Supporting Information

Influence of organic cation on the formation of hexahalotechnetates: X-ray, thermal and comparative analysis of non-valent interactions

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1. Experimental methods

1.1 Electron absorption spectroscopy and IR-spectroscopy of 1 and 2

UV-Vis spectroscopy of a stock solution of compound 4 was carried out on an Agilent Cary 100 spectrophotometer in the range of 200-800 nm. A quartz cell l = 1.01 mm was used.

Infrared spectroscopy was carried out on a Nicolet Magna 550 FTIR instrument.

1.2 Thermal analysis

We performed thermal gravimetry with simultaneous differential thermal analysis (TG-DTA) using a Netzsch STA Jupiter 449 F3 thermoanalytical complex. Heating was carried out at a rate of 10 °C/min in the temperature range 40–1000 °C. Al_2O_3 crucibles and W-Re sample carrier were used; the atmosphere was the Ar-1.5% H_2 mixture with a purity of $\omega(Ar + H_2) = 99.999\%$.

1.3 XAFS spectroscopy of 13

The X-ray absorption spectra (EXAFS, XANES) on the Tc *K*-edge were taken with the Structural Materials Science Station (Russian Research Centre Kurchatov Institute) in the transmission geometry using a Si(111) monoblock monochromator with a slit and two ionization chambers filled with an argon–xenon mixture. The EXAFS spectra were processed with Athena and Artemis programs from the IFEFFIT package[1]. The multisphere fitting of normalized EXAFS curves $\chi(k)$ was performed in the photoelectron wavenumber range k 4.0–15.0 Å–1 with the $k3$ weight scheme using the photoelectron theoretical phases and scattering amplitudes calculated with FEFF program[2]. As reference sample we used a polycrystalline powder of technetium metal.

1.4 Powder X-ray diffraction (PXRD)

PXRD measurements were performed using a Panalytical Aeris X-ray diffractometer with Cu Kα radiation and PIXcel3D detector. Diffraction patterns were recorded with a step of $2\theta = 0.011^{o}$ in the Bragg-Brentano geometry. Powders were placed on a zero-background silicon holder and covered with shellac.

1.5 Measurements of technetium concentration in saturated solutions. Beta spectrometry

The concentration of technetium in saturated solutions of various hexahalogenotechnetates was assessed by adding a sample of the dry compound into a 1.5 ml glass vial with 500 μl of solvent, which was placed in a thermostat. An aliquot was taken to determine the activity of the solution for those samples where a precipitate of the original substance remained at the bottom of the vials. If the precipitate was completely dissolved in the vial, then an additional portion of

the dry compound was added. Measurements of the activity of solutions were carried out after keeping the solvent above the sediment for at least 7 days. The experimental results are given in the SI Table S36

Activity measurements in solutions were carried out on a Tri-Carb 3180 TR/SL instrument (Perkin Elmer) using the liquid scintillation spectrometry (LSC) method. An aliquot of the analyzed solvent was mixed with HiSafe-3 liquid scintillator (Perkin Elmer) in a ratio of 1:20. The activity of technetium was taken to be 635Bk/μg[43].

2. Crystal structure data

The crystal structures of all synthesized substances were determined by X-ray structural analysis using an automatic four-circle area-detector diffractometer Bruker KAPPA APEX II with MoKα radiation. The cell parameters were refined over the entire data set together with data reduction by using SAINT-Plus software[3]. Absorption corrections were introduced using the SADABS program[4]. The structures were solved by using the SHELXT-2018/2 program[5] and refined by full-matrix least squares on F^2 in the anisotropic approximation for all non-hydrogen atoms (SHELXL-2018/3[6]). The C-H in all structures and N-H in **5** bonded hydrogen atoms were placed in geometrically calculated positions and refined in an idealized geometry with isotropic temperature factors equal to $1.2U_{eq}$(C, N) for CH-groups, and $1.5U_{eq}$(C) for CH_3-groups. N-H and O-H bonded hydrogen atoms were objectively located from the difference Fourier synthesis and refined with isotropic temperature factors equal to $1.2U_{eq}$(N) and 1.5 U_{eq}(O).

Crystal data, data collection, and structure refinement details are summarized in Table S1. Tables S2−S32 represent all other crystallographic parameters of structures **1 – 8**. The atomic coordinates were deposited at the Cambridge Crystallographic Data Centre, CCDC № 2298414-2298421for **1-8**.

Table S1. Crystal data and structure refinement for **1-8.**

Identification code	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**
CCDC number	**2298420**	**2298414**	**2298417**	**2298415**	**2298421**	**2298418**	**2298419**	**2298416**
Empirical formula	$C_{16}H_{24}Br_6N_8O_5Tc$	$C_{16}H_{22}Cl_6N_8O_4Tc$	$C_{28}H_{32}Cl_8N_4O_4S_4Tc$	$C_{14}H_{16}Cl_6N_2O_2S_2Tc$	$C_{48}H_{66}Cl_{20}N_{24}O_3Tc_2$	$C_{12}H_{14}Br_6N_4O_2Tc$	$C_8H_{24}Br_6N_2Tc$	$C_8H_{24}Cl_6N_2Tc$
Formula weight	985.89	701.11	998.41	619.11	1932.24	823.73	725.75	458.99
Temperature/K	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)
Crystal	monoc	triclini	triclini	triclini	monoc	monoc	monoc	monoc

system	linic	c	c	c	linic	linic	linic	linic
Space group	$P2_1/n$	P-1	P-1	P-1	$P2_1/c$	$P2_1/n$	$P2_1/n$	$P2_1/n$
a/Å	13.428 (2)	7.898(3)	7.1584 (4)	7.2136 (5)	28.562 3(9)	8.3100 (11)	9.1485 (5)	8.8583 (7)
b/Å	14.292 (3)	8.106(3)	9.3884 (5)	8.0612 (6)	12.861 6(4)	10.801 3(15)	10.749 7(6)	10.434 0(8)
c/Å	15.242 (3)	10.452 (4)	15.484 6(8)	9.8742 (7)	22.092 3(7)	11.899 2(16)	9.9767 (5)	9.6725 (8)
α/°	90	96.572 (16)	76.369 (2)	98.062 (3)	90	90	90	90
β/°	106.82 3(7)	91.809 (15)	79.704 (2)	100.83 0(3)	108.19 10(10)	101.54 9(6)	92.386 (2)	92.915 (3)
γ/°	90	112.38 2(14)	81.477 (2)	92.071 (3)	90	90	90	90
Volume/ $Å^3$	2800.0 (9)	612.7(4)	988.92 (9)	557.23 (7)	7710.1 (4)	1046.4 (2)	980.29 (9)	892.85 (12)
Z	4	1	1	1	4	2	2	2
$\rho_{calc}g/cm^3$	2.339	1.900	1.676	1.845	1.665	2.614	2.459	1.707
μ/mm^{-1}	9.120	1.285	1.155	1.566	1.108	12.158	12.948	1.688
F(000)	1876.0	351.0	503.0	307.0	3888.0	766.0	678.0	462.0
Crystal size/mm^3	0.1 × 0.04 × 0.03	0.1 × 0.08 × 0.05	0.2 × 0.1 × 0.07	0.13 × 0.12 × 0.04	0.3 × 0.26 × 0.2	0.12 × 0.1 × 0.09	0.28 × 0.2 × 0.14	0.22 × 0.18 × 0.17
Radiation	MoKα (λ = 0.7107 3)	MoKα (λ = 0.7107 3)	MoKα (λ = 0.7107 3)	MoKα (λ = 0.7107 3)	MoKα (λ = 0.7107 3)	MoKα (λ = 0.7107 3)	MoKα (λ = 0.7107 3)	MoKα (λ = 0.7107 3)
2Θ range for data collection/°	8.384 to 59.998	8.964 to 59.998	8.178 to 59.99	8.406 to 59.998	8.296 to 69.992	8.318 to 59.996	8.178 to 59.992	6.038 to 60.398
Index ranges	$-18 \le h \le 18$, $-20 \le k \le 20$, $-21 \le l \le 21$	$-11 \le h \le 11$, $-11 \le k \le 11$, $-14 \le l \le 14$	$-9 \le h \le 10$, $-13 \le k \le 13$, $-21 \le l \le 21$	$-10 \le h \le 9$, $-11 \le k \le 11$, $-13 \le l \le 13$	$-45 \le h \le 45$, $-20 \le k \le 20$, $-35 \le l \le 34$	$-11 \le h \le 9$, $-15 \le k \le 15$, $-16 \le l \le 16$	$-12 \le h \le 12$, $-14 \le k \le 15$, $-14 \le l \le 14$	$-12 \le h \le 12$, $-14 \le k \le 14$, $-13 \le l \le 13$
Reflections collected	43761	10321	19290	11493	205070	18373	20326	15015
Independent	8150 [R_{int} =	3569 [R_{int} =	5751 [R_{int} =	3237 [R_{int} =	33002 [R_{int} =	3039 [R_{int} =	2839 [R_{int} =	2620 [R_{int} =

reflections	0.1817, R_{sigma} = 0.1617]	0.0950, R_{sigma} = 0.1230]	0.0267, R_{sigma} = 0.0299]	0.0397, R_{sigma} = 0.0477]	0.0529, R_{sigma} = 0.0453]	0.1211, R_{sigma} = 0.1010]	0.0448, R_{sigma} = 0.0300]	0.0512, R_{sigma} = 0.0372]
Data/restraints/parameters	8150/4/326	3569/0/166	5751/0/241	3237/4/133	33002/9/892	3039/3/124	2839/0/85	2620/0/127
Goodness-of-fit on F^2	0.986	0.969	1.037	1.020	1.020	0.997	1.006	1.038
Final R indexes [I>=2σ (I)]	R_1 = 0.0610, wR_2 = 0.1058	R_1 = 0.0585, wR_2 = 0.1238	R_1 = 0.0230, wR_2 = 0.0493	R_1 = 0.0364, wR_2 = 0.0760	R_1 = 0.0358, wR_2 = 0.0640	R_1 = 0.0454, wR_2 = 0.0649	R_1 = 0.0218, wR_2 = 0.0406	R_1 = 0.0231, wR_2 = 0.0450
Final R indexes [all data]	R_1 = 0.1664, wR_2 = 0.1380	R_1 = 0.0951, wR_2 = 0.1418	R_1 = 0.0291, wR_2 = 0.0516	R_1 = 0.0519, wR_2 = 0.0827	R_1 = 0.0643, wR_2 = 0.0735	R_1 = 0.1057, wR_2 = 0.0792	R_1 = 0.0305, wR_2 = 0.0425	R_1 = 0.0321, wR_2 = 0.0485
Largest diff. peak/hole / e $Å^{-3}$	1.54/-1.92	1.21/-2.62	0.41/-0.29	0.78/-0.56	0.69/-0.60	0.98/-1.28	0.55/-0.59	0.43/-0.38

Table S2. Bond Lengths for **1.**

Atom	Atom	Length/Å		Atom	Atom	Length/Å
Tc1	Br1	2.4871(12)		N1	C2	1.414(10)
Tc1	Br2	2.5132(11)		N1	C10	1.489(10)
Tc1	Br3	2.5334(12)		N3	C12	1.469(10)
Tc1	Br4	2.5034(12)		N3	C4	1.346(9)
Tc1	Br5	2.5159(12)		N3	C2	1.373(10)
Tc1	Br6	2.5038(12)		N23	C24	1.356(10)
O13	C6	1.230(9)		N23	C22	1.387(10)
O31	C22	1.213(10)		N23	C32	1.475(10)
O11	C2	1.221(9)		N9	C4	1.361(10)
N7	C5	1.380(9)		N9	C8	1.341(11)
N7	C14	1.444(10)		N27	C25	1.380(9)
N7	C8	1.330(11)		N27	C28	1.319(10)
N21	C26	1.406(10)		N27	C34	1.479(10)
N21	C22	1.384(11)		O33	C26	1.244(10)

N21	C30	1.477(10)		C5	C6	1.419(11)
N29	C24	1.369(9)		C5	C4	1.354(11)
N29	C28	1.334(10)		C25	C24	1.354(11)
N1	C6	1.405(10)		C25	C26	1.405(11)

Table S3. Bond Angles for **1.**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
Br1	Tc1	Br2	89.47(4)	C8	N9	C4	107.8(8)
Br1	Tc1	Br3	89.20(4)	C25	N27	C34	127.7(7)
Br1	Tc1	Br4	89.85(4)	C28	N27	C25	107.2(7)
Br1	Tc1	Br5	90.18(4)	C28	N27	C34	125.1(7)
Br1	Tc1	Br6	179.75(5)	N7	C5	C6	129.6(8)
Br2	Tc1	Br3	88.63(4)	C4	C5	N7	107.7(7)
Br2	Tc1	Br5	90.19(4)	C4	C5	C6	122.7(7)
Br4	Tc1	Br2	178.72(4)	O13	C6	N1	120.7(8)
Br4	Tc1	Br3	90.28(4)	O13	C6	C5	127.9(8)
Br4	Tc1	Br5	90.90(4)	N1	C6	C5	111.5(7)
Br4	Tc1	Br6	90.37(4)	N27	C25	C26	131.9(8)
Br5	Tc1	Br3	178.67(4)	C24	C25	N27	107.7(7)
Br6	Tc1	Br2	90.31(4)	C24	C25	C26	120.4(7)
Br6	Tc1	Br3	90.68(4)	N23	C24	N29	127.8(8)
Br6	Tc1	Br5	89.93(4)	C25	C24	N29	107.3(7)
C5	N7	C14	127.1(8)	C25	C24	N23	124.9(7)
C8	N7	C5	107.1(7)	O33	C26	N21	120.3(7)
C8	N7	C14	125.7(8)	O33	C26	C25	126.2(8)
C26	N21	C30	116.5(7)	C25	C26	N21	113.4(8)
C22	N21	C26	126.1(7)	N3	C4	N9	129.0(8)
C22	N21	C30	117.4(7)	N3	C4	C5	123.4(7)
C28	N29	C24	107.5(7)	C5	C4	N9	107.6(7)
C6	N1	C2	126.3(7)	O11	C2	N1	121.2(8)
C6	N1	C10	119.0(7)	O11	C2	N3	122.1(8)
C2	N1	C10	114.6(7)	N3	C2	N1	116.6(7)
C4	N3	C12	119.5(7)	N27	C28	N29	110.4(7)
C4	N3	C2	119.4(7)	O31	C22	N21	121.5(8)
C2	N3	C12	120.7(7)	O31	C22	N23	121.5(8)
C24	N23	C22	118.0(7)	N21	C22	N23	117.0(8)
C24	N23	C32	121.0(6)	N7	C8	N9	109.8(7)
C22	N23	C32	120.5(7)				

Table S4. Hydrogen Bonds for **1**.

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
N29	H29	O13[1]	0.87(2)	1.93(4)	2.716(9)	150(7)
O1	H1B	O1[2]	0.84(2)	2.50(8)	3.134(15)	133(9)

N9	H9	O1	0.87(2)	1.94(4)	2.754(10)	154(7)
C14	H14B	O31	0.98	2.47	3.216(11)	132.2
C28	H28	O31[3]	0.95	2.44	3.119(10)	128.6
C28	H28	O11[4]	0.95	2.40	3.189(9)	140.9
C34	H34B	O31[3]	0.98	2.51	3.343(11)	142.4
C8	H8	O11[5]	0.95	2.19	3.066(10)	152.3

[1]2-X,1-Y,1-Z; [2]2-X,1-Y,2-Z; [3]5/2-X,1/2+Y,3/2-Z; [4]1+X,+Y,+Z; [5]3/2-X,-1/2+Y,3/2-Z

Table S4. Torsion Angles for **1.**

A	B	C	D	Angle/°		A	B	C	D	Angle/°
N7	C5	C6	O13	-0.7(13)		C2	N1	C6	C5	0.7(10)
N7	C5	C6	N1	178.1(7)		C2	N3	C4	N9	-179.4(7)
N7	C5	C4	N3	-178.4(7)		C2	N3	C4	C5	0.1(11)
N7	C5	C4	N9	1.2(9)		C14	N7	C5	C6	4.0(13)
N27	C25	C24	N29	-1.5(8)		C14	N7	C5	C4	-176.4(7)
N27	C25	C24	N23	179.0(7)		C14	N7	C8	N9	175.7(7)
N27	C25	C26	N21	178.4(7)		C28	N29	C24	N23	-178.8(7)
N27	C25	C26	O33	1.1(14)		C28	N29	C24	C25	1.8(8)
C5	N7	C8	N9	-0.2(9)		C28	N27	C25	C24	0.7(8)
C12	N3	C4	N9	-6.3(11)		C28	N27	C25	C26	-179.4(8)
C12	N3	C4	C5	173.2(7)		C22	N21	C26	O33	179.7(8)
C12	N3	C2	O11	5.2(11)		C22	N21	C26	C25	2.2(11)
C12	N3	C2	N1	-173.9(6)		C22	N23	C24	N29	-176.0(7)
C6	N1	C2	O11	-178.6(7)		C22	N23	C24	C25	3.4(11)
C6	N1	C2	N3	0.4(10)		C34	N27	C25	C24	-178.8(7)
C6	C5	C4	N3	1.2(12)		C34	N27	C25	C26	1.1(13)
C6	C5	C4	N9	-179.2(7)		C34	N27	C28	N29	180.0(7)
C25	N27	C28	N29	0.4(8)		C30	N21	C26	O33	-1.1(11)
C24	N29	C28	N27	-1.4(8)		C30	N21	C26	C25	-178.5(7)
C24	N23	C22	O31	177.1(7)		C30	N21	C22	O31	0.9(12)
C24	N23	C22	N21	-2.8(10)		C30	N21	C22	N23	-179.1(7)
C24	C25	C26	N21	-1.8(11)		C8	N7	C5	C6	179.8(8)
C24	C25	C26	O33	-179.1(8)		C8	N7	C5	C4	-0.6(9)
C26	N21	C22	O31	-179.8(8)		C8	N9	C4	N3	178.3(7)
C26	N21	C22	N23	0.1(11)		C8	N9	C4	C5	-1.3(9)
C26	C25	C24	N29	178.6(7)		C32	N23	C24	N29	-3.8(11)
C26	C25	C24	N23	-0.9(12)		C32	N23	C24	C25	175.6(7)
C4	N3	C2	O11	178.2(7)		C32	N23	C22	O31	4.8(12)
C4	N3	C2	N1	-0.8(10)		C32	N23	C22	N21	-175.1(7)
C4	N9	C8	N7	1.0(9)		C10	N1	C6	O13	-3.7(10)
C4	C5	C6	O13	179.8(7)		C10	N1	C6	C5	177.4(6)

C4	C5	C6	N1	-1.5(10)		C10	N1	C2	O11	4.5(10)
C2	N1	C6	O13	179.6(7)		C10	N1	C2	N3	-176.4(6)

Table S5. Bond Lengths for **2.**

Atom	Atom	Length/Å		Atom	Atom	Length/Å
Tc1	Cl3	2.3380(14)		N1	C2	1.415(6)
Tc1	Cl3[1]	2.3380(14)		N1	C6	1.391(6)
Tc1	Cl2[1]	2.3490(14)		N1	C10	1.465(5)
Tc1	Cl2	2.3490(14)		N9	C4	1.367(5)
Tc1	Cl1	2.3684(14)		N9	C8	1.335(6)
Tc1	Cl1[1]	2.3684(14)		N7	C5	1.377(6)
O1	C2	1.199(6)		N7	C8	1.336(6)
O2	C6	1.219(5)		N7	C12	1.473(6)
N3	C4	1.341(6)		C4	C5	1.363(6)
N3	C2	1.390(5)		C6	C5	1.445(6)
N3	C11	1.471(6)				

[1]2-X,2-Y,1-Z

Table S6. Bond Angles for **2.**

Atom	Atom	Atom	Angle/°		Atom	Atom	Atom	Angle/°
Cl3	Tc1	Cl3[1]	180.0		C6	N1	C2	127.1(4)
Cl3[1]	Tc1	Cl2	90.04(4)		C6	N1	C10	116.5(4)
Cl3	Tc1	Cl2	89.96(4)		C8	N9	C4	109.0(4)
Cl3[1]	Tc1	Cl2[1]	89.96(4)		C5	N7	C12	126.6(4)
Cl3	Tc1	Cl2[1]	90.04(4)		C8	N7	C5	107.7(4)
Cl3[1]	Tc1	Cl1	89.87(4)		C8	N7	C12	125.6(4)
Cl3	Tc1	Cl1	90.13(4)		N3	C4	N9	129.7(4)
Cl3	Tc1	Cl1[1]	89.87(4)		N3	C4	C5	123.8(4)
Cl3[1]	Tc1	Cl1[1]	90.13(4)		C5	C4	N9	106.5(4)
Cl2[1]	Tc1	Cl2	180.00(6)		O1	C2	N3	121.6(4)
Cl2[1]	Tc1	Cl1	90.73(4)		O1	C2	N1	122.2(4)
Cl2	Tc1	Cl1	89.27(4)		N3	C2	N1	116.3(4)
Cl2	Tc1	Cl1[1]	90.73(4)		O2	C6	N1	122.1(4)
Cl2[1]	Tc1	Cl1[1]	89.27(4)		O2	C6	C5	126.5(5)
Cl1	Tc1	Cl1[1]	180.0		N1	C6	C5	111.4(4)
C4	N3	C2	119.3(4)		N7	C5	C6	130.3(4)
C4	N3	C11	123.6(4)		C4	C5	N7	107.8(4)
C2	N3	C11	117.1(4)		C4	C5	C6	121.9(4)
C2	N1	C10	116.3(4)		N9	C8	N7	108.9(4)

[1]2-X,2-Y,1-Z

Table S7. Hydrogen Bonds for **2.**

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
N9	H9	Cl1	0.84(5)	2.45(5)	3.275(4)	168(5)
C10	H10B	O1[1]	0.98	2.42	3.345(6)	157.6

[1]1-X,-Y,2-Z

Table S8. Torsion Angles for **2.**

A	B	C	D	Angle/°		A	B	C	D	Angle/°
O2	C6	C5	N7	-0.5(8)		C5	N7	C8	N9	0.3(5)
O2	C6	C5	C4	177.6(4)		C8	N9	C4	N3	-178.3(4)
N3	C4	C5	N7	178.6(4)		C8	N9	C4	C5	0.5(5)
N3	C4	C5	C6	0.1(7)		C8	N7	C5	C4	0.0(5)
N1	C6	C5	N7	-179.6(4)		C8	N7	C5	C6	178.3(4)
N1	C6	C5	C4	-1.5(6)		C11	N3	C4	N9	-0.3(7)
N9	C4	C5	N7	-0.3(5)		C11	N3	C4	C5	-178.9(4)
N9	C4	C5	C6	-178.8(4)		C11	N3	C2	O1	-1.5(6)
C4	N3	C2	O1	175.8(4)		C11	N3	C2	N1	176.6(4)
C4	N3	C2	N1	-6.1(6)		C12	N7	C5	C4	-179.8(4)
C4	N9	C8	N7	-0.5(5)		C12	N7	C5	C6	-1.5(7)
C2	N3	C4	N9	-177.5(4)		C12	N7	C8	N9	-179.8(4)
C2	N3	C4	C5	3.9(6)		C10	N1	C2	O1	0.2(6)
C2	N1	C6	O2	179.7(4)		C10	N1	C2	N3	-178.0(4)
C2	N1	C6	C5	-1.1(6)		C10	N1	C6	O2	2.6(6)
C6	N1	C2	O1	-177.0(4)		C10	N1	C6	C5	-178.2(4)
C6	N1	C2	N3	4.9(6)						

Table S9. Bond Lengths for **3.**

Atom	Atom	Length/Å		Atom	Atom	Length/Å
Tc1	Cl1	2.3652(4)		N11	C19	1.3936(18)
Tc1	Cl1[1]	2.3652(4)		C9	C8	1.397(2)
Tc1	Cl2[1]	2.3684(3)		C9	C4	1.3989(19)
Tc1	Cl2	2.3684(3)		C8	C7	1.380(2)
Tc1	Cl3[1]	2.3574(3)		C14	C15	1.3951(19)
Tc1	Cl3	2.3575(3)		C14	C19	1.3973(19)
S13	C12	1.6990(16)		C15	C16	1.387(2)
S13	C14	1.7466(14)		C16	C17	1.406(2)
S3	C4	1.7441(15)		C17	C18	1.380(2)
S3	C2	1.6938(16)		C5	C4	1.392(2)
N1	C9	1.3891(19)		C5	C6	1.379(2)
N1	C2	1.3140(19)		C19	C18	1.3959(19)
N11	C12	1.3081(19)		C7	C6	1.407(2)

[1]1-X,2-Y,-Z

Table S10. Bond Angles for **3.**

Atom	Atom	Atom	Angle/°		Atom	Atom	Atom	Angle/°
Cl1	Tc1	Cl1[1]	180.0		N1	C9	C4	111.13(13)
Cl1[1]	Tc1	Cl2[1]	88.657(12)		C8	C9	C4	121.49(14)
Cl1[1]	Tc1	Cl2	91.343(12)		C7	C8	C9	117.11(14)
Cl1	Tc1	Cl2	88.657(12)		C15	C14	S13	128.85(11)
Cl1	Tc1	Cl2[1]	91.343(12)		C15	C14	C19	121.09(12)
Cl2[1]	Tc1	Cl2	180.0		C19	C14	S13	110.01(10)
Cl3[1]	Tc1	Cl1[1]	90.001(12)		C16	C15	C14	117.27(14)
Cl3	Tc1	Cl1[1]	89.999(12)		C15	C16	C17	121.46(14)
Cl3	Tc1	Cl1	90.001(12)		C18	C17	C16	121.31(13)
Cl3[1]	Tc1	Cl1	89.998(12)		C6	C5	C4	117.53(13)
Cl3	Tc1	Cl2	89.828(12)		C9	C4	S3	110.25(11)
Cl3	Tc1	Cl2[1]	90.171(12)		C5	C4	S3	128.73(11)
Cl3[1]	Tc1	Cl2[1]	89.829(12)		C5	C4	C9	121.02(13)
Cl3[1]	Tc1	Cl2	90.172(12)		N1	C2	S3	113.66(12)
Cl3[1]	Tc1	Cl3	180.000(17)		N11	C19	C14	111.53(12)
C12	S13	C14	90.31(7)		N11	C19	C18	126.99(14)
C2	S3	C4	90.45(7)		C18	C19	C14	121.46(13)
C2	N1	C9	114.51(13)		C17	C18	C19	117.38(14)
C12	N11	C19	114.11(13)		C8	C7	C6	121.38(14)
N11	C12	S13	113.99(11)		C5	C6	C7	121.47(14)
N1	C9	C8	127.38(13)					

[1]1-X,2-Y,-Z

Table S11. Hydrogen Bonds for **3.**

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
O1	H1A	Cl4[1]	0.83(2)	2.34(2)	3.1683(14)	178(2)
O1	H1B	Cl4	0.83(2)	2.35(2)	3.1738(14)	173(2)
O2	H2A	Cl4[2]	0.80(2)	2.48(2)	3.2141(13)	153(2)
O2	H2B	O1	0.79(2)	1.88(2)	2.6732(18)	173(2)
N1	H1	Cl4	0.877(18)	2.213(18)	3.0736(13)	166.8(16)
N11	H11	O2	0.861(18)	1.803(19)	2.6577(17)	171.3(17)
C12	H12	Cl2[3]	0.95	2.74	3.3970(15)	127.1
C2	H2	Cl2[4]	0.95	2.72	3.3435(16)	124.0
C2	H2	O2[2]	0.95	2.56	3.291(2)	134.4

[1]2-X,2-Y,1-Z; [2]1-X,2-Y,1-Z; [3]1+X,+Y,+Z; [4]+X,+Y,1+Z

Table S12. Torsion Angles for **3.**

A	B	C	D	Angle/°		A	B	C	D	Angle/°

S13	C14	C15	C16	175.74(11)		C14	C15	C16	C17	0.7(2)
S13	C14	C19	N11	2.29(14)		C14	C19	C18	C17	0.1(2)
S13	C14	C19	C18	-176.56(11)		C15	C14	C19	N11	-179.96(12)
N1	C9	C8	C7	-179.85(14)		C15	C14	C19	C18	1.2(2)
N1	C9	C4	S3	0.02(14)		C15	C16	C17	C18	0.5(2)
N1	C9	C4	C5	179.95(12)		C16	C17	C18	C19	-0.9(2)
N11	C19	C18	C17	-178.60(13)		C4	S3	C2	N1	0.14(12)
C12	S13	C14	C15	-179.36(13)		C4	C9	C8	C7	-0.5(2)
C12	S13	C14	C19	-1.84(10)		C4	C5	C6	C7	-0.3(2)
C12	N11	C19	C14	-1.66(17)		C2	S3	C4	C9	-0.09(11)
C12	N11	C19	C18	177.11(13)		C2	S3	C4	C5	179.98(13)
C9	N1	C2	S3	-0.16(16)		C2	N1	C9	C8	179.51(15)
C9	C8	C7	C6	0.1(2)		C2	N1	C9	C4	0.09(17)
C8	C9	C4	S3	-179.45(11)		C19	N11	C12	S13	0.21(16)
C8	C9	C4	C5	0.5(2)		C19	C14	C15	C16	-1.5(2)
C8	C7	C6	C5	0.3(2)		C6	C5	C4	S3	179.82(11)
C14	S13	C12	N11	0.96(11)		C6	C5	C4	C9	-0.1(2)

Table S13. Bond Lengths for **4.**

Atom	Atom	Length/Å		Atom	Atom	Length/Å
Tc1	Cl1	2.3728(6)		N3	C2	1.311(4)
Tc1	Cl1[1]	2.3728(6)		N3	C4	1.387(3)
Tc1	Cl2[1]	2.3539(6)		C4	C5	1.395(4)
Tc1	Cl2	2.3539(6)		C4	C9	1.398(4)
Tc1	Cl3	2.3283(7)		C5	C6	1.390(4)
Tc1	Cl3[1]	2.3283(7)		C6	C7	1.396(4)
S1	C2	1.692(3)		C7	C8	1.378(4)
S1	C9	1.745(3)		C8	C9	1.403(4)

[1]2-X,1-Y,1-Z

Table S14. Bond Angles for **4.**

Atom	Atom	Atom	Angle/°		Atom	Atom	Atom	Angle/°
Cl1	Tc1	Cl1[1]	180.0		Cl3	Tc1	Cl3[1]	180.0
Cl2	Tc1	Cl1	90.78(2)		C2	S1	C9	90.27(14)
Cl2	Tc1	Cl1[1]	89.22(2)		C2	N3	C4	114.6(2)
Cl2[1]	Tc1	Cl1[1]	90.78(2)		N3	C2	S1	113.8(2)
Cl2[1]	Tc1	Cl1	89.22(2)		N3	C4	C5	127.5(2)
Cl2	Tc1	Cl2[1]	180.0		N3	C4	C9	111.0(2)
Cl3	Tc1	Cl1	89.30(2)		C5	C4	C9	121.5(2)
Cl3[1]	Tc1	Cl1	90.70(2)		C6	C5	C4	117.0(3)
Cl3[1]	Tc1	Cl1[1]	89.30(2)		C5	C6	C7	121.3(3)
Cl3	Tc1	Cl1[1]	90.70(2)		C8	C7	C6	122.2(3)
Cl3	Tc1	Cl2	89.50(2)		C7	C8	C9	116.9(3)
Cl3[1]	Tc1	Cl2[1]	89.50(2)		C4	C9	S1	110.29(19)
Cl3[1]	Tc1	Cl2	90.50(2)		C4	C9	C8	121.1(3)
Cl3	Tc1	Cl2[1]	90.50(2)		C8	C9	S1	128.6(2)

[1]2-X,1-Y,1-Z

Table S15. Hydrogen Bonds for **4.**

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
O1W	H1WB	Cl1	0.799(17)	2.49(2)	3.259(2)	162(3)
N3	H3	O1W	0.80(3)	1.91(3)	2.711(3)	176(3)

Table S16. Torsion Angles for **4.**

A	B	C	D	Angle/°		A	B	C	D	Angle/°
N3	C4	C5	C6	179.9(2)		C5	C4	C9	S1	179.15(18)
N3	C4	C9	S1	-0.3(2)		C5	C4	C9	C8	-0.5(3)
N3	C4	C9	C8	-179.9(2)		C5	C6	C7	C8	0.1(4)
C2	S1	C9	C4	0.07(18)		C6	C7	C8	C9	0.0(4)
C2	S1	C9	C8	179.7(2)		C7	C8	C9	S1	-179.41(19)
C2	N3	C4	C5	-179.0(2)		C7	C8	C9	C4	0.2(3)
C2	N3	C4	C9	0.4(3)		C9	S1	C2	N3	0.2(2)
C4	N3	C2	S1	-0.4(3)		C9	C4	C5	C6	0.6(3)
C4	C5	C6	C7	-0.4(4)						

Table S17. Bond Lengths for **5.**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Tc1	Cl11	2.3668(4)	N16	C30	1.332(2)
Tc1	Cl12	2.3523(4)	N16	C31	1.327(2)
Tc1	Cl13	2.3485(4)	N17	C33	1.328(2)
Tc1	Cl14	2.3503(4)	N17	C36	1.338(2)
Tc1	Cl15	2.3505(4)	N18	C34	1.337(2)

Tc1	Cl16	2.3641(4)	N18	C35	1.335(2)
Tc2	Cl21	2.3658(4)	N19	C37	1.329(2)
Tc2	Cl22	2.3564(4)	N19	C40	1.334(2)
Tc2	Cl23	2.3531(4)	N20	C38	1.330(2)
Tc2	Cl24	2.3448(4)	N20	C39	1.337(2)
Tc2	Cl25	2.3438(4)	N21	C41	1.327(2)
Tc2	Cl26	2.3647(4)	N21	C44	1.337(2)
N1	C1	1.330(2)	N22	C42	1.333(2)
N1	C4	1.336(2)	N22	C43	1.335(2)
N2	C2	1.336(2)	N23	C45	1.332(2)
N2	C3	1.342(2)	N23	C48	1.325(2)
N3	C5	1.332(2)	N24	C46	1.333(2)
N3	C8	1.333(2)	N24	C47	1.331(2)
N4	C6	1.337(2)	C1	C2	1.377(2)
N4	C7	1.338(2)	C3	C4	1.378(2)
N5	C9	1.328(2)	C5	C6	1.382(3)
N5	C12	1.332(2)	C7	C8	1.379(2)
N6	C10	1.331(2)	C9	C10	1.382(2)
N6	C11	1.333(2)	C11	C12	1.380(3)
N7	C13	1.332(2)	C13	C14	1.386(2)
N7	C16	1.325(2)	C15	C16	1.382(2)
N8	C14	1.331(2)	C17	C18	1.384(2)
N8	C15	1.333(2)	C19	C20	1.376(2)
N9	C17	1.333(2)	C21	C22	1.385(2)
N9	C20	1.339(2)	C23	C24	1.374(2)
N10	C18	1.331(2)	C25	C26	1.383(2)
N10	C19	1.340(2)	C27	C28	1.377(2)
N11	C21	1.328(2)	C29	C30	1.379(3)
N11	C24	1.330(2)	C31	C32	1.387(2)
N12	C22	1.334(2)	C33	C34	1.385(2)
N12	C23	1.339(2)	C35	C36	1.379(2)
N13	C25	1.326(2)	C37	C38	1.384(2)
N13	C28	1.332(2)	C39	C40	1.378(2)
N14	C26	1.328(2)	C41	C42	1.385(2)
N14	C27	1.340(2)	C43	C44	1.376(2)
N15	C29	1.326(2)	C45	C46	1.381(2)
N15	C32	1.324(2)	C47	C48	1.387(2)

Table S18. Bond Angles for **5.**

Atom	**Atom**	**Atom**	**Angle/°**		**Atom**	**Atom**	**Atom**	**Angle/°**
Cl12	Tc1	Cl11	90.398(14)		C42	N22	C43	117.07(14)
Cl12	Tc1	Cl16	88.765(13)		C48	N23	C45	121.83(15)
Cl13	Tc1	Cl11	88.847(13)		C47	N24	C46	117.44(14)

Cl13	Tc1	Cl12	90.669(14)		N1	C1	C2	118.57(15)
Cl13	Tc1	Cl14	89.450(14)		N2	C2	C1	122.61(15)
Cl13	Tc1	Cl15	177.378(14)		N2	C3	C4	122.52(15)
Cl13	Tc1	Cl16	91.388(13)		N1	C4	C3	118.35(15)
Cl14	Tc1	Cl11	92.050(14)		N3	C5	C6	118.21(16)
Cl14	Tc1	Cl12	177.551(14)		N4	C6	C5	122.65(16)
Cl14	Tc1	Cl15	89.875(14)		N4	C7	C8	122.13(15)
Cl14	Tc1	Cl16	88.786(13)		N3	C8	C7	118.78(15)
Cl15	Tc1	Cl11	88.646(13)		N5	C9	C10	118.16(16)
Cl15	Tc1	Cl12	90.115(14)		N6	C10	C9	122.60(16)
Cl15	Tc1	Cl16	91.130(13)		N6	C11	C12	122.70(17)
Cl16	Tc1	Cl11	179.134(15)		N5	C12	C11	118.04(16)
Cl22	Tc2	Cl21	91.080(14)		N7	C13	C14	117.83(15)
Cl22	Tc2	Cl26	89.472(14)		N8	C14	C13	122.43(15)
Cl23	Tc2	Cl21	88.706(14)		N8	C15	C16	122.46(16)
Cl23	Tc2	Cl22	89.985(14)		N7	C16	C15	118.17(15)
Cl23	Tc2	Cl26	91.153(14)		N9	C17	C18	118.08(14)
Cl24	Tc2	Cl21	90.643(14)		N10	C18	C17	122.52(15)
Cl24	Tc2	Cl22	178.270(14)		N10	C19	C20	122.28(15)
Cl24	Tc2	Cl23	90.212(14)		N9	C20	C19	118.33(15)
Cl24	Tc2	Cl26	88.806(14)		N11	C21	C22	118.19(15)
Cl25	Tc2	Cl21	88.798(14)		N12	C22	C21	122.37(16)
Cl25	Tc2	Cl22	89.599(14)		N12	C23	C24	122.66(16)
Cl25	Tc2	Cl23	177.462(14)		N11	C24	C23	118.26(15)
Cl25	Tc2	Cl24	90.279(14)		N13	C25	C26	118.30(15)
Cl25	Tc2	Cl26	91.346(14)		N14	C26	C25	122.15(16)
Cl26	Tc2	Cl21	179.431(15)		N14	C27	C28	122.13(16)
C1	N1	C4	121.26(15)		N13	C28	C27	118.17(15)
C2	N2	C3	116.68(15)		N15	C29	C30	118.24(18)
C5	N3	C8	121.26(15)		N16	C30	C29	122.47(18)
C6	N4	C7	116.96(15)		N16	C31	C32	122.28(17)
C9	N5	C12	121.61(15)		N15	C32	C31	118.21(17)
C10	N6	C11	116.88(16)		N17	C33	C34	118.12(15)
C16	N7	C13	121.94(15)		N18	C34	C33	122.41(15)
C14	N8	C15	117.16(15)		N18	C35	C36	122.58(16)
C17	N9	C20	121.51(14)		N17	C36	C35	118.07(16)
C18	N10	C19	117.28(14)		N19	C37	C38	117.91(16)
C21	N11	C24	121.65(14)		N20	C38	C37	122.39(16)
C22	N12	C23	116.79(14)		N20	C39	C40	122.36(16)
C25	N13	C28	121.79(14)		N19	C40	C39	117.96(16)
C26	N14	C27	117.46(14)		N21	C41	C42	118.26(15)
C32	N15	C29	121.68(16)		N22	C42	C41	122.40(15)
C31	N16	C30	117.13(16)		N22	C43	C44	122.51(15)

C33	N17	C36	121.74(15)		N21	C44	C43	118.32(15)
C35	N18	C34	117.07(14)		N23	C45	C46	118.19(16)
C37	N19	C40	122.02(15)		N24	C46	C45	122.19(16)
C38	N20	C39	117.37(15)		N24	C47	C48	122.22(16)
C41	N21	C44	121.43(14)		N23	C48	C47	118.11(15)

Table S19. Hydrogen Bonds for **5.**

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
O1W	H1A	Cl1	0.789(15)	2.297(17)	3.0572(14)	162(2)
O1W	H1B	Cl2	0.828(15)	2.461(17)	3.2502(14)	160(2)
O2W	H2A	Cl7	0.879(16)	2.350(16)	3.1927(17)	161(2)
O2W	H2B	Cl4	0.891(16)	2.287(16)	3.1593(16)	166(2)
O3W	H3A	Cl2	0.801(14)	2.344(16)	3.1135(13)	161(2)
O3W	H3B	Cl1	0.822(14)	2.469(16)	3.2528(14)	159.7(19)
N1	H1	O1W	0.88	1.80	2.6743(19)	170.1
N3	H3	O3W	0.88	1.83	2.6931(19)	164.9
N5	H5	Cl1	0.88	2.16	3.0196(15)	165.7
N7	H7	Cl2	0.88	2.17	3.0112(14)	159.4
N9	H9	Cl3	0.88	2.59	3.2138(13)	128.2
N9	H9	Cl4	0.88	2.43	3.1282(14)	137.1
N11	H11	Cl3	0.88	2.41	3.1009(14)	135.4
N11	H11	Cl4	0.88	2.68	3.3277(14)	131.7
N13	H13	Cl3	0.88	2.16	3.0100(14)	161.4
N15	H15	Cl5	0.88	2.12	2.9697(15)	162.1
N17	H17	Cl7	0.88	2.55	3.2463(15)	136.7
N17	H17	Cl8	0.88	2.54	3.1845(14)	130.5
N19	H19	Cl8	0.88	2.16	3.0182(14)	165.1
N21	H21	Cl7	0.88	2.41	3.1217(14)	137.8
N21	H21	Cl8	0.88	2.66	3.2794(14)	128.5
N23	H23	Cl6	0.88	2.18	2.9922(14)	153.9

Table S20. Torsion Angles for **5.**

A	B	C	D	Angle/°		A	B	C	D	Angle/°
N1	C1	C2	N2	0.7(3)		C13	N7	C16	C15	-0.3(2)
N2	C3	C4	N1	0.1(2)		C14	N8	C15	C16	0.3(2)
N3	C5	C6	N4	-0.5(3)		C15	N8	C14	C13	0.3(2)
N4	C7	C8	N3	-0.9(3)		C16	N7	C13	C14	0.8(2)
N5	C9	C10	N6	-0.6(3)		C17	N9	C20	C19	-1.0(2)
N6	C11	C12	N5	-0.1(3)		C18	N10	C19	C20	-0.4(2)
N7	C13	C14	N8	-0.8(2)		C19	N10	C18	C17	0.0(2)
N8	C15	C16	N7	-0.3(2)		C20	N9	C17	C18	0.5(2)
N9	C17	C18	N10	0.0(2)		C21	N11	C24	C23	2.5(2)
N10	C19	C20	N9	0.9(2)		C22	N12	C23	C24	-1.8(2)
N11	C21	C22	N12	0.5(3)		C23	N12	C22	C21	1.6(2)

N12	C23	C24	N11	-0.2(3)		C24	N11	C21	C22	-2.7(2)
N13	C25	C26	N14	0.2(2)		C25	N13	C28	C27	-0.8(2)
N14	C27	C28	N13	0.1(2)		C26	N14	C27	C28	0.7(2)
N15	C29	C30	N16	0.1(3)		C27	N14	C26	C25	-0.9(2)
N16	C31	C32	N15	0.6(3)		C28	N13	C25	C26	0.6(2)
N17	C33	C34	N18	0.5(3)		C29	N15	C32	C31	-0.8(2)
N18	C35	C36	N17	0.1(3)		C30	N16	C31	C32	-0.1(3)
N19	C37	C38	N20	0.0(2)		C31	N16	C30	C29	-0.3(3)
N20	C39	C40	N19	0.5(3)		C32	N15	C29	C30	0.5(3)
N21	C41	C42	N22	0.6(2)		C33	N17	C36	C35	1.2(2)
N22	C43	C44	N21	1.2(3)		C34	N18	C35	C36	-1.0(2)
N23	C45	C46	N24	0.8(3)		C35	N18	C34	C33	0.7(2)
N24	C47	C48	N23	-0.6(2)		C36	N17	C33	C34	-1.5(2)
C1	N1	C4	C3	0.1(2)		C37	N19	C40	C39	-1.0(2)
C2	N2	C3	C4	0.2(2)		C38	N20	C39	C40	0.2(3)
C3	N2	C2	C1	-0.6(2)		C39	N20	C38	C37	-0.4(2)
C4	N1	C1	C2	-0.5(2)		C40	N19	C37	C38	0.7(2)
C5	N3	C8	C7	0.6(2)		C41	N21	C44	C43	-1.1(2)
C6	N4	C7	C8	0.4(3)		C42	N22	C43	C44	-0.4(2)
C7	N4	C6	C5	0.2(3)		C43	N22	C42	C41	-0.6(2)
C8	N3	C5	C6	0.0(2)		C44	N21	C41	C42	0.3(2)
C9	N5	C12	C11	-0.7(2)		C45	N23	C48	C47	0.3(2)
C10	N6	C11	C12	0.6(3)		C46	N24	C47	C48	1.0(2)
C11	N6	C10	C9	-0.2(3)		C47	N24	C46	C45	-1.0(2)
C12	N5	C9	C10	1.0(2)		C48	N23	C45	C46	-0.4(2)

Table S21. Bond Lengths for **6.**

Atom	Atom	Length/Å		Atom	Atom	Length/Å
Tc1	Br3[1]	2.4932(6)		N1	C2	1.339(7)
Tc1	Br3	2.4933(6)		N2	C7	1.327(8)
Tc1	Br1[1]	2.5258(7)		C4	C3	1.385(8)
Tc1	Br1	2.5258(7)		C4	C5	1.375(8)
Tc1	Br2	2.5103(7)		C3	C7	1.498(8)
Tc1	Br2[1]	2.5103(7)		C3	C2	1.376(8)
O1	C7	1.239(7)		C5	C6	1.377(9)
N1	C6	1.328(8)				

[1]1-X,1-Y,1-Z

Table S22. Bond Angles for **6.**

Atom	Atom	Atom	Angle/°		Atom	Atom	Atom	Angle/°
Br3[1]	Tc1	Br3	180.0		Br2[1]	Tc1	Br1	90.12(2)
Br3	Tc1	Br1[1]	89.536(19)		Br2[1]	Tc1	Br2	180.00(3)

Br3[1]	Tc1	Br1	89.536(19)		C6	N1	C2	123.4(6)
Br3[1]	Tc1	Br1[1]	90.465(19)		C5	C4	C3	120.0(6)
Br3	Tc1	Br1	90.464(19)		C4	C3	C7	120.5(5)
Br3[1]	Tc1	Br2[1]	90.56(2)		C2	C3	C4	118.9(5)
Br3	Tc1	Br2	90.56(2)		C2	C3	C7	120.3(6)
Br3	Tc1	Br2[1]	89.44(2)		C4	C5	C6	119.3(6)
Br3[1]	Tc1	Br2	89.44(2)		O1	C7	N2	124.5(6)
Br1	Tc1	Br1[1]	180.0		O1	C7	C3	118.2(6)
Br2	Tc1	Br1[1]	90.12(2)		N2	C7	C3	117.3(6)
Br2[1]	Tc1	Br1[1]	89.88(2)		N1	C6	C5	119.2(6)
Br2	Tc1	Br1	89.88(2)		N1	C2	C3	119.2(6)

[1]1-X,1-Y,1-Z

Table S23. Hydrogen Bonds for **6.**

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
N1	H1	O1[1]	0.83(4)	1.85(4)	2.671(7)	173(7)
C4	H4	O1[2]	0.95	2.61	3.225(7)	123.2

[1]-1/2+X,3/2-Y,-1/2+Z; [2]2-X,2-Y,1-Z

Table S24. Torsion Angles for **6.**

A	B	C	D	Angle/°		A	B	C	D	Angle/°
C4	C3	C7	O1	23.5(9)		C5	C4	C3	C2	-2.6(9)
C4	C3	C7	N2	-154.5(6)		C7	C3	C2	N1	174.7(5)
C4	C3	C2	N1	1.6(9)		C6	N1	C2	C3	-0.5(9)
C4	C5	C6	N1	-1.4(9)		C2	N1	C6	C5	0.4(9)
C3	C4	C5	C6	2.5(10)		C2	C3	C7	O1	-149.5(6)
C5	C4	C3	C7	-175.8(6)		C2	C3	C7	N2	32.5(9)

Table S25. Bond Lengths for **7.**

Atom	Atom	Length/Å		Atom	Atom	Length/Å
Tc1	Br1	2.5073(2)		Tc1	Br3	2.5145(2)
Tc1	Br1[1]	2.5073(2)		N1	C1	1.500(3)
Tc1	Br2	2.5149(2)		N1	C3	1.495(3)
Tc1	Br2[1]	2.5149(2)		C1	C2	1.519(3)
Tc1	Br3[1]	2.5145(2)		C3	C4	1.515(3)

[1]1-X,1-Y,1-Z

Table S26. Bond Angles for **7.**

Atom	Atom	Atom	Angle/°		Atom	Atom	Atom	Angle/°
Br1	Tc1	Br1[1]	180.0		Br2[1]	Tc1	Br2	180.0

Br1[1]	Tc1	Br2	90.988(8)		Br3[1]	Tc1	Br2[1]	90.400(8)
Br1	Tc1	Br2	89.012(8)		Br3	Tc1	Br2	90.400(8)
Br1[1]	Tc1	Br2[1]	89.012(8)		Br3	Tc1	Br2[1]	89.600(8)
Br1	Tc1	Br2[1]	90.988(8)		Br3[1]	Tc1	Br2	89.600(8)
Br1	Tc1	Br3	90.211(8)		Br3	Tc1	Br3[1]	180.0
Br1[1]	Tc1	Br3	89.789(8)		C3	N1	C1	115.17(18)
Br1[1]	Tc1	Br3[1]	90.211(8)		N1	C1	C2	109.6(2)
Br1	Tc1	Br3[1]	89.789(9)		N1	C3	C4	110.5(2)

[1]1-X,1-Y,1-Z

Table S27. Hydrogen Bonds for **7.**

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
N1	H1A	Br3[1]	0.92(3)	2.62(3)	3.491(2)	157(2)
N1	H1B	Br1	0.84(3)	2.65(3)	3.407(2)	150(2)
N1	H1B	Br2[2]	0.84(3)	2.82(3)	3.413(2)	129(2)
C1	H1D	Br2[1]	0.99	3.07	3.740(2)	126.3
C4	H4B	Br1[1]	0.98	3.07	3.766(3)	128.8

[1]3/2-X,1/2+Y,3/2-Z; [2]1-X,1-Y,1-Z

Table S28. Torsion Angles for **7.**

A	B	C	D	Angle/°		A	B	C	D	Angle/°
C1	N1	C3	C4	-174.4(2)		C3	N1	C1	C2	176.71(19)

Table S29. Bond Lengths for **8.**

Atom	Atom	Length/Å		Atom	Atom	Length/Å
Tc1	Cl1[1]	2.3586(4)		Tc1	Cl3[1]	2.3562(4)
Tc1	Cl1	2.3586(4)		N1	C3	1.497(2)
Tc1	Cl2	2.3499(4)		N1	C1	1.499(2)
Tc1	Cl2[1]	2.3499(4)		C3	C4	1.507(3)
Tc1	Cl3	2.3562(4)		C1	C2	1.509(2)

[1]1-X,1-Y,1-Z

Table S30. Bond Angles for **8.**

Atom	Atom	Atom	Angle/°		Atom	Atom	Atom	Angle/°
Cl1	Tc1	Cl1[1]	180.0		Cl2[1]	Tc1	Cl3	89.907(17)
Cl2	Tc1	Cl1	90.164(16)		Cl3[1]	Tc1	Cl1	89.987(15)
Cl2[1]	Tc1	Cl1	89.836(15)		Cl3	Tc1	Cl1[1]	89.986(16)
Cl2[1]	Tc1	Cl1[1]	90.163(15)		Cl3	Tc1	Cl1	90.013(15)
Cl2	Tc1	Cl1[1]	89.837(15)		Cl3[1]	Tc1	Cl1[1]	90.014(16)
Cl2	Tc1	Cl2[1]	180.0		Cl3[1]	Tc1	Cl3	180.0

Cl2	Tc1	Cl3[1]	89.907(17)		C3	N1	C1	114.35(14)
Cl2	Tc1	Cl3	90.093(17)		N1	C3	C4	110.05(16)
Cl2[1]	Tc1	Cl3[1]	90.093(17)		N1	C1	C2	109.55(15)

[1]1-X,1-Y,1-Z

Table S31. Hydrogen Bonds for **8.**

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
N1	H1A	Cl3[1]	0.89(2)	2.48(2)	3.3353(16)	160.8(17)
N1	H1B	Cl1	0.93(2)	2.66(2)	3.3179(16)	128.9(16)
N1	H1B	Cl2	0.93(2)	2.48(2)	3.3172(15)	150.0(17)

[1]1/2+X,3/2-Y,1/2+Z

Table S32. Torsion Angles for **8.**

A	B	C	D	Angle/°		A	B	C	D	Angle/°
C3	N1	C1	C2	177.82(15)		C1	N1	C3	C4	-178.26(15)

Table S33. Parameters of π-stacking interactions.

Structure	Rings		Angle	Centroid-centroid distance	Shift distance
2	C4N3C2N1C6C5	C4N3C2N1C6C5 (symmetry code: 1-X,1-Y,2-Z)	0.000	3.677	1.550
3	C14C19C18C17C16C15	C4C5C6C7C8C9 (symmetry code: 2-X,1-Y,1-Z)	6.601	3.650	0.976
		C2S3C4C9N1 (symmetry code: 1-X,1-Y,1-Z)	6.337	3.660	1.619
		C2S3C4C9N1 (symmetry code: 2-X,1-Y,1-Z)	6.337	3.640	1.366
	C12S13C14C19N11	C4C5C6C7C8C9 (symmetry code: 2-X,1-Y,1-Z)	9.055	3.857	1.516
4	C9C8C7C6C5C4	C9C8C7C6C5C4 (symmetry code: 1-	0.000	3.587	1.073

		X,-Y,-Z)			
		C2S1C9C4N3 (symmetry code: -X,-Y,-Z)	0.515	3.754	1.303
		C2S1C9C4N3 (symmetry code: 1-X,-Y,-Z)	0.515	3.709	1.443

Table S34. Distances and angles of anion-π interactions.

Structure	Hal	C_z (centroid of ring)	Distance Hal···C_z, Å	Angle α between the ring plane and the Cz···Hal vector, °
1	Br4	N1C2N3C4C5C6	3.82	68.2
	Br6	N21C22N23C24C25C26	3.41	73.5
		C4C5N7C8C9	3.31	84.7
2	Cl2	N1C2N3C4C5C6 (symmetry code: 1-X,1-Y,1-Z)	3.63	62.6
	Cl1	C4C5N7C8N9 (symmetry code: 1-X,1-Y,1-Z)	3.46	81.4
5	Cl16	N15C29C30N16C31C32 (symmetry code: X,3/2-Y,-1/2+Z	3.34	80.7
		N14C27C28N13C25C26	3.28	84.0
	Cl11	N23C45C46N24C47C48 (symmetry code: X,1+Y,Z	3.51	83.55
	Cl21	N15C29C30N16C31C32	3.49	84.87
		N14C27C28N13C25C26 (symmetry code: X,1/2-Y,1/2+Z)	3.76	71.3
	Cl26	N19C37C38N20C39C40 (symmetry code: X,1/2-Y,-1/2+Z)	3.54	77.4
6	Br3	N1C2C3C4C5C6 (symmetry code: 3/2-X,-1/2+Y,1/2-Z	3.65	70.3
	Br1	N1C2C3C4C5C6 (symmetry code: 1-X,1-Y,1-Z)	3.83	72.0

Table S35. Presence of $TcHal_6$ structures in ICSD.

	TcF_6	$TcCl_6$	$TcBr_6$	TcI_6
Na	+			
NH_4	+	+		
K	+	+		+
Rb	+			
Cs	+			
H_3O			+	+

3. Solubility of some $Tc(Hal)_6^{2-}$ compounds

Table S36. Technetium concentrations in saturated solutions of hexahalide compounds.

Solvent[T°]	Concentration of technetium in solution, mg/L*					
	3	**4**	K_2TcCl_6	K_2TcBr_6	**7**	**13**
Acrylonitrile[6]					490	
n-propanol[23]	<10	<10				20
n-heptanol[23]	<10	<10				<10
n-Octanol[23]	<10	<10				<10
Decanol[23]	<10	<10				<10
CH_2Cl_2[6]			<10	140		<10
CH_2Cl_2[-28]			<10	30		
H_2O[23]	5640***	40	91020***	58270***		
H_2O[6]	110		28236***	57950***		
CCl_4[23]		<10			70	<10
CCl_4[6]		<10				
$CHCl_3$[23]					480	
$CHCl_3$[6]					350	<10
MeOH[23]	2830**	2150**	180	920		80
MeOH[6]	240	200	40	300		
MeOH[-28]			40	300		
CH3COOH[23]						20

TGF[23]						<10
Acrylonitrile[23]						620**

* Measurement error 5%;

** The substance reacts slowly with the solvent;

*** Hydrolytic processes take place.

4. Thermal analysis

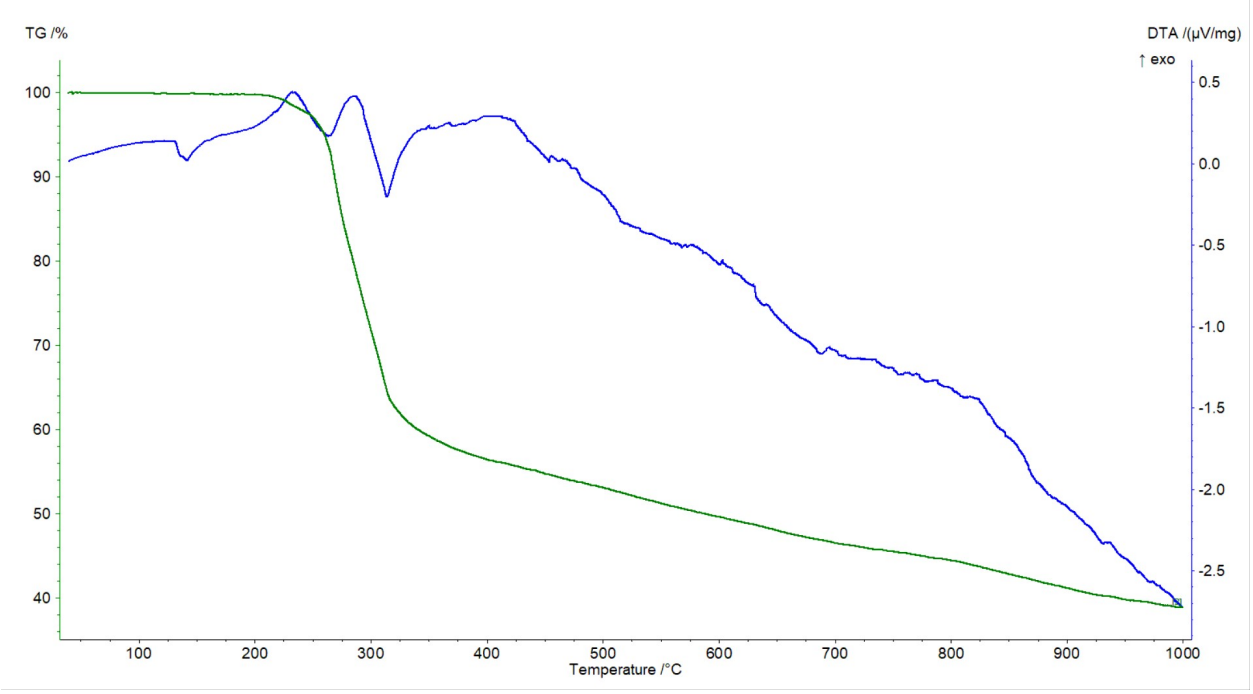


Figure S1. TG and DTA curves of compound **7**

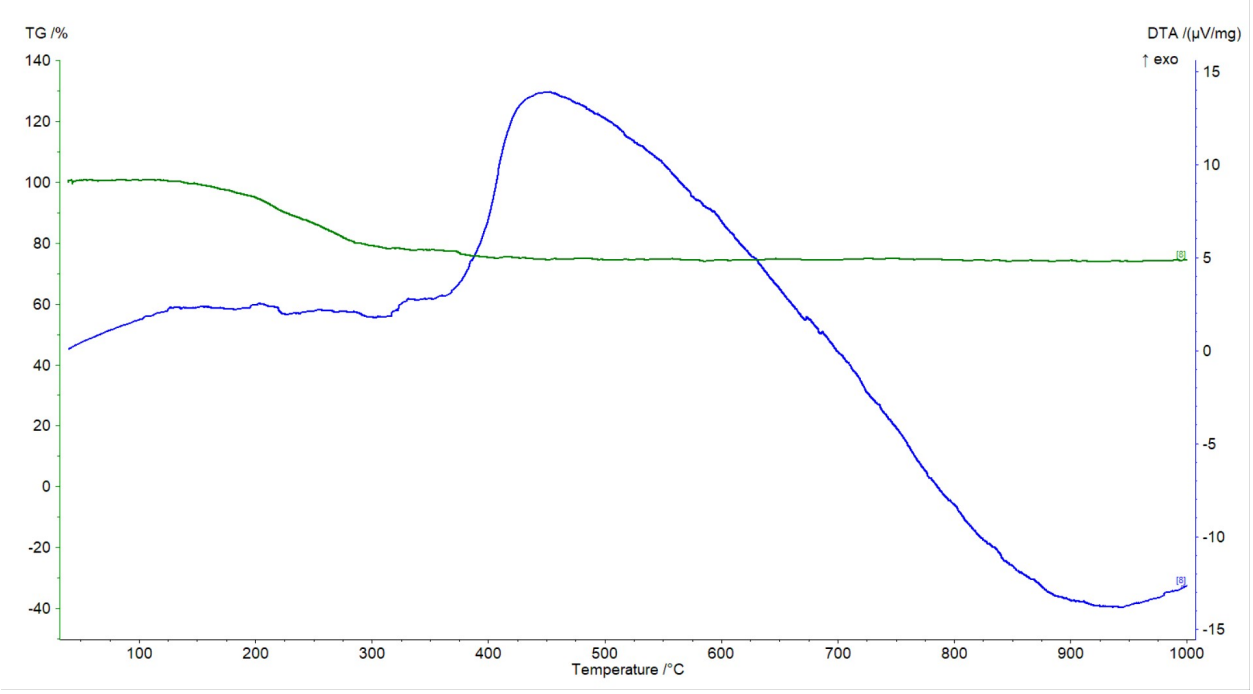


Figure S2. TG and DTA curves of compound **2**

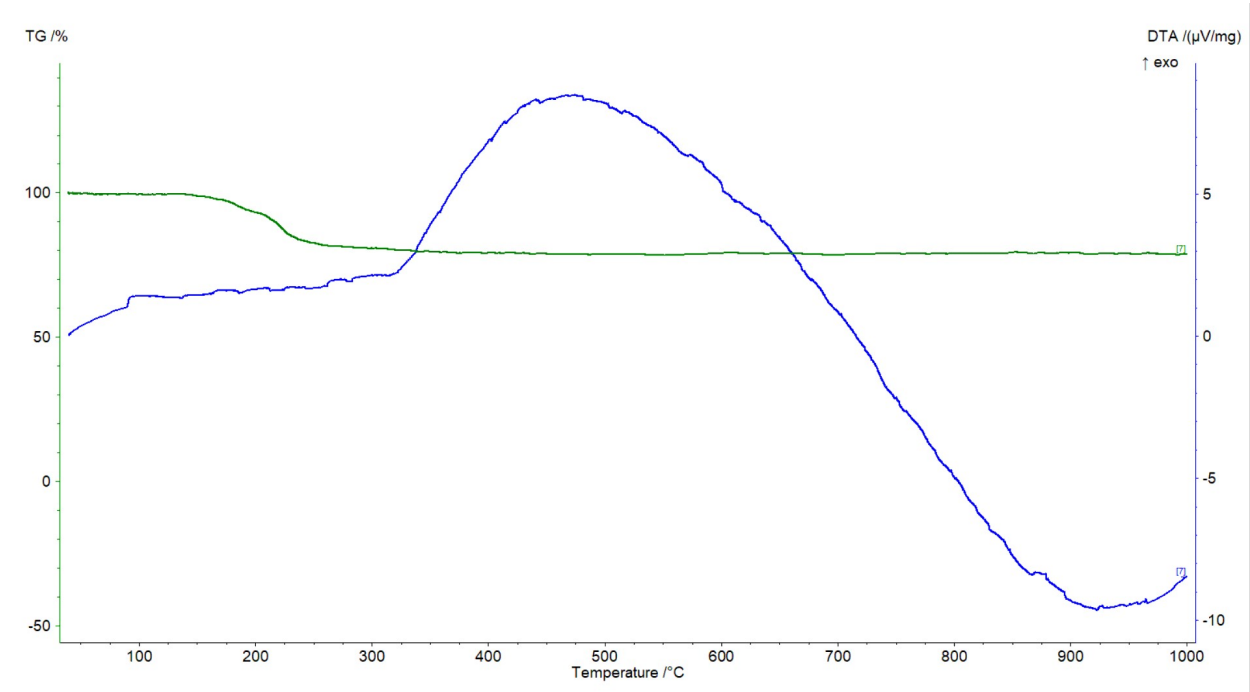


Figure S3. TG and DTA curves of compound **1**

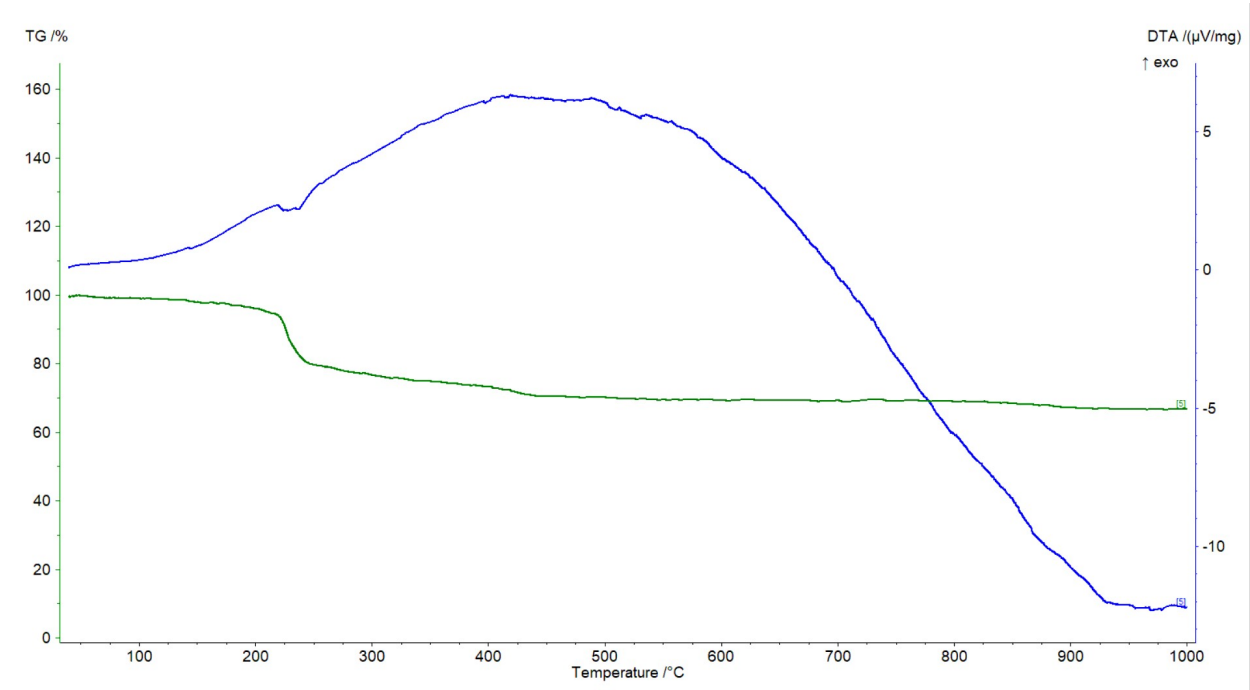


Figure S4. TG and DTA curves of compound **9**

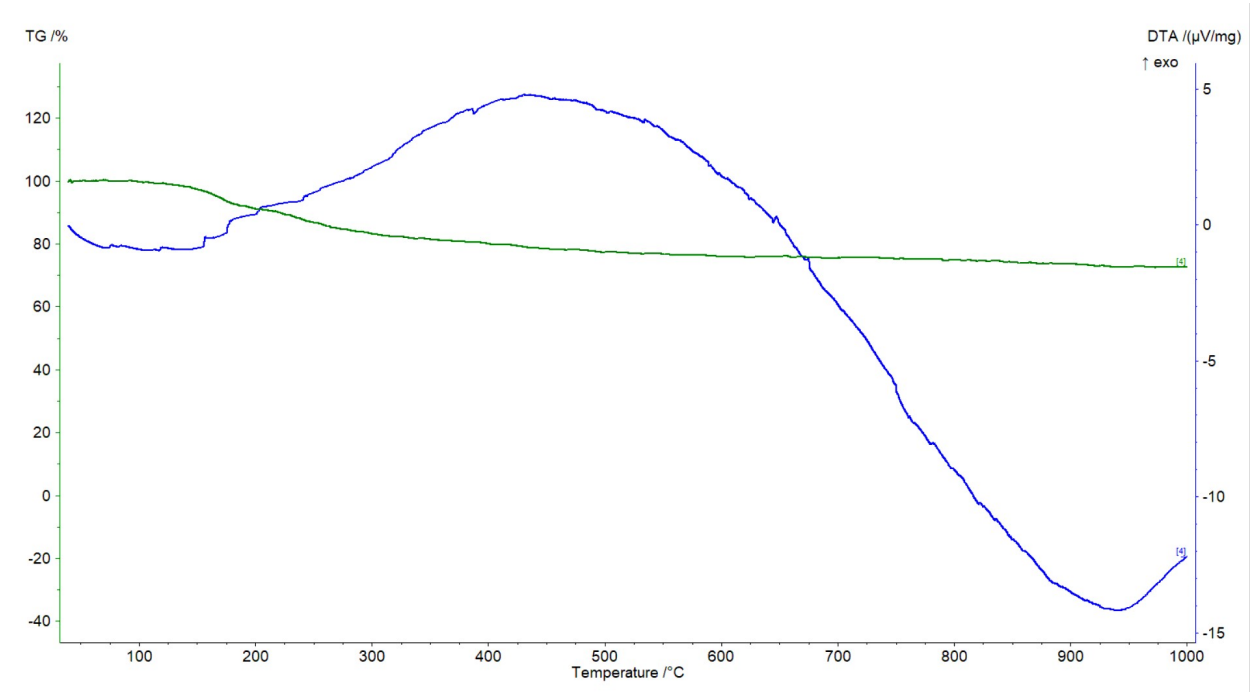


Figure S5. TG and DTA curves of compound **10**

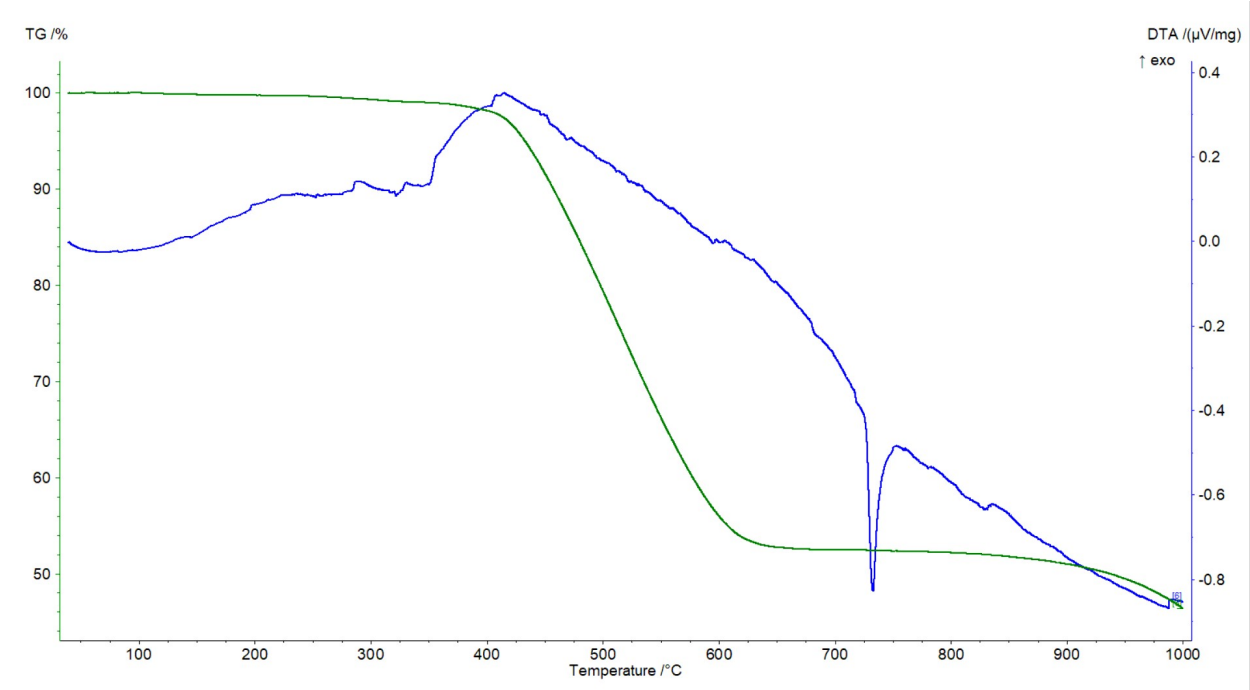


Figure S6. TG and DTA curves of K_2TcBr_6

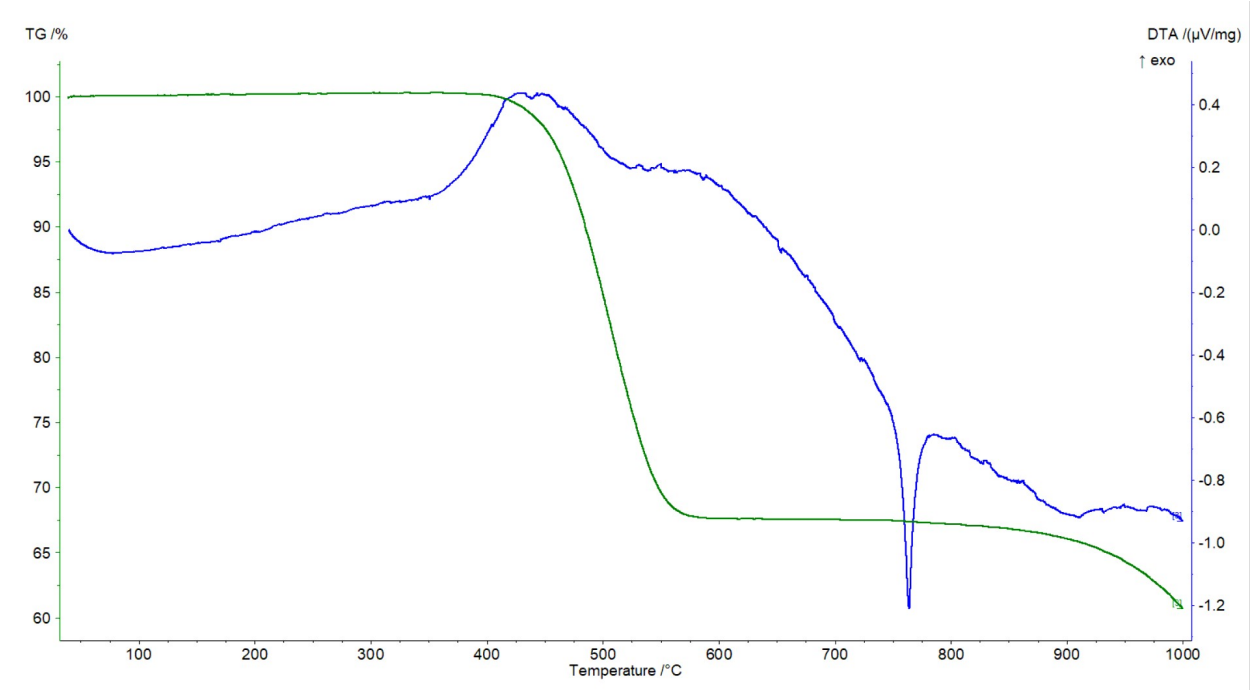


Figure S7. TG and DTA curves of K_2TcCl_6

5. X-ray phase analysis of thermolysis products and some initial substances

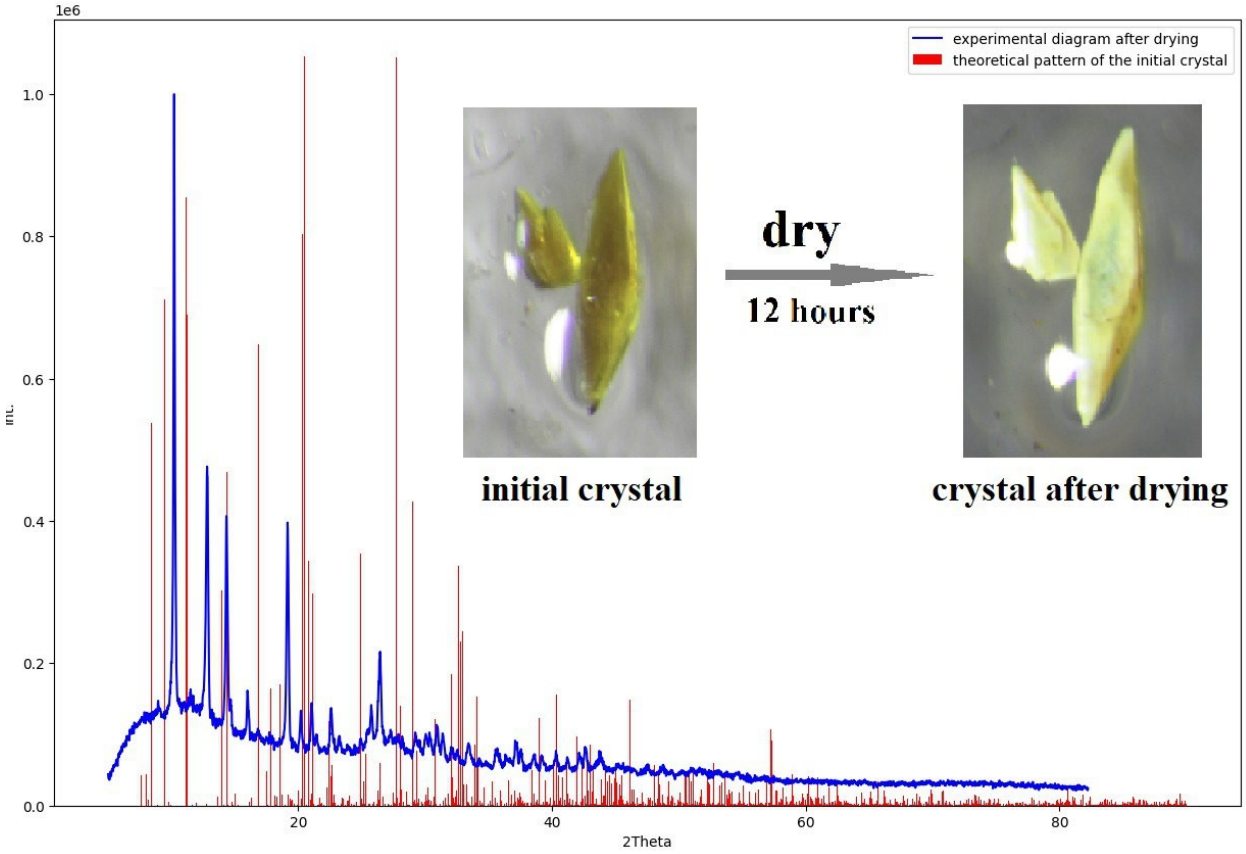


Figure S8. pXRD of dried compound **5** compared to the theoretical profile calculated from the structure of compound **5**

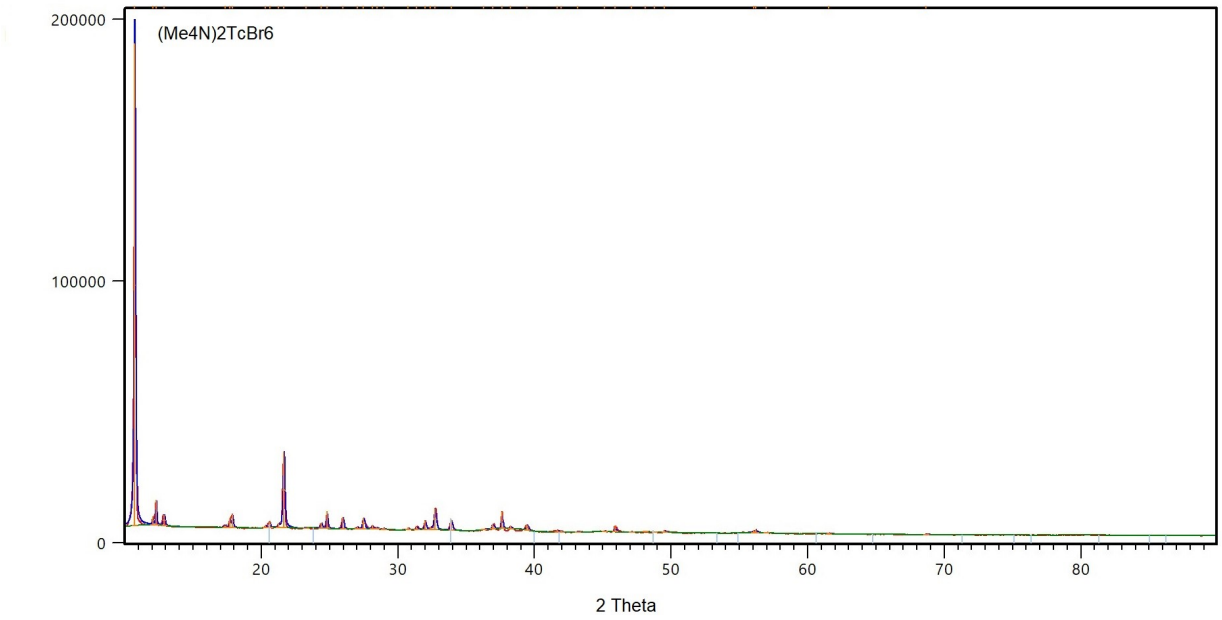


Figure S9. pXRD compound **13**

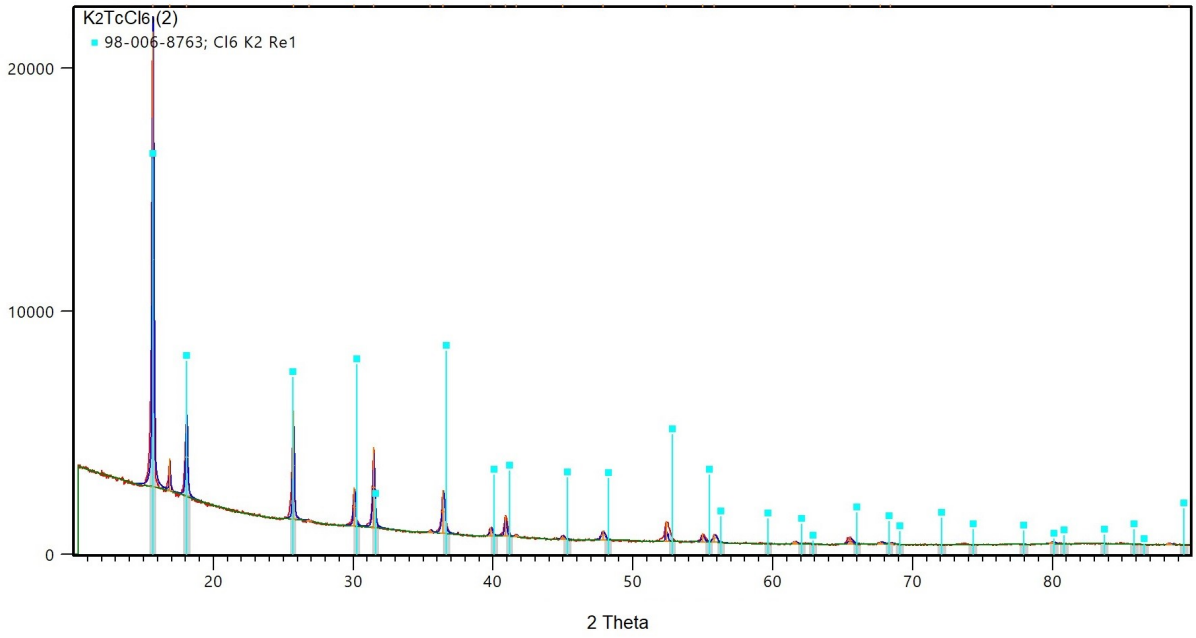


Figure S10. pXRD K_2TcCl_6 with comparing to K_2ReCl_6

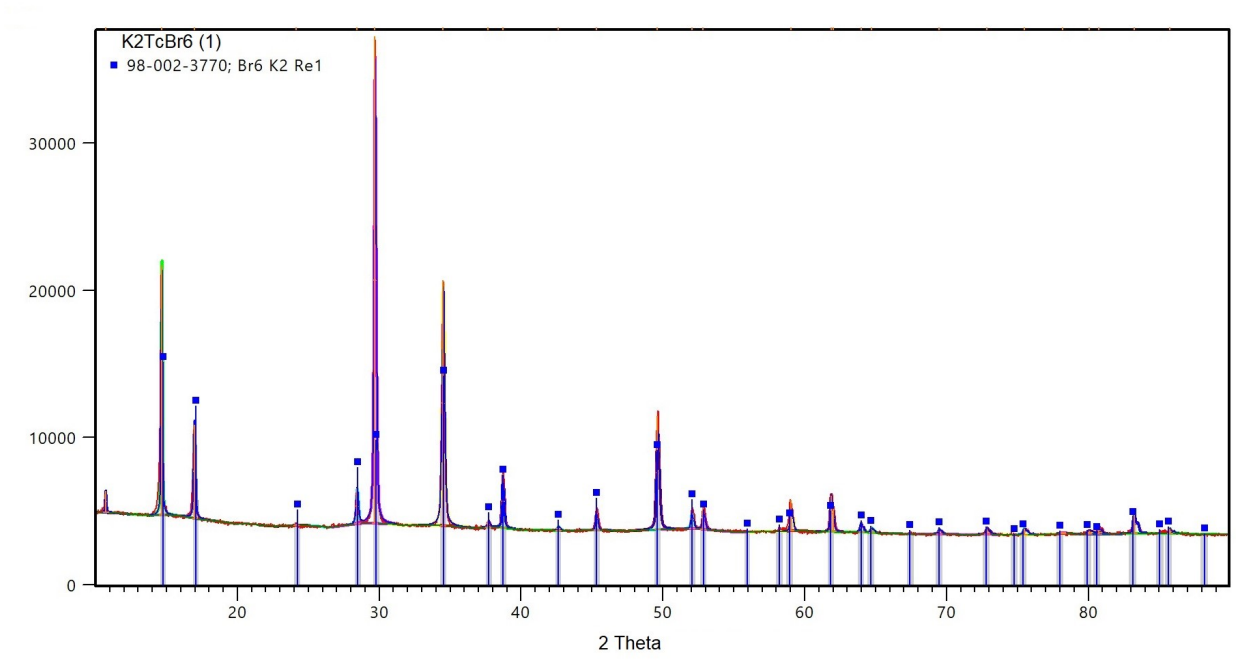


Figure S11. pXRD K_2TcBr_6 with comparing to K_2ReBr_6

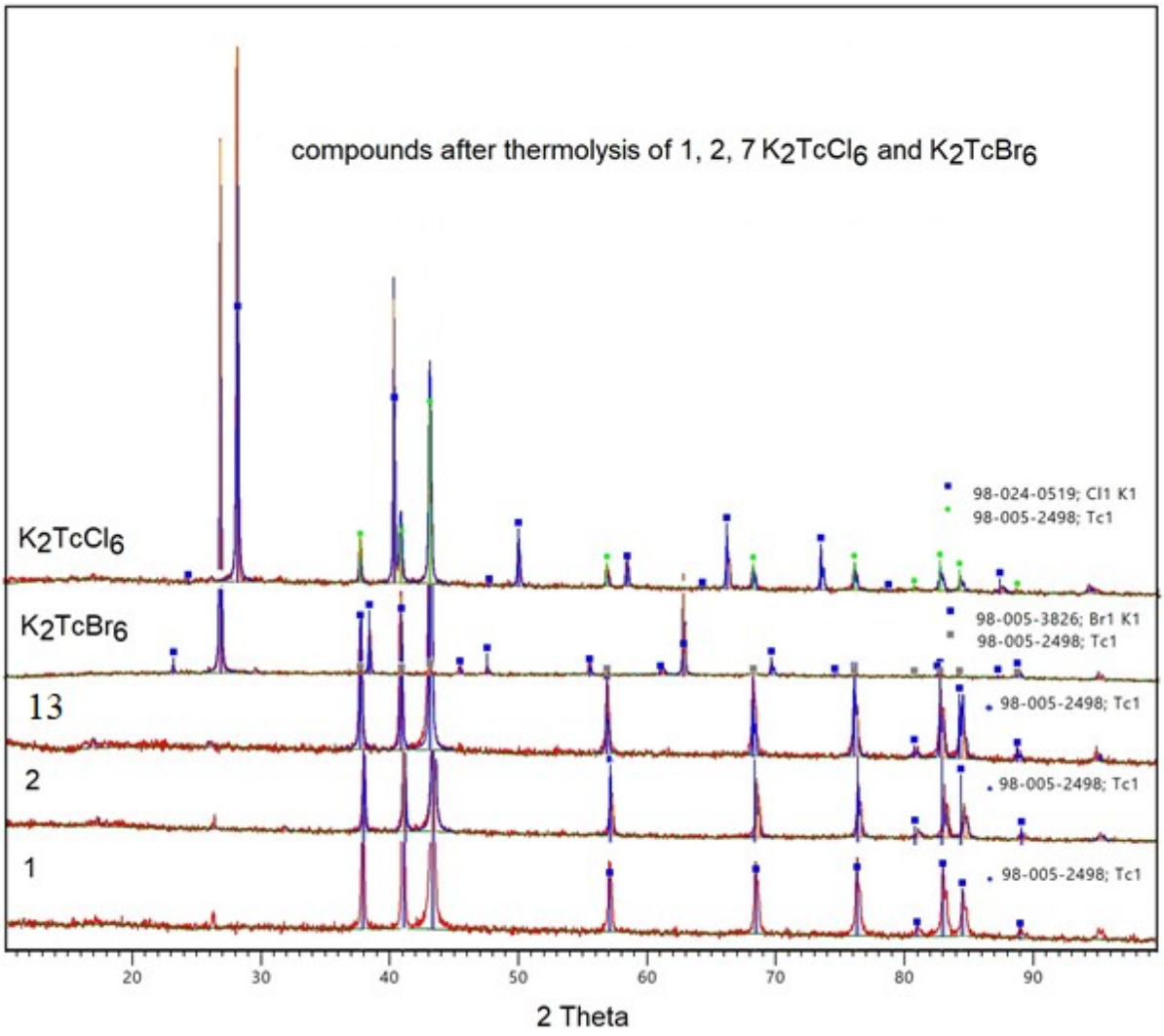


Figure S12. PXRD of **1**, **2**, **13**, K_2TcCl_6 and K_2TcBr_6 thermolysis products

6. Hirshfeld surface analysis

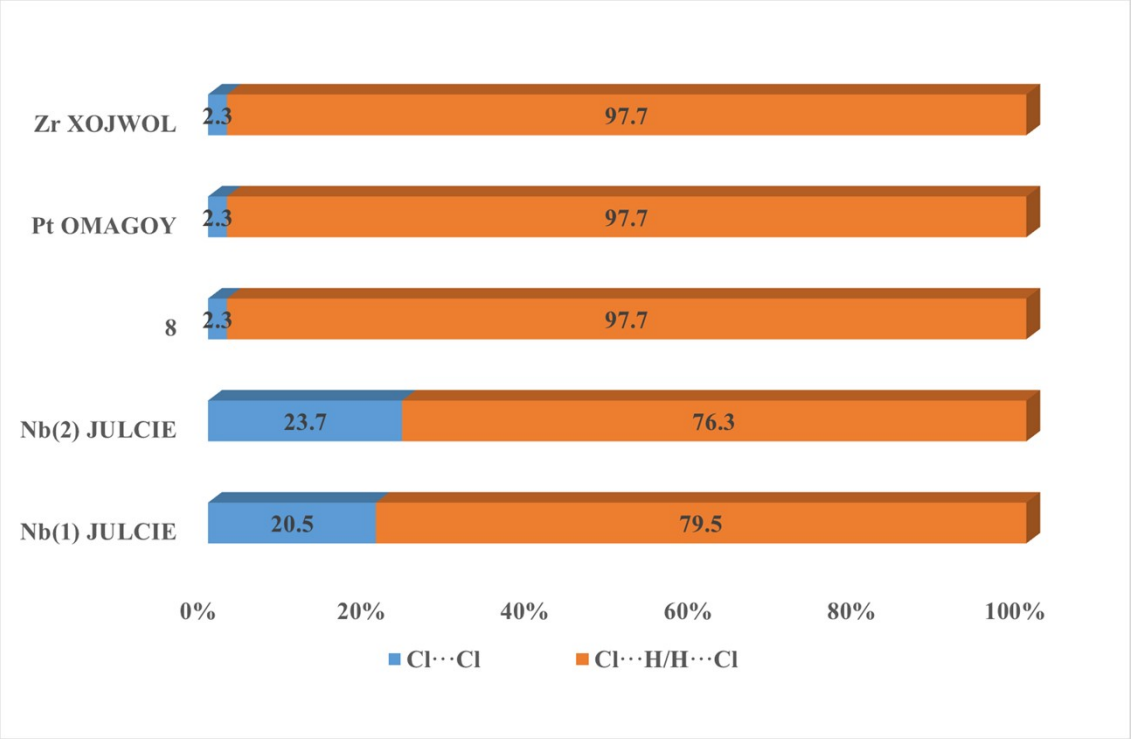


Figure S13. Percentage contribution of each type of non-valent interactions to the Hirshfeld surface in anions of similar octahedral structure with a transition metal ($TRCl_6^{2-}$) and a diethylammonium (DEA) cation.

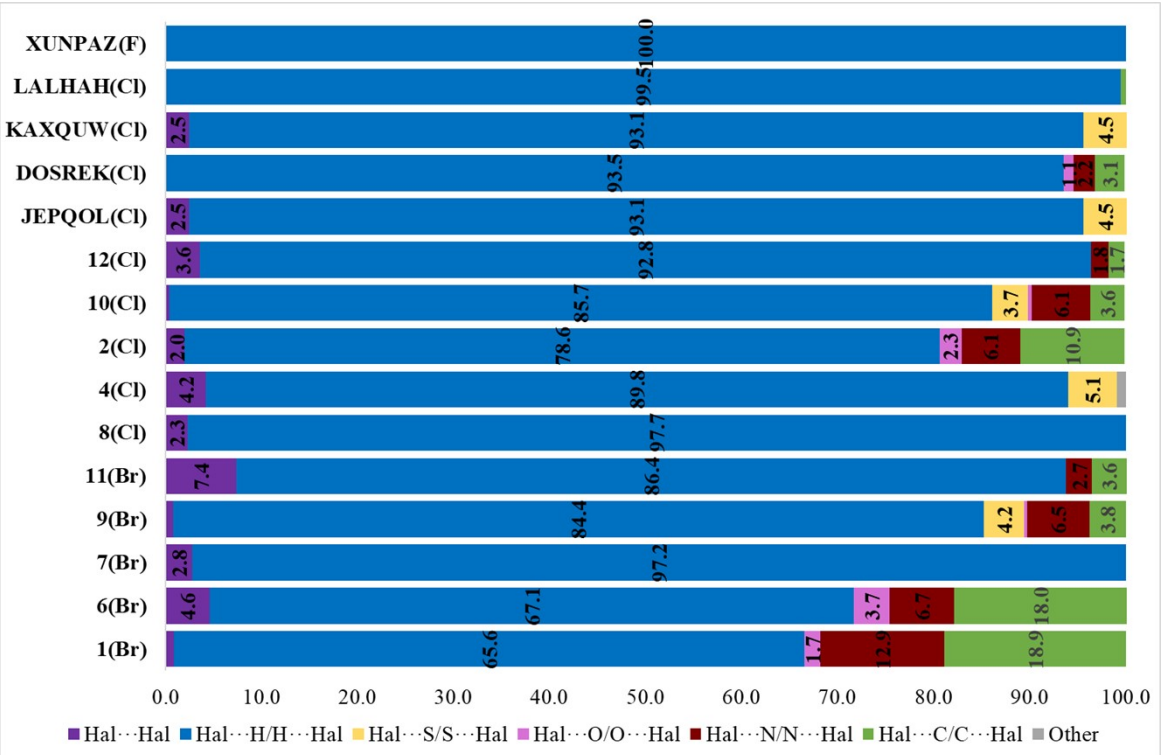
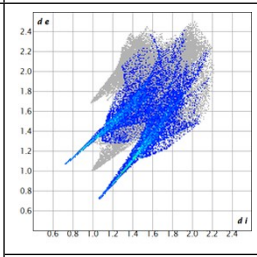
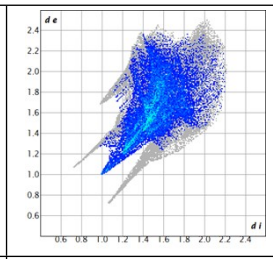
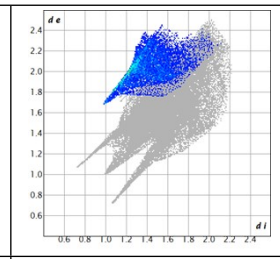
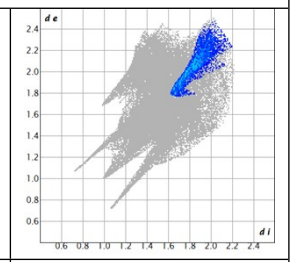
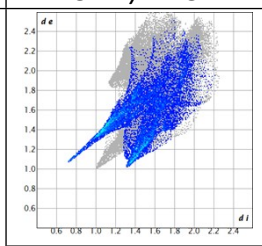
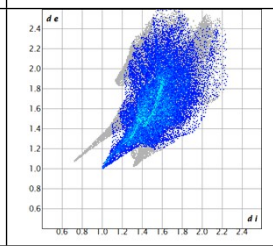
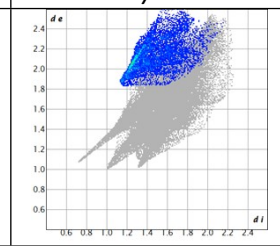
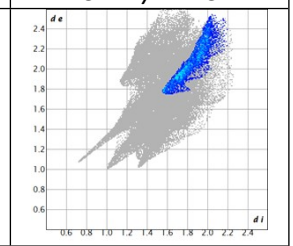
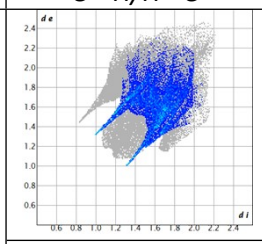
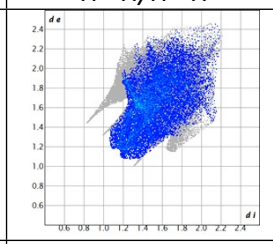
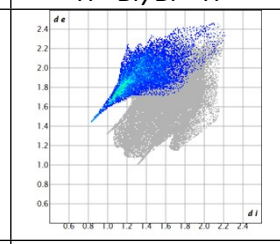
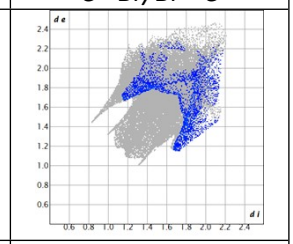
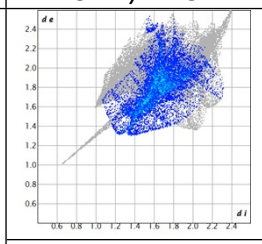
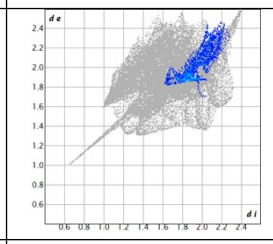
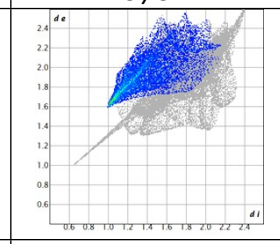
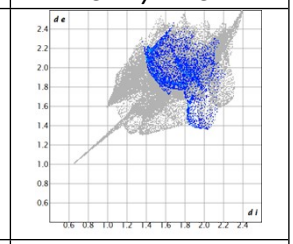
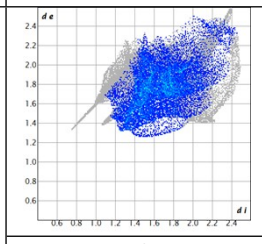
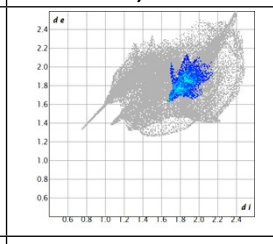
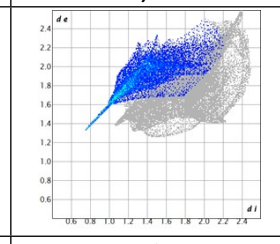
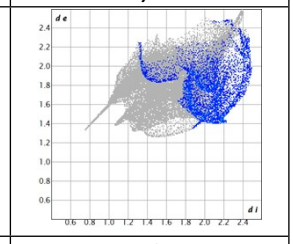
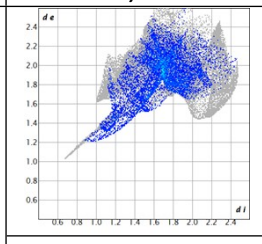
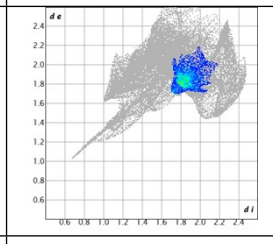
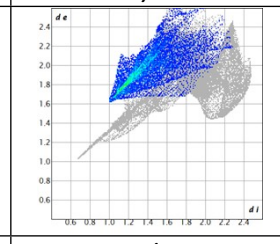
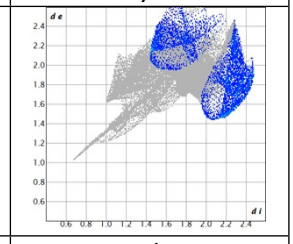
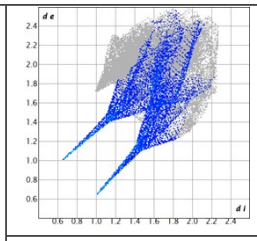
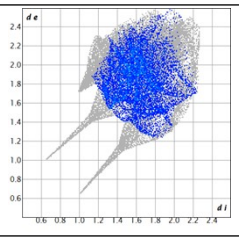
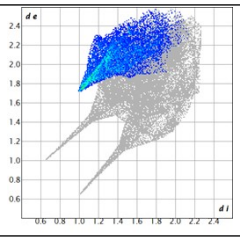
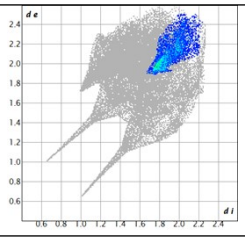
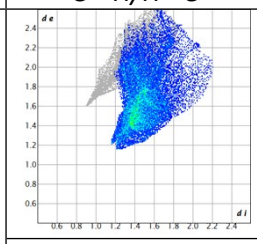
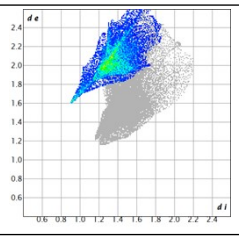


Figure S14. Percentage contribution of each type of non-valent interactions to the Hirshfeld surface in $TcHal_6^{2-}$ anions, described for the first time in this work and found in the CSD.

Table S37. Two-dimensional fingerprint plots for cations of **1**- **7**.

Structure	Interactions			
1 (Cat. 1)				
	O···H/H···O	*H···H*	*H···Br/Br···H*	*C···Br/Br···C*
1 (Cat .2)				
	O···H/H···O	*H···H/H···H*	*H···Br/Br···H*	*C···Br/Br···C*
2				
	O···H/H···O	*H···H*	*H···Cl/Cl···H*	*C···H/H···C*
3 (Cat. 1)				
	H···H	*C···S/S···C*	*H···Cl/Cl···H*	*C···H/H···C*
3 (Cat. 2)				
	H···H/H···H	*C···C*	*H···Cl/Cl···H*	*C···H/H···C*
4				
	H···H	*C···C*	*H···Cl/Cl···H*	*H···S/S···H*

6				
	O···H/H···O	*H···H*	*H···Br/Br···H*	*C···Br/Br···C*
7				
	H···H	*H···Br/Br···H*		

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