222-239.