Electronic supplementary materials for the paper

The influence of the alkoxy substituent length on the crystal structures of Tc(V) complexes with pyrazine

Anton P. Novikov,* Mikhail A. Volkov

Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences, 31 Bldg 4, Leninsky prosp., Moscow, 119071, Russian Federation

* Correspondence: tony.novickoff@yandex.ru

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XRD part

Table S1. Crystal data and structure refinement for **1-10.**

Identification code	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
CCDC number	**2302025**	**2302026**	**2302027**	**2302028**	**2302029**	**2302030**	**2302031**	**2302032**	**2302033**	**2302034**
Chemical formula	**$Tc(V)OCl_2(Pyrz)_2OMe$**	**$Tc(V)OCl_2(Pyrz)_2OEt$**	**$Tc(V)OCl_2(Pyrz)_2On\text{-}Pr$**	**$Tc(V)OCl_2(Pyrz)_2On\text{-}Bu$**	**$Tc(V)OCl_2(Pyrz)_2OPent$**	**$Tc(V)OCl_2(Pyrz)_2OHex$**	**$Tc(V)OCl_2(Pyrz)_2OHept$**	**$Tc(V)OCl_2(Pyrz)_2OOct$**	**$Tc(V)OCl_2(Pyrz)_2ONon$**	**$Tc(V)OCl_2(Pyrz)_2ODec$**
Empirical formula	$C_9H_{11}Cl_2N_4O_2Tc$	$C_{10}H_{13}Cl_2N_4O_2Tc$	$C_{22}H_{30}Cl_4N_8O_4Tc_2$	$C_{24}H_{34}Cl_4N_8O_4Tc_2$	$C_{13}H_{19}Cl_2N_4O_2Tc$	$C_{14}H_{21}Cl_2N_4O_2Tc$	$C_{15}H_{23}Cl_2N_4O_2Tc$	$C_{16}H_{25}Cl_2N_4O_2Tc$	$C_{34}H_{54}Cl_4N_8O_4Tc_2$	$C_{18}H_{29}Cl_2N_4O_2Tc$
Formula weight	376.12	390.14	808.34	836.39	432.22	446.25	460.27	474.30	976.65	502.35
Crystal system	monoclinic	monoclinic	monoclinic	triclinic	monoclinic	triclinic	monoclinic	triclinic	triclinic	triclinic
Space group	$P2_1/c$	$P2_1/n$	$P2_1/n$	P-1	$P2_1/n$	P-1	$P2_1/c$	P-1	P-1	P-1
a/Å	7.0073(8)	11.6629(6)	8.0605(6)	9.0647(11)	14.0797(10)	9.0399(5)	14.089(2)	6.8651(6)	9.612(4)	6.8766(4)
b/Å	11.8847(12)	9.0674(5)	33.630(3)	12.8136(15)	8.8218(6)	14.1450(8)	9.1069(15)	7.6286(7)	10.482(4)	7.6359(5)
c/Å	15.9967(17)	14.0443(7)	12.0796(9)	14.4134(17)	14.5189(9)	14.9860(8)	16.009(3)	19.7846(18)	21.517(8)	21.6350(13)
α/°	90	90	90	74.521(5)	90	69.993(2)	90	86.031(3)	101.141(17)	92.223(2)
β/°	101.950(4)	105.197(2)	108.857(3)	82.598(6)	109.072(2)	84.129(2)	113.149(6)	89.719(4)	99.638(16)	94.493(2)
γ/°	90	90	90	83.057(5)	90	83.815(2)	90	72.288(4)	90.665(16)	107.672(2)
Volume/Å^3	1303.3(2)	1433.28(13)	3098.7(4)	1593.4(3)	1704.4(2)	1785.73(17)	1888.7(5)	984.52(16)	2094.9(14)	1076.75(11)
Z	4	4	4	2	4	4	4	2	2	2
ρ_{calc}g/cm^3	1.917	1.808	1.733	1.743	1.684	1.660	1.619	1.600	1.548	1.549
μ/mm^{-1}	1.513	1.379	1.279	1.247	1.169	1.119	1.060	1.020	0.961	0.937
F(000)	744.0	776.0	1616.0	840.0	872.0	904.0	936.0	484.0	1000.0	516.0
Crystal size/mm^3	0.23 × 0.2 × 0.12	0.24 × 0.2 × 0.17	0.15 × 0.13 × 0.12	0.12 × 0.09 × 0.07	0.3 × 0.18 × 0.09	0.4 × 0.2 × 0.13	0.1 × 0.03 × 0.02	0.21 × 0.1 × 0.03	0.13 × 0.12 × 0.02	0.2 × 0.18 × 0.03
2Θ range for data collection/°	8.532 to 60	8.384 to 59.994	8.172 to 59.996	8.282 to 59.996	8.39 to 59.996	8.204 to 54.998	8.62 to 54.996	8.262 to 59.994	8.266 to 50	8.246 to 59.998
Index ranges	$-9 \le h \le 9$, -	$-16 \le h \le$	$-11 \le h \le$	$-12 \le h \le$	$-19 \le h \le$	$-11 \le h \le$	$-18 \le h \le$	$-8 \le h \le 9$, -	$-11 \le h \le$	$-9 \le h \le 9$, -

	$16 \le k \le 14$, $-22 \le l \le 22$	$16, -12 \le k \le 12$, $-19 \le l \le 19$	$11, -47 \le k \le 47$, $-16 \le l \le 16$	$12, -18 \le k \le 18$, $-20 \le l \le 20$	$19, -12 \le k \le 12$, $-20 \le l \le 20$	$11, -18 \le k \le 18$, $-19 \le l \le 19$	$18, -11 \le k \le 11$, $-20 \le l \le 20$	$10 \le k \le 10$, $-27 \le l \le 27$	$11, -12 \le k \le 11$, $-25 \le l \le 25$	$10 \le k \le 10$, $0 \le l \le 30$
Reflections collected	23680	21488	54400	28315	28302	24202	23971	17271	24079	6253
Independent reflections	3791 [R_{int} = 0.0751, R_{sigma} = 0.0581]	4174 [R_{int} = 0.0339, R_{sigma} = 0.0278]	9011 [R_{int} = 0.0797, R_{sigma} = 0.0636]	9273 [R_{int} = 0.1220, R_{sigma} = 0.1631]	4961 [R_{int} = 0.0662, R_{sigma} = 0.0526]	8008 [R_{int} = 0.0559, R_{sigma} = 0.0659]	4324 [R_{int} = 0.2009, R_{sigma} = 0.1649]	5723 [R_{int} = 0.0704, R_{sigma} = 0.0929]	7336 [R_{int} = 0.3360, R_{sigma} = 0.4121]	6253 [R_{int} = ?, R_{sigma} = 0.0540]
Data/restraints/parameters	3791/0/164	4174/1/214	9011/0/363	9273/0/381	4961/0/200	8008/6/417	4324/0/217	5723/0/227	7336/276/469	6253/0/358
Goodness-of-fit on F^2	1.029	1.022	1.017	0.949	1.006	1.037	0.965	0.984	0.935	1.033
Final R indexes [I>=2σ (I)]	R_1 = 0.0363, wR_2 = 0.0712	R_1 = 0.0228, wR_2 = 0.0456	R_1 = 0.0461, wR_2 = 0.0833	R_1 = 0.0633, wR_2 = 0.1015	R_1 = 0.0321, wR_2 = 0.0561	R_1 = 0.0407, wR_2 = 0.0814	R_1 = 0.0614, wR_2 = 0.1111	R_1 = 0.0466, wR_2 = 0.0799	R_1 = 0.0925, wR_2 = 0.1586	R_1 = 0.0346, wR_2 = 0.0608
Final R indexes [all data]	R_1 = 0.0591, wR_2 = 0.0784	R_1 = 0.0310, wR_2 = 0.0488	R_1 = 0.0787, wR_2 = 0.0956	R_1 = 0.1207, wR_2 = 0.1238	R_1 = 0.0539, wR_2 = 0.0628	R_1 = 0.0572, wR_2 = 0.0886	R_1 = 0.1658, wR_2 = 0.1478	R_1 = 0.0748, wR_2 = 0.0886	R_1 = 0.2912, wR_2 = 0.2352	R_1 = 0.0496, wR_2 = 0.0654
Largest diff. peak/hole / e Å^{-3}	0.64/-0.86	0.47/-0.37	0.61/-0.91	0.92/-1.04	0.48/-0.68	2.81/-2.13	0.73/-1.32	0.74/-0.86	0.86/-1.27	0.67/-0.49

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

Atom	Atom	Length/Å		Atom	Atom	Length/Å
Tc1	Cl2	2.3843(8)		N2	C3	1.337(4)
Tc1	Cl1	2.4258(8)		N3	C5	1.345(4)
Tc1	O2	1.675(2)		N3	C8	1.338(4)
Tc1	O1	1.857(2)		N4	C6	1.328(4)
Tc1	N1	2.134(2)		N4	C7	1.340(4)
Tc1	N3	2.160(2)		C1	C2	1.385(4)
O1	C9	1.407(4)		C3	C4	1.379(4)
N1	C1	1.342(4)		C5	C6	1.396(4)
N1	C4	1.342(4)		C7	C8	1.385(4)
N2	C2	1.327(4)				

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

Atom	Atom	Atom	Angle/°		Atom	Atom	Atom	Angle/°

Cl2	Tc1	Cl1	176.06(3)		C1	N1	Tc1	121.8(2)
O2	Tc1	Cl2	94.17(8)		C4	N1	Tc1	120.50(19)
O2	Tc1	Cl1	89.52(8)		C4	N1	C1	117.6(3)
O2	Tc1	O1	174.15(10)		C2	N2	C3	115.5(3)
O2	Tc1	N1	92.61(10)		C5	N3	Tc1	120.3(2)
O2	Tc1	N3	91.64(10)		C8	N3	Tc1	121.63(19)
O1	Tc1	Cl2	91.42(7)		C8	N3	C5	117.7(3)
O1	Tc1	Cl1	84.94(7)		C6	N4	C7	115.9(3)
O1	Tc1	N1	89.29(9)		N1	C1	C2	120.5(3)
O1	Tc1	N3	86.67(9)		N2	C2	C1	122.9(3)
N1	Tc1	Cl2	87.96(7)		N2	C3	C4	123.4(3)
N1	Tc1	Cl1	90.49(7)		N1	C4	C3	120.1(3)
N1	Tc1	N3	175.31(10)		N3	C5	C6	119.9(3)
N3	Tc1	Cl2	89.74(7)		N4	C6	C5	123.0(3)
N3	Tc1	Cl1	91.54(7)		N4	C7	C8	122.5(3)
C9	O1	Tc1	154.5(2)		N3	C8	C7	120.8(3)

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

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
C4	H4	N4[1]	0.93	2.50	3.351(4)	152.8

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

Table S5. Torsion Angles for **1.**

A	B	C	D	Angle/°		A	B	C	D	Angle/°
Tc1	N1	C1	C2	-175.8(2)		N3	C5	C6	N4	-0.4(5)
Tc1	N1	C4	C3	176.2(2)		N4	C7	C8	N3	1.0(5)
Tc1	N3	C5	C6	-170.7(2)		C1	N1	C4	C3	-0.6(5)
Tc1	N3	C8	C7	170.3(2)		C2	N2	C3	C4	1.2(5)
Cl2	Tc1	O1	C9	164.9(5)		C3	N2	C2	C1	-0.8(5)
Cl1	Tc1	O1	C9	-16.6(5)		C4	N1	C1	C2	1.0(4)
N1	Tc1	O1	C9	-107.1(5)		C5	N3	C8	C7	-2.7(4)
N1	C1	C2	N2	-0.3(5)		C6	N4	C7	C8	1.0(5)
N2	C3	C4	N1	-0.5(5)		C7	N4	C6	C5	-1.3(5)
N3	Tc1	O1	C9	75.3(5)		C8	N3	C5	C6	2.4(4)

Table S6. Bond Lengths for **2.**

Atom	Atom	Length/Å		Atom	Atom	Length/Å
Tc1	Cl1	2.4429(4)		N4	C6	1.335(2)
Tc1	Cl2	2.3695(4)		N4	C7	1.333(2)
Tc1	O1	1.8643(12)		N3	C5	1.344(2)
Tc1	O2	1.6687(12)		N3	C8	1.338(2)
Tc1	N1	2.1275(13)		C3	C4	1.384(2)
Tc1	N3	2.1474(14)		C2	C1	1.389(2)
O1	C9	1.421(2)		C6	C5	1.385(2)
N2	C3	1.340(2)		C7	C8	1.389(2)
N2	C2	1.333(2)		C9	C10	1.458(5)
N1	C1	1.340(2)		C9	C10A	1.496(8)

N1	C4	1.349(2)				

Table S7. Bond Angles for **2.**

Atom	Atom	Atom	Angle/°		Atom	Atom	Atom	Angle/°
Cl2	Tc1	Cl1	174.958(16)		C1	N1	Tc1	120.18(11)
O1	Tc1	Cl1	84.59(4)		C1	N1	C4	117.88(14)
O1	Tc1	Cl2	90.69(4)		C4	N1	Tc1	121.87(11)
O1	Tc1	N1	90.38(5)		C7	N4	C6	115.70(16)
O1	Tc1	N3	87.32(5)		C5	N3	Tc1	120.77(11)
O2	Tc1	Cl1	87.30(5)		C8	N3	Tc1	121.86(11)
O2	Tc1	Cl2	97.51(5)		C8	N3	C5	117.29(15)
O2	Tc1	O1	171.28(6)		N2	C3	C4	122.85(16)
O2	Tc1	N1	92.54(5)		N2	C2	C1	122.41(16)
O2	Tc1	N3	89.88(6)		N1	C1	C2	120.63(16)
N1	Tc1	Cl1	88.10(4)		N4	C6	C5	122.57(17)
N1	Tc1	Cl2	90.15(4)		N4	C7	C8	123.04(17)
N1	Tc1	N3	177.49(5)		N1	C4	C3	120.01(15)
N3	Tc1	Cl1	92.69(4)		N3	C5	C6	120.93(16)
N3	Tc1	Cl2	88.87(4)		N3	C8	C7	120.47(16)
C9	O1	Tc1	146.52(12)		O1	C9	C10	110.8(3)
C2	N2	C3	116.17(15)		O1	C9	C10A	111.3(4)

Table S8. Hydrogen Bonds for **2.**

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
C3	H3	O2[1]	0.90(2)	2.55(2)	3.160(2)	125.8(16)
C1	H1	N4[2]	0.88(2)	2.59(2)	3.362(2)	147.0(16)
C8	H8	N2[3]	0.94(2)	2.43(2)	3.312(2)	156.6(16)

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

Table S9. Torsion Angles for **2.**

A	B	C	D	Angle/°		A	B	C	D	Angle/°
Tc1	O1	C9	C10	101.4(6)		N4	C6	C5	N3	-0.5(3)
Tc1	O1	C9	C10A	135.7(13)		N4	C7	C8	N3	-0.5(3)
Tc1	N1	C1	C2	174.84(12)		N3	Tc1	O1	C9	82.2(2)
Tc1	N1	C4	C3	-175.48(12)		C3	N2	C2	C1	1.3(3)
Tc1	N3	C5	C6	176.47(15)		C2	N2	C3	C4	-2.0(3)
Tc1	N3	C8	C7	-175.94(14)		C1	N1	C4	C3	1.3(2)
Cl1	Tc1	O1	C9	-10.7(2)		C6	N4	C7	C8	-0.2(3)
Cl2	Tc1	O1	C9	171.1(2)		C7	N4	C6	C5	0.7(3)
N2	C3	C4	N1	0.8(3)		C4	N1	C1	C2	-2.0(2)
N2	C2	C1	N1	0.7(3)		C5	N3	C8	C7	0.7(3)
N1	Tc1	O1	C9	-98.8(2)		C8	N3	C5	C6	-0.2(3)

Table S10. Bond Lengths for **3.**

Atom	Atom	Length/Å		Atom	Atom	Length/Å
Tc1	Cl1	2.4382(8)		N23	C28	1.337(4)

Tc1	Cl2	2.3869(8)		N4	C6	1.339(5)
Tc1	O1	1.842(3)		N4	C7	1.335(5)
Tc1	O2	1.676(3)		N2	C2	1.333(5)
Tc1	N3	2.145(3)		N2	C3	1.334(5)
Tc1	N1	2.144(3)		N22	C22	1.337(5)
Tc2	Cl21	2.4443(8)		N22	C23	1.333(5)
Tc2	Cl22	2.3815(8)		N24	C26	1.338(5)
Tc2	O22	1.678(3)		N24	C27	1.331(5)
Tc2	O21	1.850(3)		C2	C1	1.387(5)
Tc2	N21	2.145(3)		C3	C4	1.380(5)
Tc2	N23	2.143(3)		C8	C7	1.363(5)
O1	C9	1.424(4)		C6	C5	1.386(5)
O21	C29	1.419(4)		C21	C22	1.388(5)
N21	C21	1.341(4)		C26	C25	1.380(5)
N21	C24	1.342(4)		C23	C24	1.386(5)
N3	C8	1.341(4)		C30	C29	1.510(5)
N3	C5	1.346(4)		C30	C31	1.517(5)
N1	C1	1.344(4)		C11	C10	1.522(5)
N1	C4	1.342(4)		C10	C9	1.506(5)
N23	C25	1.343(4)		C28	C27	1.391(5)

Table S11. Bond Angles for **3.**

Atom	**Atom**	**Atom**	**Angle/°**		**Atom**	**Atom**	**Atom**	**Angle/°**
Cl2	Tc1	Cl1	177.15(4)		C24	N21	Tc2	121.7(2)
O1	Tc1	Cl1	85.68(7)		C8	N3	Tc1	121.5(2)
O1	Tc1	Cl2	91.54(7)		C8	N3	C5	117.4(3)
O1	Tc1	N3	88.81(10)		C5	N3	Tc1	121.1(2)
O1	Tc1	N1	88.55(10)		C1	N1	Tc1	121.3(2)
O2	Tc1	Cl1	87.28(7)		C4	N1	Tc1	121.2(2)
O2	Tc1	Cl2	95.50(7)		C4	N1	C1	117.4(3)
O2	Tc1	O1	172.94(10)		C25	N23	Tc2	121.3(2)
O2	Tc1	N3	91.67(11)		C28	N23	Tc2	121.4(2)
O2	Tc1	N1	90.75(11)		C28	N23	C25	117.3(3)
N3	Tc1	Cl1	89.77(7)		C7	N4	C6	115.5(3)
N3	Tc1	Cl2	90.77(7)		C2	N2	C3	115.3(3)
N1	Tc1	Cl1	88.47(7)		C23	N22	C22	115.4(3)
N1	Tc1	Cl2	90.86(7)		C27	N24	C26	115.6(3)
N1	Tc1	N3	176.93(12)		N2	C2	C1	123.4(3)
Cl22	Tc2	Cl21	177.17(4)		N1	C1	C2	120.1(3)
O22	Tc2	Cl21	86.69(7)		N2	C3	C4	123.0(3)
O22	Tc2	Cl22	96.04(8)		N3	C8	C7	121.0(3)
O22	Tc2	O21	171.55(9)		N4	C6	C5	122.7(3)
O22	Tc2	N21	91.69(11)		N21	C21	C22	120.8(3)
O22	Tc2	N23	90.70(11)		N4	C7	C8	123.2(3)
O21	Tc2	Cl21	84.96(7)		N22	C22	C21	122.6(3)
O21	Tc2	Cl22	92.29(7)		N3	C5	C6	120.1(3)
O21	Tc2	N21	89.62(10)		N24	C26	C25	123.0(3)
O21	Tc2	N23	87.87(10)		N23	C25	C26	120.6(3)
N21	Tc2	Cl21	90.21(7)		N22	C23	C24	123.5(3)

N21	Tc2	Cl22	90.46(7)		C29	C30	C31	109.3(3)
N23	Tc2	Cl21	88.91(7)		N1	C4	C3	120.8(3)
N23	Tc2	Cl22	90.30(7)		N21	C24	C23	120.2(3)
N23	Tc2	N21	177.40(12)		C9	C10	C11	109.5(3)
C9	O1	Tc1	155.5(2)		N23	C28	C27	120.8(3)
C29	O21	Tc2	150.6(2)		O1	C9	C10	112.1(3)
C21	N21	Tc2	120.8(2)		N24	C27	C28	122.7(4)
C21	N21	C24	117.5(3)		O21	C29	C30	112.2(3)

Table S12. Hydrogen Bonds for **3.**

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
C5	H5	O22[1]	0.95	2.37	3.246(4)	153.9
C25	H25	O2	0.95	2.43	3.248(4)	143.8
C4	H4	O22	0.95	2.42	3.238(4)	144.0
C24	H24	O2[2]	0.95	2.36	3.253(4)	155.8

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

Table S13. Torsion Angles for **3.**

A	B	C	D	Angle/°		A	B	C	D	Angle/°
Tc1	O1	C9	C10	168.9(3)		N2	C2	C1	N1	0.0(6)
Tc1	N3	C8	C7	-179.0(3)		N2	C3	C4	N1	-0.2(6)
Tc1	N3	C5	C6	178.2(3)		N22	C23	C24	N21	-0.9(6)
Tc1	N1	C1	C2	176.3(2)		N24	C26	C25	N23	0.2(6)
Tc1	N1	C4	C3	-176.3(3)		C2	N2	C3	C4	0.3(5)
Tc2	O21	C29	C30	-166.7(3)		C1	N1	C4	C3	0.0(5)
Tc2	N21	C21	C22	-179.2(3)		C3	N2	C2	C1	-0.2(5)
Tc2	N21	C24	C23	179.7(3)		C8	N3	C5	C6	-0.3(5)
Tc2	N23	C25	C26	178.1(3)		C6	N4	C7	C8	0.8(6)
Tc2	N23	C28	C27	-178.3(3)		C21	N21	C24	C23	0.7(5)
Cl21	Tc2	O21	C29	-4.7(4)		C7	N4	C6	C5	-1.6(6)
Cl1	Tc1	O1	C9	1.4(5)		C22	N22	C23	C24	0.5(5)
Cl2	Tc1	O1	C9	-178.0(5)		C5	N3	C8	C7	-0.5(5)
Cl22	Tc2	O21	C29	174.6(4)		C26	N24	C27	C28	0.4(6)
N21	Tc2	O21	C29	-94.9(4)		C25	N23	C28	C27	-0.5(5)
N21	C21	C22	N22	-0.3(6)		C23	N22	C22	C21	0.1(5)
N3	Tc1	O1	C9	91.2(5)		C4	N1	C1	C2	0.1(5)
N3	C8	C7	N4	0.3(6)		C24	N21	C21	C22	-0.1(5)
N1	Tc1	O1	C9	-87.2(5)		C11	C10	C9	O1	177.0(3)
N23	Tc2	O21	C29	84.4(4)		C28	N23	C25	C26	0.4(5)
N23	C28	C27	N24	0.2(6)		C27	N24	C26	C25	-0.5(6)
N4	C6	C5	N3	1.4(6)		C31	C30	C29	O21	-174.3(3)

Table S14. Bond Lengths for **4.**

Atom	Atom	Length/Å		Atom	Atom	Length/Å
Tc1	Cl1	2.4335(13)		N2	C2	1.336(7)
Tc1	Cl2	2.3748(13)		N2	C3	1.332(7)
Tc1	O1	1.857(3)		N22	C22	1.335(7)

Tc1	O2	1.667(4)		N22	C23	1.353(6)
Tc1	N3	2.126(4)		N23	C28	1.324(6)
Tc1	N1	2.148(4)		N23	C25	1.363(6)
Tc2	Cl21	2.4420(14)		N1	C4	1.335(7)
Tc2	Cl22	2.3721(14)		N1	C1	1.343(6)
Tc2	O21	1.861(3)		C6	C5	1.390(7)
Tc2	O22	1.677(3)		C11	C10	1.524(7)
Tc2	N21	2.146(4)		C11	C12	1.524(7)
Tc2	N23	2.127(4)		C8	C7	1.387(7)
O1	C9	1.425(5)		C22	C21	1.380(7)
O21	C29	1.422(6)		C23	C24	1.386(7)
N4	C6	1.332(7)		C27	C28	1.393(7)
N4	C7	1.336(7)		C26	C25	1.385(7)
N24	C27	1.336(6)		C9	C10	1.517(7)
N24	C26	1.341(7)		C31	C32	1.541(7)
N3	C8	1.347(6)		C31	C30	1.522(8)
N3	C5	1.350(6)		C2	C1	1.372(7)
N21	C24	1.336(6)		C4	C3	1.387(7)
N21	C21	1.353(6)		C30	C29	1.525(7)

Table S15. Bond Angles for **4.**

Atom	**Atom**	**Atom**	**Angle/°**		**Atom**	**Atom**	**Atom**	**Angle/°**
Cl2	Tc1	Cl1	175.57(5)		C8	N3	C5	118.0(4)
O1	Tc1	Cl1	84.49(11)		C5	N3	Tc1	120.0(4)
O1	Tc1	Cl2	91.35(11)		C24	N21	Tc2	120.6(3)
O1	Tc1	N3	90.14(16)		C24	N21	C21	117.1(5)
O1	Tc1	N1	88.05(16)		C21	N21	Tc2	122.3(4)
O2	Tc1	Cl1	88.11(12)		C3	N2	C2	115.2(5)
O2	Tc1	Cl2	96.09(12)		C22	N22	C23	115.6(5)
O2	Tc1	O1	172.47(16)		C28	N23	Tc2	121.1(3)
O2	Tc1	N3	91.00(17)		C28	N23	C25	117.5(4)
O2	Tc1	N1	90.66(17)		C25	N23	Tc2	121.4(3)
N3	Tc1	Cl1	88.08(11)		C4	N1	Tc1	120.9(4)
N3	Tc1	Cl2	90.43(11)		C4	N1	C1	116.5(5)
N3	Tc1	N1	177.91(15)		C1	N1	Tc1	122.6(4)
N1	Tc1	Cl1	90.70(12)		N4	C6	C5	123.1(5)
N1	Tc1	Cl2	90.67(12)		C10	C11	C12	114.0(4)
Cl22	Tc2	Cl21	175.74(5)		N3	C8	C7	120.2(5)
O21	Tc2	Cl21	84.64(12)		N4	C7	C8	122.9(5)
O21	Tc2	Cl22	91.11(12)		N22	C22	C21	122.9(5)
O21	Tc2	N21	87.42(15)		N22	C23	C24	122.3(5)
O21	Tc2	N23	91.19(15)		N24	C27	C28	122.1(5)
O22	Tc2	Cl21	87.50(13)		N21	C24	C23	121.1(5)
O22	Tc2	Cl22	96.74(13)		N24	C26	C25	123.3(5)
O22	Tc2	O21	171.13(17)		N3	C5	C6	119.8(5)
O22	Tc2	N21	88.59(16)		O1	C9	C10	110.5(4)
O22	Tc2	N23	92.92(16)		C30	C31	C32	112.5(5)
N21	Tc2	Cl21	90.70(12)		N2	C2	C1	122.5(5)
N21	Tc2	Cl22	88.97(12)		N1	C4	C3	120.7(5)

N23	Tc2	Cl21	90.19(12)		C9	C10	C11	113.1(4)
N23	Tc2	Cl22	90.04(12)		N21	C21	C22	120.9(5)
N23	Tc2	N21	178.28(16)		N2	C3	C4	123.3(6)
C9	O1	Tc1	146.6(3)		N23	C28	C27	121.6(5)
C29	O21	Tc2	147.0(3)		N23	C25	C26	119.7(5)
C6	N4	C7	115.9(5)		C31	C30	C29	114.7(4)
C27	N24	C26	115.7(4)		N1	C1	C2	121.8(5)
C8	N3	Tc1	122.0(4)		O21	C29	C30	110.9(4)

Table S16. Hydrogen Bonds for **4.**

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
C6	H6	O22[1]	0.95	2.69	3.301(7)	122.8
C24	H24	N4[2]	0.95	2.43	3.292(7)	150.2
C26	H26	O2	0.95	2.54	3.144(7)	121.7
C4	H4	N24[3]	0.95	2.60	3.355(7)	137.2
C28	H28	N2[4]	0.95	2.50	3.344(7)	147.3

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

Table S17. Torsion Angles for **4.**

A	B	C	D	Angle/°		A	B	C	D	Angle/°
Tc1	O1	C9	C10	-106.1(6)		N22	C23	C24	N21	2.0(8)
Tc1	N3	C8	C7	-175.1(3)		N23	Tc2	O21	C29	116.6(6)
Tc1	N3	C5	C6	176.1(3)		N1	Tc1	O1	C9	-87.2(6)
Tc1	N1	C4	C3	178.4(4)		N1	C4	C3	N2	-0.1(8)
Tc1	N1	C1	C2	-178.1(4)		C6	N4	C7	C8	0.3(7)
Tc2	O21	C29	C30	168.9(4)		C8	N3	C5	C6	-1.2(7)
Tc2	N21	C24	C23	174.5(4)		C7	N4	C6	C5	0.7(7)
Tc2	N21	C21	C22	-175.7(4)		C22	N22	C23	C24	1.1(8)
Tc2	N23	C28	C27	-175.6(4)		C23	N22	C22	C21	-2.4(8)
Tc2	N23	C25	C26	176.6(4)		C27	N24	C26	C25	3.0(8)
Cl1	Tc1	O1	C9	3.7(6)		C24	N21	C21	C22	2.5(8)
Cl21	Tc2	O21	C29	26.6(6)		C26	N24	C27	C28	-1.9(7)
Cl2	Tc1	O1	C9	-177.8(6)		C5	N3	C8	C7	2.2(7)
Cl22	Tc2	O21	C29	-153.3(6)		C31	C30	C29	O21	72.5(6)
O1	C9	C10	C11	-70.0(6)		C2	N2	C3	C4	0.3(8)
N4	C6	C5	N3	-0.2(8)		C4	N1	C1	C2	0.8(8)
N24	C27	C28	N23	-0.5(8)		C32	C31	C30	C29	-173.2(5)
N24	C26	C25	N23	-1.7(8)		C21	N21	C24	C23	-3.7(7)
N3	Tc1	O1	C9	91.8(6)		C3	N2	C2	C1	0.0(8)
N3	C8	C7	N4	-1.8(8)		C12	C11	C10	C9	170.9(4)
N21	Tc2	O21	C29	-64.4(6)		C28	N23	C25	C26	-0.9(7)
N2	C2	C1	N1	-0.6(9)		C25	N23	C28	C27	1.9(7)
N22	C22	C21	N21	0.6(9)		C1	N1	C4	C3	-0.5(7)

Table S18. Bond Lengths for **5.**

Atom	Atom	Length/Å		Atom	Atom	Length/Å
Tc1	Cl1	2.4321(6)		N1	C1	1.347(3)

Tc1	Cl2	2.3746(6)		N2	C3	1.333(3)
Tc1	O1	1.8562(15)		N2	C2	1.338(3)
Tc1	O2	1.6737(16)		C7	C8	1.388(3)
Tc1	N3	2.1268(18)		C3	C4	1.383(3)
Tc1	N1	2.1416(18)		C2	C1	1.385(3)
O1	C9	1.421(3)		C6	C5	1.381(3)
N3	C8	1.339(3)		C10	C11	1.532(3)
N3	C5	1.352(3)		C10	C9	1.518(3)
N4	C7	1.337(3)		C11	C12	1.517(3)
N4	C6	1.338(3)		C13	C12	1.522(3)
N1	C4	1.342(3)				

Table S19. Bond Angles for **5.**

Atom	Atom	Atom	Angle/°		Atom	Atom	Atom	Angle/°
Cl2	Tc1	Cl1	174.93(2)		C5	N3	Tc1	121.51(14)
O1	Tc1	Cl1	84.75(5)		C7	N4	C6	115.90(19)
O1	Tc1	Cl2	90.27(5)		C4	N1	Tc1	121.33(15)
O1	Tc1	N3	89.98(7)		C4	N1	C1	116.82(19)
O1	Tc1	N1	87.55(7)		C1	N1	Tc1	121.84(15)
O2	Tc1	Cl1	88.34(6)		C3	N2	C2	116.0(2)
O2	Tc1	Cl2	96.67(6)		N4	C7	C8	122.3(2)
O2	Tc1	O1	172.74(7)		N2	C3	C4	122.7(2)
O2	Tc1	N3	92.21(7)		N2	C2	C1	122.4(2)
O2	Tc1	N1	90.11(7)		N4	C6	C5	123.0(2)
N3	Tc1	Cl1	89.55(5)		N1	C4	C3	121.1(2)
N3	Tc1	Cl2	89.51(5)		N3	C8	C7	121.1(2)
N3	Tc1	N1	177.28(7)		N1	C1	C2	121.0(2)
N1	Tc1	Cl1	89.08(5)		C9	C10	C11	114.1(2)
N1	Tc1	Cl2	91.65(5)		C12	C11	C10	113.8(2)
C9	O1	Tc1	151.24(14)		N3	C5	C6	120.4(2)
C8	N3	Tc1	121.26(15)		C11	C12	C13	113.8(2)
C8	N3	C5	117.20(19)		O1	C9	C10	109.89(19)

Table S20. Hydrogen Bonds for **5.**

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
C6	H6	O2[1]	0.95	2.66	3.287(3)	123.8
C4	H4	N4[2]	0.95	2.50	3.314(3)	143.3
C8	H8	N2[3]	0.95	2.53	3.302(3)	138.6
C5	H5	O2[1]	0.95	2.70	3.292(3)	121.4

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

Table S21. Torsion Angles for **5.**

A	B	C	D	Angle/°		A	B	C	D	Angle/°
Tc1	O1	C9	C10	-175.4(2)		N2	C2	C1	N1	1.0(4)
Tc1	N3	C8	C7	-176.98(17)		C7	N4	C6	C5	1.4(4)
Tc1	N3	C5	C6	178.09(17)		C3	N2	C2	C1	0.2(4)
Tc1	N1	C4	C3	-178.94(17)		C2	N2	C3	C4	-1.1(4)

Tc1	N1	C1	C2	178.05(17)		C6	N4	C7	C8	-0.2(4)
Cl1	Tc1	O1	C9	8.2(3)		C4	N1	C1	C2	-1.2(3)
Cl2	Tc1	O1	C9	-172.8(3)		C8	N3	C5	C6	0.0(3)
N3	Tc1	O1	C9	97.7(3)		C1	N1	C4	C3	0.3(3)
N4	C7	C8	N3	-1.0(4)		C10	C11	C12	C13	174.8(2)
N4	C6	C5	N3	-1.4(4)		C11	C10	C9	O1	-65.0(3)
N1	Tc1	O1	C9	-81.1(3)		C5	N3	C8	C7	1.1(3)
N2	C3	C4	N1	0.9(4)		C9	C10	C11	C12	-72.6(3)

Table S22. Bond Lengths for **6.**

Atom	Atom	Length/Å		Atom	Atom	Length/Å
Tc1	Cl1	2.4418(9)		N24	C26	1.340(5)
Tc1	Cl2	2.3718(9)		N24	C27	1.340(5)
Tc1	O1	1.872(2)		N23	C28	1.344(4)
Tc1	O2	1.676(3)		N23	C25	1.350(4)
Tc1	N1	2.145(3)		N4	C6	1.336(5)
Tc1	N3	2.138(3)		N4	C7	1.338(5)
Tc2	Cl22	2.3819(8)		C12	C13	1.525(5)
Tc2	Cl21	2.4327(9)		C12	C11	1.523(5)
Tc2	O21	1.858(2)		C24	C23	1.381(5)
Tc2	O22	1.670(2)		C13	C14	1.517(5)
Tc2	N21	2.117(3)		C11	C10	1.533(5)
Tc2	N23	2.155(3)		C22	C21	1.379(5)
O21	C29	1.420(4)		C4	C3	1.391(5)
O1	C9	1.426(4)		C26	C25	1.378(5)
N21	C24	1.354(4)		C2	C1	1.386(5)
N21	C21	1.342(4)		C5	C6	1.391(5)
N1	C4	1.346(4)		C28	C27	1.374(5)
N1	C1	1.348(4)		C34	C33	1.474(6)
N22	C22	1.339(4)		C10	C9	1.509(5)
N22	C23	1.347(5)		C7	C8	1.388(5)
N3	C5	1.350(4)		C30	C29	1.505(6)
N3	C8	1.342(5)		C30	C31	1.493(7)
N2	C2	1.338(5)		C31	C32	1.564(8)
N2	C3	1.343(5)		C32	C33	1.309(9)

Table S23. Bond Angles for **6.**

Atom	Atom	Atom	Angle/°		Atom	Atom	Atom	Angle/°
Cl2	Tc1	Cl1	175.85(3)		C1	N1	Tc1	120.7(2)
O1	Tc1	Cl1	84.05(8)		C22	N22	C23	115.7(3)
O1	Tc1	Cl2	91.80(8)		C5	N3	Tc1	120.7(2)
O1	Tc1	N1	86.21(10)		C8	N3	Tc1	122.2(2)
O1	Tc1	N3	91.89(10)		C8	N3	C5	117.1(3)
O2	Tc1	Cl1	87.19(9)		C2	N2	C3	115.8(3)
O2	Tc1	Cl2	96.94(9)		C26	N24	C27	115.3(3)
O2	Tc1	O1	169.96(11)		C28	N23	Tc2	122.4(2)
O2	Tc1	N1	88.84(11)		C28	N23	C25	116.6(3)
O2	Tc1	N3	93.08(11)		C25	N23	Tc2	121.0(2)

N1	Tc1	Cl1	89.61(8)		C6	N4	C7	116.0(3)
N1	Tc1	Cl2	90.08(8)		C11	C12	C13	114.6(3)
N3	Tc1	Cl1	90.44(8)		N21	C24	C23	120.8(3)
N3	Tc1	Cl2	89.73(8)		C14	C13	C12	112.2(3)
N3	Tc1	N1	178.08(12)		C12	C11	C10	112.3(3)
Cl22	Tc2	Cl21	175.07(3)		N22	C22	C21	122.8(3)
O21	Tc2	Cl22	90.20(7)		N22	C23	C24	122.4(3)
O21	Tc2	Cl21	85.15(7)		N21	C21	C22	121.0(3)
O21	Tc2	N21	91.61(11)		N1	C4	C3	120.7(3)
O21	Tc2	N23	85.99(11)		N24	C26	C25	123.1(3)
O22	Tc2	Cl22	96.04(9)		N2	C2	C1	123.0(4)
O22	Tc2	Cl21	88.76(9)		N2	C3	C4	122.5(4)
O22	Tc2	O21	171.56(11)		N3	C5	C6	120.4(4)
O22	Tc2	N21	94.07(12)		N23	C28	C27	121.5(3)
O22	Tc2	N23	88.20(12)		N4	C6	C5	123.0(4)
N21	Tc2	Cl22	89.96(7)		N1	C1	C2	120.4(3)
N21	Tc2	Cl21	88.53(8)		N24	C27	C28	122.7(3)
N21	Tc2	N23	177.36(11)		N23	C25	C26	120.8(3)
N23	Tc2	Cl22	91.14(8)		C9	C10	C11	114.8(3)
N23	Tc2	Cl21	90.17(8)		N4	C7	C8	122.2(4)
C29	O21	Tc2	148.4(2)		N3	C8	C7	121.4(4)
C9	O1	Tc1	140.9(2)		C31	C30	C29	114.3(4)
C24	N21	Tc2	121.1(2)		O1	C9	C10	113.2(3)
C21	N21	Tc2	121.7(2)		O21	C29	C30	111.6(3)
C21	N21	C24	117.1(3)		C30	C31	C32	108.3(5)
C4	N1	Tc1	121.7(2)		C33	C32	C31	120.6(6)
C4	N1	C1	117.5(3)		C32	C33	C34	125.2(5)

Table S24. Hydrogen Bonds for **6.**

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
C24	H24	O2[1]	0.95	2.63	3.235(4)	122.3
C23	H23	O2[1]	0.95	2.64	3.252(4)	122.3
C3	H3	O22	0.95	2.62	3.238(5)	123.5
C5	H5	N22[2]	0.95	2.48	3.297(5)	143.9
C1	H1	N24[3]	0.95	2.59	3.369(5)	139.7
C25	H25	N2[4]	0.95	2.54	3.347(4)	142.9

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

Table S25. Torsion Angles for **6.**

A	B	C	D	Angle/°		A	B	C	D	Angle/°
Tc1	O1	C9	C10	176.9(2)		N4	C7	C8	N3	-1.1(6)
Tc1	N1	C4	C3	-177.7(3)		C12	C11	C10	C9	-167.2(3)
Tc1	N1	C1	C2	177.7(3)		C24	N21	C21	C22	-2.0(5)
Tc1	N3	C5	C6	-176.9(3)		C13	C12	C11	C10	178.7(3)
Tc1	N3	C8	C7	177.7(3)		C11	C12	C13	C14	-173.5(3)
Tc2	O21	C29	C30	161.1(3)		C11	C10	C9	O1	-62.1(4)
Tc2	N21	C24	C23	-176.0(3)		C22	N22	C23	C24	-2.7(5)

Tc2	N21	C21	C22	174.6(3)		C23	N22	C22	C21	1.3(5)
Tc2	N23	C28	C27	178.7(3)		C21	N21	C24	C23	0.6(5)
Tc2	N23	C25	C26	-178.2(3)		C4	N1	C1	C2	-0.7(5)
Cl1	Tc1	O1	C9	26.0(3)		C26	N24	C27	C28	1.3(6)
Cl2	Tc1	O1	C9	-154.0(3)		C2	N2	C3	C4	-1.1(5)
Cl22	Tc2	O21	C29	146.6(5)		C3	N2	C2	C1	1.1(5)
Cl21	Tc2	O21	C29	-35.1(5)		C5	N3	C8	C7	-0.1(5)
N21	Tc2	O21	C29	-123.5(5)		C28	N23	C25	C26	0.4(5)
N21	C24	C23	N22	1.8(6)		C6	N4	C7	C8	1.3(6)
O2	Tc1	O1	C9	-3.4(8)		C1	N1	C4	C3	0.6(5)
N1	Tc1	O1	C9	-64.0(3)		C27	N24	C26	C25	-0.7(6)
N1	C4	C3	N2	0.3(6)		C25	N23	C28	C27	0.1(5)
N22	C22	C21	N21	1.1(6)		C7	N4	C6	C5	-0.5(6)
N3	Tc1	O1	C9	116.2(3)		C8	N3	C5	C6	0.9(5)
N3	C5	C6	N4	-0.6(6)		C30	C31	C32	C33	-159.6(8)
N2	C2	C1	N1	-0.2(6)		C29	C30	C31	C32	174.9(5)
N24	C26	C25	N23	-0.1(6)		C31	C30	C29	O21	-70.3(5)
N23	Tc2	O21	C29	55.4(5)		C31	C32	C33	C34	-175.3(6)
N23	C28	C27	N24	-1.0(6)						

Table S26. Bond Lengths for **7.**

Atom	Atom	Length/Å		Atom	Atom	Length/Å
Tc1	Cl1	2.442(2)		N2	C2	1.345(10)
Tc1	Cl2	2.367(2)		N2	C3	1.326(9)
Tc1	O1	1.867(5)		C11	C10	1.519(10)
Tc1	O2	1.667(5)		C11	C12	1.548(10)
Tc1	N1	2.146(6)		C8	C7	1.384(9)
Tc1	N3	2.121(6)		C10	C9	1.526(10)
O1	C9	1.411(8)		C12	C13	1.515(10)
N1	C4	1.362(9)		C4	C3	1.385(10)
N1	C1	1.341(8)		C13	C14	1.521(10)
N3	C8	1.349(8)		C6	C5	1.361(10)
N3	C5	1.340(9)		C1	C2	1.401(10)
N4	C7	1.334(9)		C14	C15	1.522(10)
N4	C6	1.341(9)				

Table S27. Bond Angles for **7.**

Atom	Atom	Atom	Angle/°		Atom	Atom	Atom	Angle/°
Cl2	Tc1	Cl1	175.15(7)		C8	N3	Tc1	119.7(5)
O1	Tc1	Cl1	84.28(16)		C5	N3	Tc1	122.9(5)
O1	Tc1	Cl2	90.90(16)		C5	N3	C8	117.3(6)
O1	Tc1	N1	86.4(2)		C7	N4	C6	116.1(7)
O1	Tc1	N3	91.3(2)		C3	N2	C2	115.5(7)
O2	Tc1	Cl1	87.66(18)		C10	C11	C12	111.7(6)
O2	Tc1	Cl2	97.18(18)		N3	C8	C7	120.3(7)
O2	Tc1	O1	170.7(2)		C11	C10	C9	114.4(6)
O2	Tc1	N1	88.9(2)		C13	C12	C11	113.7(6)
O2	Tc1	N3	93.2(2)		N1	C4	C3	120.3(7)

N1	Tc1	Cl1	90.13(17)		C12	C13	C14	112.2(6)
N1	Tc1	Cl2	90.08(17)		O1	C9	C10	112.8(6)
N3	Tc1	Cl1	88.63(16)		N4	C7	C8	122.3(7)
N3	Tc1	Cl2	90.97(17)		N4	C6	C5	122.8(7)
N3	Tc1	N1	177.5(2)		N1	C1	C2	121.7(7)
C9	O1	Tc1	142.7(4)		N3	C5	C6	121.1(7)
C4	N1	Tc1	121.0(5)		N2	C2	C1	121.9(7)
C1	N1	Tc1	122.5(5)		N2	C3	C4	124.1(7)
C1	N1	C4	116.4(6)		C13	C14	C15	114.2(7)

Table S28. Hydrogen Bonds for **7.**

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
C6	H6	O2[1]	0.95	2.49	3.172(9)	129.1

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

Table S29. Torsion Angles for **7.**

A	B	C	D	Angle/°		A	B	C	D	Angle/°
Tc1	O1	C9	C10	171.1(5)		C11	C10	C9	O1	81.0(9)
Tc1	N1	C4	C3	178.5(5)		C11	C12	C13	C14	-179.9(7)
Tc1	N1	C1	C2	-178.0(5)		C8	N3	C5	C6	-2.7(11)
Tc1	N3	C8	C7	-176.0(5)		C10	C11	C12	C13	-167.3(7)
Tc1	N3	C5	C6	177.2(6)		C12	C11	C10	C9	-176.7(7)
Cl1	Tc1	O1	C9	27.9(8)		C12	C13	C14	C15	-172.0(7)
Cl2	Tc1	O1	C9	-152.6(8)		C4	N1	C1	C2	0.9(11)
N1	Tc1	O1	C9	-62.6(8)		C7	N4	C6	C5	2.5(12)
N1	C4	C3	N2	0.9(13)		C6	N4	C7	C8	-1.1(11)
N1	C1	C2	N2	-2.0(12)		C1	N1	C4	C3	-0.3(11)
N3	Tc1	O1	C9	116.4(8)		C5	N3	C8	C7	3.9(11)
N3	C8	C7	N4	-2.1(12)		C2	N2	C3	C4	-1.9(12)
N4	C6	C5	N3	-0.6(12)		C3	N2	C2	C1	2.4(12)

Table S30. Bond Lengths for **8.**

Atom	Atom	Length/Å		Atom	Atom	Length/Å
Tc1	Cl2	2.3690(9)		N3	C8	1.355(4)
Tc1	Cl1	2.4510(9)		N3	C5	1.347(4)
Tc1	O1	1.866(2)		C15	C16	1.528(4)
Tc1	O2	1.674(2)		C15	C14	1.515(4)
Tc1	N1	2.134(2)		C3	C4	1.386(4)
Tc1	N3	2.147(3)		C9	C10	1.520(4)
O1	C9	1.418(3)		C7	C8	1.383(4)
N1	C4	1.340(4)		C13	C14	1.522(4)
N1	C1	1.342(4)		C13	C12	1.516(4)
N2	C3	1.336(4)		C1	C2	1.382(4)
N2	C2	1.339(4)		C6	C5	1.390(4)
N4	C7	1.331(4)		C11	C10	1.526(4)
N4	C6	1.338(4)		C11	C12	1.525(4)

Table S31. Bond Angles for **8.**

Atom	Atom	Atom	Angle/°		Atom	Atom	Atom	Angle/°
Cl2	Tc1	Cl1	175.05(3)		C7	N4	C6	115.6(3)
O1	Tc1	Cl2	91.44(7)		C8	N3	Tc1	120.8(2)
O1	Tc1	Cl1	83.71(7)		C5	N3	Tc1	122.0(2)
O1	Tc1	N1	90.83(9)		C5	N3	C8	117.2(3)
O1	Tc1	N3	88.15(9)		C14	C15	C16	114.7(3)
O2	Tc1	Cl2	98.29(8)		N2	C3	C4	122.4(3)
O2	Tc1	Cl1	86.59(8)		N1	C4	C3	121.2(3)
O2	Tc1	O1	170.07(10)		O1	C9	C10	110.4(3)
O2	Tc1	N1	91.26(10)		N4	C7	C8	123.4(3)
O2	Tc1	N3	89.92(10)		C12	C13	C14	115.3(3)
N1	Tc1	Cl2	89.05(7)		N1	C1	C2	120.5(3)
N1	Tc1	Cl1	90.04(7)		C15	C14	C13	112.5(3)
N1	Tc1	N3	178.56(10)		N4	C6	C5	122.9(3)
N3	Tc1	Cl2	89.97(7)		C12	C11	C10	113.2(3)
N3	Tc1	Cl1	90.85(7)		N2	C2	C1	123.2(3)
C9	O1	Tc1	148.04(19)		C9	C10	C11	112.9(3)
C4	N1	Tc1	121.75(19)		C13	C12	C11	113.8(3)
C4	N1	C1	117.2(3)		N3	C8	C7	120.3(3)
C1	N1	Tc1	121.1(2)		N3	C5	C6	120.6(3)
C3	N2	C2	115.5(3)					

Table S32. Hydrogen Bonds for **8.**

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
C3	H3	N2[1]	0.93	2.56	3.225(4)	128.9

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

Table S33. Torsion Angles for **8.**

A	B	C	D	Angle/°		A	B	C	D	Angle/°
Tc1	O1	C9	C10	170.7(3)		C3	N2	C2	C1	-0.3(5)
Tc1	N1	C4	C3	178.8(2)		C16	C15	C14	C13	-179.9(3)
Tc1	N1	C1	C2	-179.6(2)		C4	N1	C1	C2	-0.8(4)
Tc1	N3	C8	C7	-178.9(2)		C7	N4	C6	C5	0.4(5)
Tc1	N3	C5	C6	179.3(2)		C1	N1	C4	C3	0.0(4)
Cl2	Tc1	O1	C9	174.7(4)		C14	C13	C12	C11	-178.8(3)
Cl1	Tc1	O1	C9	-6.3(4)		C6	N4	C7	C8	0.0(5)
O1	C9	C10	C11	-178.9(3)		C2	N2	C3	C4	-0.5(5)
N1	Tc1	O1	C9	-96.2(4)		C10	C11	C12	C13	178.4(3)
N1	C1	C2	N2	1.0(5)		C12	C13	C14	C15	-179.4(3)
N2	C3	C4	N1	0.7(5)		C12	C11	C10	C9	179.2(3)
N4	C7	C8	N3	-1.4(5)		C8	N3	C5	C6	-1.8(4)
N4	C6	C5	N3	0.5(5)		C5	N3	C8	C7	2.2(5)
N3	Tc1	O1	C9	84.8(4)						

Table S34. Bond Lengths for **9.**

Atom	Atom	Length/Å		Atom	Atom	Length/Å
Tc1	Cl1	2.439(4)		N21	C24	1.36(2)
Tc1	Cl2	2.373(4)		N22	C22	1.311(19)
Tc1	O2	1.668(11)		N22	C23	1.34(2)
Tc1	O1	1.853(12)		C8	C7	1.37(2)
Tc1	N3	2.116(13)		C6	C5	1.37(2)
Tc1	N1	2.128(13)		C4	C3	1.37(2)
Tc2	Cl21	2.451(4)		C2	C1	1.39(2)
Tc2	Cl22	2.376(4)		C9	C10	1.46(2)
Tc2	O22	1.658(11)		C10	C11	1.60(2)
Tc2	O21	1.901(11)		C11	C12	1.51(2)
Tc2	N23	2.138(12)		C12	C13	1.56(2)
Tc2	N21	2.127(13)		C13	C14	1.54(2)
O1	C9	1.451(18)		C14	C15	1.56(2)
O21	C29	1.405(18)		C15	C16	1.50(2)
N3	C8	1.37(2)		C16	C17	1.50(2)
N3	C5	1.36(2)		C25	C26	1.40(2)
N4	C7	1.32(2)		C27	C28	1.37(2)
N4	C6	1.351(18)		C21	C22	1.37(2)
N1	C4	1.33(2)		C23	C24	1.38(2)
N1	C1	1.35(2)		C29	C30	1.46(2)
N2	C3	1.33(2)		C30	C31	1.54(2)
N2	C2	1.32(2)		C31	C32	1.51(2)
N23	C25	1.335(17)		C32	C33	1.51(2)
N23	C28	1.353(19)		C33	C34	1.54(2)
N24	C26	1.352(19)		C34	C35	1.53(2)
N24	C27	1.333(19)		C35	C36	1.52(3)
N21	C21	1.362(18)		C36	C37	1.49(2)

Table S35. Bond Angles for **9.**

Atom	Atom	Atom	Angle/°		Atom	Atom	Atom	Angle/°
Cl2	Tc1	Cl1	174.6(2)		C25	N23	Tc2	123.8(10)
O2	Tc1	Cl1	86.9(4)		C25	N23	C28	114.9(14)
O2	Tc1	Cl2	98.5(4)		C28	N23	Tc2	121.2(11)
O2	Tc1	O1	170.8(5)		C27	N24	C26	118.8(15)
O2	Tc1	N3	89.5(5)		C21	N21	Tc2	121.5(10)
O2	Tc1	N1	92.2(5)		C24	N21	Tc2	119.7(11)
O1	Tc1	Cl1	84.7(3)		C24	N21	C21	118.8(15)
O1	Tc1	Cl2	90.0(3)		C22	N22	C23	111.7(15)
O1	Tc1	N3	87.1(5)		C7	C8	N3	120.3(16)
O1	Tc1	N1	91.2(5)		N4	C7	C8	125.2(16)
N3	Tc1	Cl1	90.7(3)		N4	C6	C5	122.2(15)
N3	Tc1	Cl2	89.8(3)		N3	C5	C6	122.7(15)
N3	Tc1	N1	178.3(6)		N1	C4	C3	123.4(17)
N1	Tc1	Cl1	89.0(3)		N2	C3	C4	121.3(17)
N1	Tc1	Cl2	90.3(3)		N2	C2	C1	123.3(16)
Cl22	Tc2	Cl21	175.6(2)		N1	C1	C2	120.2(15)
O22	Tc2	Cl21	86.4(4)		O1	C9	C10	112.5(14)
O22	Tc2	Cl22	97.9(4)		C9	C10	C11	112.4(15)

O22	Tc2	O21	169.3(5)		C12	C11	C10	109.3(16)
O22	Tc2	N23	87.2(5)		C11	C12	C13	112.3(16)
O22	Tc2	N21	95.0(5)		C14	C13	C12	110.3(15)
O21	Tc2	Cl21	85.0(3)		C13	C14	C15	113.4(15)
O21	Tc2	Cl22	90.7(3)		C16	C15	C14	110.6(16)
O21	Tc2	N23	86.3(5)		C15	C16	C17	112.6(19)
O21	Tc2	N21	91.4(5)		N23	C25	C26	124.0(15)
N23	Tc2	Cl21	89.7(4)		N24	C26	C25	118.4(15)
N23	Tc2	Cl22	90.2(4)		N24	C27	C28	121.0(16)
N21	Tc2	Cl21	90.2(4)		N23	C28	C27	122.9(16)
N21	Tc2	Cl22	89.7(4)		N21	C21	C22	117.6(15)
N21	Tc2	N23	177.7(6)		N22	C22	C21	127.7(16)
C9	O1	Tc1	145.7(10)		N22	C23	C24	126.8(18)
C29	O21	Tc2	141.4(10)		N21	C24	C23	117.3(17)
C8	N3	Tc1	121.8(11)		O21	C29	C30	116.2(14)
C5	N3	Tc1	123.5(11)		C29	C30	C31	112.4(15)
C5	N3	C8	114.7(15)		C32	C31	C30	114.4(15)
C7	N4	C6	114.7(15)		C31	C32	C33	110.3(14)
C4	N1	Tc1	121.8(12)		C32	C33	C34	114.6(15)
C4	N1	C1	115.7(15)		C35	C34	C33	112.0(15)
C1	N1	Tc1	122.3(11)		C36	C35	C34	115.2(17)
C2	N2	C3	116.1(16)		C37	C36	C35	115.2(18)

Table S36. Hydrogen Bonds for **9.**

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
C7	H7	N4[1]	0.95	2.62	3.31(2)	129.5
C27	H27	N24[2]	0.95	2.70	3.36(2)	127.0

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

Table S37. Torsion Angles for **9.**

A	B	C	D	Angle/°		A	B	C	D	Angle/°
Tc1	O1	C9	C10	99.5(19)		C6	N4	C7	C8	-2(3)
Tc1	N3	C8	C7	177.6(12)		C5	N3	C8	C7	-3(2)
Tc1	N3	C5	C6	-176.6(12)		C4	N1	C1	C2	2(2)
Tc1	N1	C4	C3	-177.8(13)		C3	N2	C2	C1	1(3)
Tc1	N1	C1	C2	178.0(12)		C2	N2	C3	C4	-1(3)
Tc2	O21	C29	C30	97.9(19)		C1	N1	C4	C3	-2(3)
Tc2	N23	C25	C26	-178.6(12)		C9	C10	C11	C12	75.0(19)
Tc2	N23	C28	C27	178.8(13)		C10	C11	C12	C13	178.7(15)
Tc2	N21	C21	C22	179.4(11)		C11	C12	C13	C14	176.7(15)
Tc2	N21	C24	C23	-177.8(13)		C12	C13	C14	C15	-175.6(15)
Cl1	Tc1	O1	C9	-21.2(17)		C13	C14	C15	C16	172.7(15)
Cl2	Tc1	O1	C9	159.5(17)		C14	C15	C16	C17	-174.3(16)
O1	C9	C10	C11	-178.8(14)		C25	N23	C28	C27	2(2)
O21	C29	C30	C31	-176.0(15)		C26	N24	C27	C28	1(3)
N3	Tc1	O1	C9	69.8(18)		C27	N24	C26	C25	-1(2)
N3	C8	C7	N4	2(3)		C28	N23	C25	C26	-2(2)

N4	C6	C5	N3	-4(3)		C21	N21	C24	C23	0(3)
N1	Tc1	O1	C9	-110.1(18)		C22	N22	C23	C24	0(3)
N1	C4	C3	N2	1(3)		C23	N22	C22	C21	2(3)
N2	C2	C1	N1	-2(3)		C24	N21	C21	C22	1(2)
N23	C25	C26	N24	2(3)		C29	C30	C31	C32	179.0(16)
N24	C27	C28	N23	-2(3)		C30	C31	C32	C33	173.3(16)
N21	C21	C22	N22	-3(3)		C31	C32	C33	C34	-171.6(15)
N22	C23	C24	N21	-1(3)		C32	C33	C34	C35	173.7(15)
C8	N3	C5	C6	4(2)		C33	C34	C35	C36	178.4(16)
C7	N4	C6	C5	2(2)		C34	C35	C36	C37	-71(2)

Table S38. Bond Lengths for **10.**

Atom	Atom	Length/Å		Atom	Atom	Length/Å
Tc1	Cl2	2.3689(6)		N2	C3	1.333(3)
Tc1	Cl1	2.4508(6)		C6	C5	1.385(3)
Tc1	O1	1.8673(14)		C16	C17	1.511(3)
Tc1	O2	1.6743(14)		C16	C15	1.523(3)
Tc1	N3	2.1340(19)		C9	C10	1.521(3)
Tc1	N1	2.1501(19)		C10	C11	1.524(3)
O1	C9	1.425(3)		C12	C13	1.520(3)
N3	C5	1.344(3)		C12	C11	1.523(3)
N3	C8	1.351(3)		C13	C14	1.522(3)
N1	C1	1.343(3)		C17	C18	1.517(3)
N1	C4	1.348(3)		C15	C14	1.524(3)
N4	C6	1.336(3)		C1	C2	1.378(3)
N4	C7	1.337(3)		C8	C7	1.382(3)
N2	C2	1.339(3)		C4	C3	1.383(3)

Table S39. Bond Angles for **10.**

Atom	Atom	Atom	Angle/°		Atom	Atom	Atom	Angle/°
Cl2	Tc1	Cl1	175.11(2)		C4	N1	Tc1	122.33(15)
O1	Tc1	Cl2	91.36(5)		C6	N4	C7	115.8(2)
O1	Tc1	Cl1	83.85(5)		C3	N2	C2	115.8(2)
O1	Tc1	N3	90.79(7)		N4	C6	C5	122.6(2)
O1	Tc1	N1	88.36(7)		N3	C5	C6	120.9(2)
O2	Tc1	Cl2	98.18(5)		C17	C16	C15	112.9(2)
O2	Tc1	Cl1	86.65(5)		O1	C9	C10	109.95(18)
O2	Tc1	O1	170.25(7)		C9	C10	C11	113.29(19)
O2	Tc1	N3	91.38(7)		C13	C12	C11	113.8(2)
O2	Tc1	N1	89.66(7)		C12	C13	C14	114.7(2)
N3	Tc1	Cl2	89.01(5)		C16	C17	C18	115.3(2)
N3	Tc1	Cl1	90.11(5)		C16	C15	C14	115.3(2)
N3	Tc1	N1	178.53(7)		C13	C14	C15	113.3(2)
N1	Tc1	Cl2	89.81(5)		C12	C11	C10	112.91(19)
N1	Tc1	Cl1	91.00(5)		N1	C1	C2	121.4(2)
C9	O1	Tc1	147.84(13)		N3	C8	C7	120.4(2)
C5	N3	Tc1	121.74(14)		N2	C2	C1	122.5(2)
C5	N3	C8	117.19(19)		N1	C4	C3	120.9(2)

C8	N3	Tc1	121.07(15)		N2	C3	C4	122.8(2)
C1	N1	Tc1	121.12(15)		N4	C7	C8	123.1(2)
C1	N1	C4	116.5(2)					

Table S40. Hydrogen Bonds for **10.**

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
C9	H9A	N2[1]	0.97(2)	2.55(2)	3.438(3)	151.6(19)
C6	H6	N4[2]	0.93(3)	2.56(3)	3.233(3)	130(2)

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

Table S41. Torsion Angles for **10.**

A	B	C	D	Angle/°		A	B	C	D	Angle/°
Tc1	O1	C9	C10	-170.83(19)		C5	N3	C8	C7	0.4(3)
Tc1	N3	C5	C6	-179.12(16)		C16	C15	C14	C13	-179.8(2)
Tc1	N3	C8	C7	179.60(17)		C9	C10	C11	C12	-178.6(2)
Tc1	N1	C1	C2	178.87(18)		C12	C13	C14	C15	178.8(2)
Tc1	N1	C4	C3	-179.63(16)		C13	C12	C11	C10	-177.4(2)
Cl2	Tc1	O1	C9	-174.2(3)		C17	C16	C15	C14	178.9(2)
Cl1	Tc1	O1	C9	6.7(3)		C15	C16	C17	C18	179.5(2)
O1	C9	C10	C11	178.8(2)		C11	C12	C13	C14	179.1(2)
N3	Tc1	O1	C9	96.7(3)		C1	N1	C4	C3	0.9(3)
N3	C8	C7	N4	-0.6(4)		C8	N3	C5	C6	0.1(3)
N1	Tc1	O1	C9	-84.5(3)		C2	N2	C3	C4	-1.0(3)
N1	C1	C2	N2	1.2(4)		C4	N1	C1	C2	-1.7(3)
N1	C4	C3	N2	0.4(3)		C3	N2	C2	C1	0.2(3)
N4	C6	C5	N3	-0.4(3)		C7	N4	C6	C5	0.2(3)
C6	N4	C7	C8	0.3(3)						

Hirshfeld surface analysis and DFT colculations part

Table S42. Energies (kJ/mol) of intermolecular interactions for structure **1**.

	N	Symop	R	Electron Density	E_ele	E_pol	E_dis	E_rep	E_tot
	2	x, y, z	7.01	HF/3-21G	-9.1	-4.2	-8.6	4.0	-16.5
	1	-	6.95	HF/3-21G	0.0	nan	0.0	0.0	nan
	2	x, y, z	11.88	HF/3-21G	3.4	-0.4	-2.0	0.0	1.4
	2	x, -y+1/2, z+1/2	9.37	HF/3-21G	-10.8	-4.6	-12.4	11.0	-16.3
	2	-x, y+1/2, -z+1/2	6.91	HF/3-21G	-10.6	-9.2	-43.2	31.8	-29.9
	1	-x, -y, -z	7.35	HF/3-21G	-45.2	-12.8	-26.3	25.6	-57.3
	1	-	2.00	HF/3-21G	-10.6	-9.2	-43.2	31.8	-29.9
	1	-	5.51	HF/3-21G	3.4	-0.4	-2.0	0.0	1.4
	1	-	8.03	HF/3-21G	0.5	-0.1	-2.8	0.0	-2.1

	2	x, -y+1/2, z+1/2	10.63	HF/3-21G	-2.0	-1.4	-8.3	4.3	-6.9
	2	-x, y+1/2, -z+1/2	6.97	HF/3-21G	-49.1	-14.9	-49.5	44.0	-68.6
	1	-x, -y, -z	8.83	HF/3-21G	1.0	-1.0	-10.4	6.7	-3.5
	1	-x, -y, -z	8.88	HF/3-21G	-36.2	-8.6	-13.6	29.2	-31.0

Energy Model	k_ele	k_pol	k_disp	k_rep
CE-HF ... HF/3-21G electron densities	1.019	0.651	0.901	0.811
CE-B3LYP ... B3LYP/6-31G(d,p) electron densities	1.057	0.740	0.871	0.618

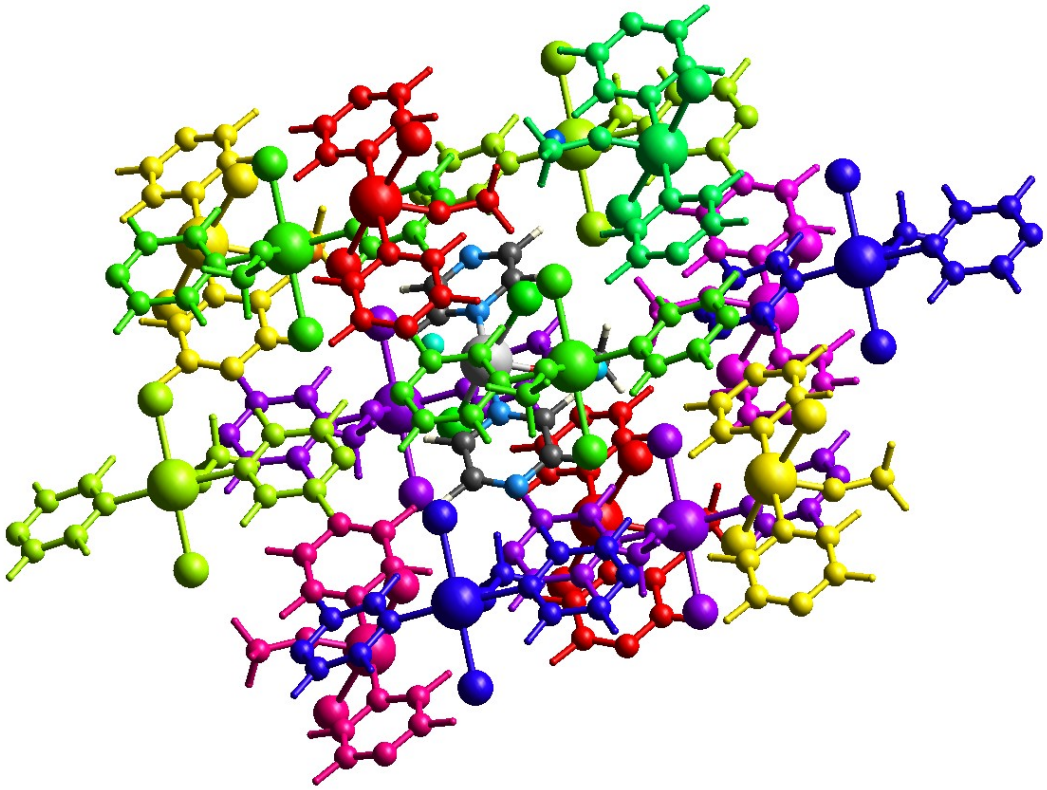

Figure S1. Cluster of molecules around the selected molecule of **1** (3.8 Å) for generate energies.

Table S43. Energies (kJ/mol) of intermolecular interactions for structure **5**.

	N	Symop	R	Electron Density	E_ele	E_pol	E_dis	E_rep	E_tot
	2	x+1/2, -y+1/2, z+1/2	9.94	HF/3-21G	-27.1	-6.5	-14.4	17.1	-31.0
	1	-x, -y, -z	8.01	HF/3-21G	-18.3	-9.0	-18.3	20.8	-24.2
	1	-	8.49	HF/3-21G	0.0	nan	0.0	0.0	nan
	2	-x+1/2, y+1/2, -z+1/2	7.12	HF/3-21G	4.6	-9.6	-31.8	16.0	-17.1
	2	x+1/2, -y+1/2, z+1/2	8.95	HF/3-21G	-27.7	-6.8	-26.7	19.0	-41.4
	1	-x, -y, -z	12.68	HF/3-21G	-1.7	-0.7	-8.6	0.0	-10.0

	2	x, y, z	8.82	HF/3-21G	-22.9	-11.4	-38.1	33.0	-38.3
	1	-x, -y, -z	10.30	HF/3-21G	-4.1	-1.0	-33.5	16.4	-21.6
	2	-x+1/2, y+1/2, -z+1/2	10.18	HF/3-21G	-0.9	-0.4	-16.7	6.8	-10.7
	1	-x, -y, -z	6.86	HF/3-21G	-15.8	-14.0	-31.1	26.1	-32.1
	1	-	2.55	HF/3-21G	-27.1	-6.5	-14.4	17.1	-31.0
	1	-	4.71	HF/3-21G	-18.3	-9.0	-18.3	20.8	-24.2
	1	-	6.44	HF/3-21G	-1.7	-0.7	-8.6	0.0	-10.0

Energy Model	k_ele	k_pol	k_disp	k_rep
CE-HF ... HF/3-21G electron densities	1.019	0.651	0.901	0.811
CE-B3LYP ... B3LYP/6-31G(d,p) electron densities	1.057	0.740	0.871	0.618

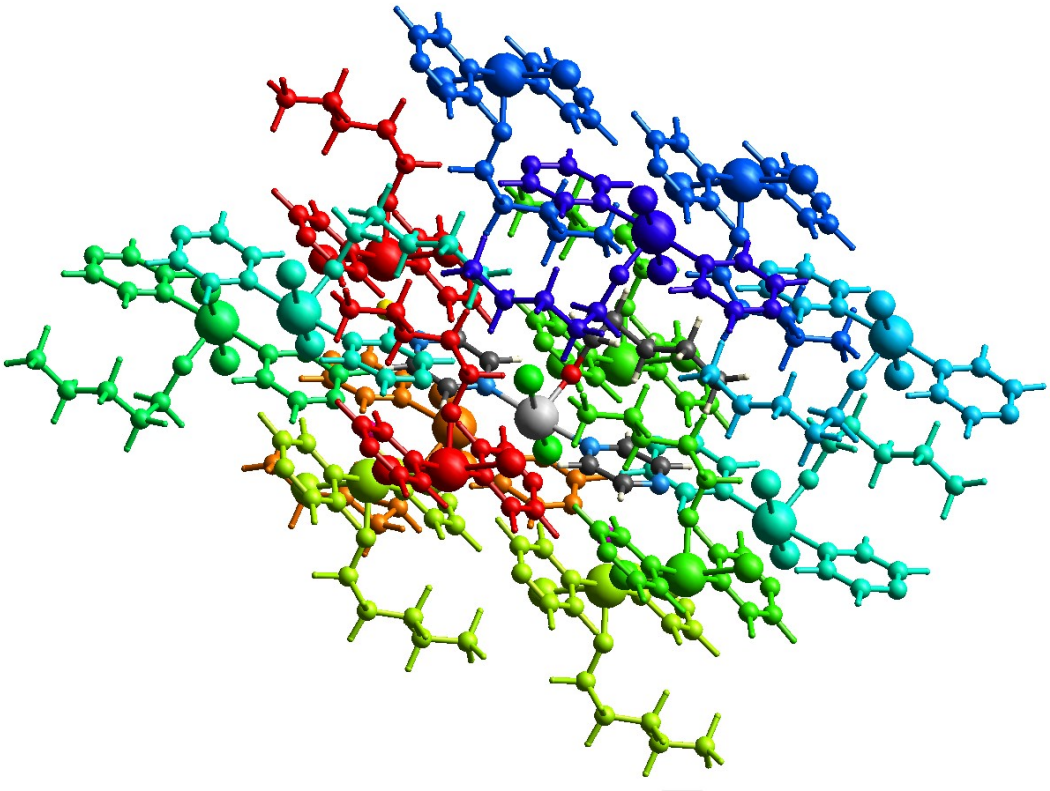

Figure S2. Cluster of molecules around the selected molecule of **5** (3.8 Å) for generate energies.

Table S44. Energies (kJ/mol) of intermolecular interactions for structure **1**.

	N	Symop	R	Electron Density	E_ele	E_pol	E_dis	E_rep	E_tot
	1	-x, -y, -z	13.99	HF/3-21G	-6.5	-4.1	-11.4	0.0	-19.6
	2	x, y, z	8.59	HF/3-21G	-10.7	-7.4	-47.0	32.3	-32.0
	1	-x, -y, -z	10.80	HF/3-21G	-33.1	-14.7	-29.8	27.0	-48.3

	2	x, y, z	6.88	HF/3-21G	-42.3	-22.0	-69.4	54.8	-75.5
	1	-x, -y, -z	13.22	HF/3-21G	-23.1	-4.1	-36.9	0.0	-59.5
	1	-	5.09	HF/3-21G	0.0	nan	0.0	0.0	nan
	1	-x, -y, -z	12.01	HF/3-21G	4.7	-0.8	-19.2	0.0	-13.0
	1	-x, -y, -z	17.25	HF/3-21G	20.9	-0.1	-36.0	0.0	-11.2
	1	-x, -y, -z	14.29	HF/3-21G	29.4	-2.6	-68.6	0.0	-33.6
	1	x, y, z	13.55	HF/3-21G	1.6	-0.2	-1.7	0.0	0.0
	1	-x, -y, -z	18.95	HF/3-21G	-6.0	-0.0	-13.1	0.0	-17.9
	2	x, y, z	7.64	HF/3-21G	-27.4	-10.1	-18.8	16.9	-37.7
	1	-	7.23	HF/3-21G	7.4	-1.5	-7.3	0.4	0.3
	1	-	4.30	HF/3-21G	-42.3	-22.0	-69.4	54.8	-75.5
Energy Model						k_ele	k_pol	k_disp	k_rep
CE-HF ... HF/3-21G electron densities						1.019	0.651	0.901	0.811
CE-B3LYP ... B3LYP/6-31G(d,p) electron densities						1.057	0.740	0.871	0.618

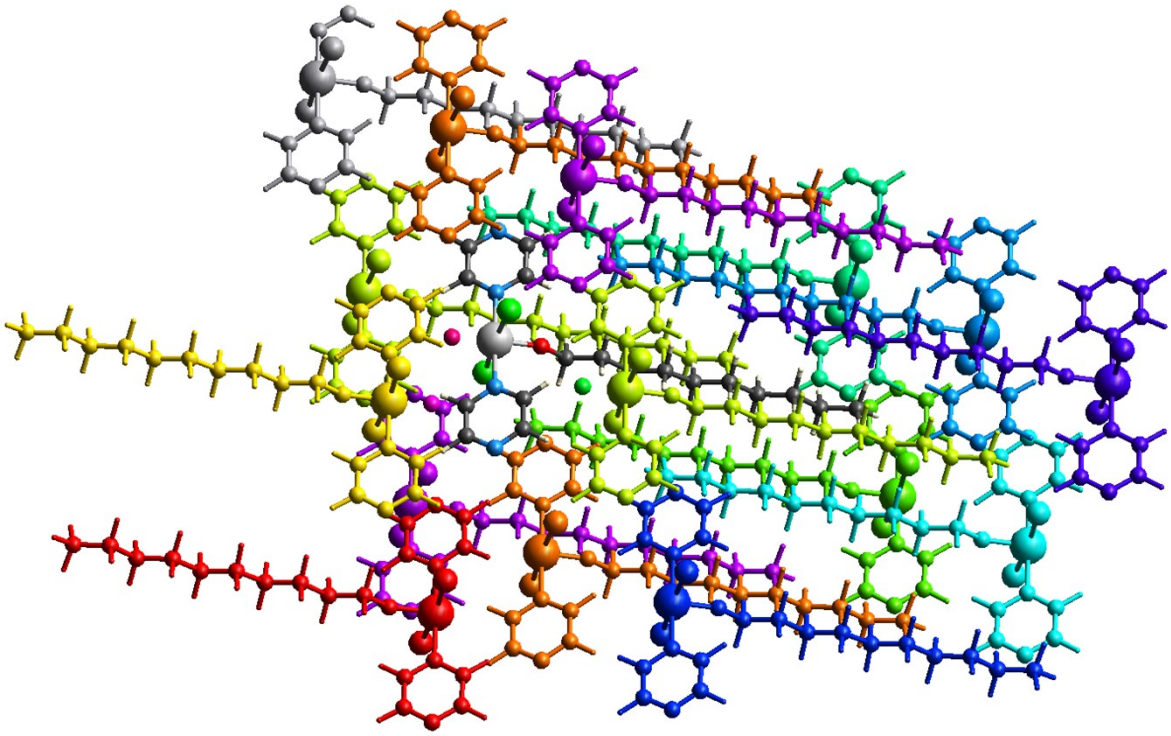

Figure S3. Cluster of molecules around the selected molecule of **10** (3.8 Å) for generate energies.

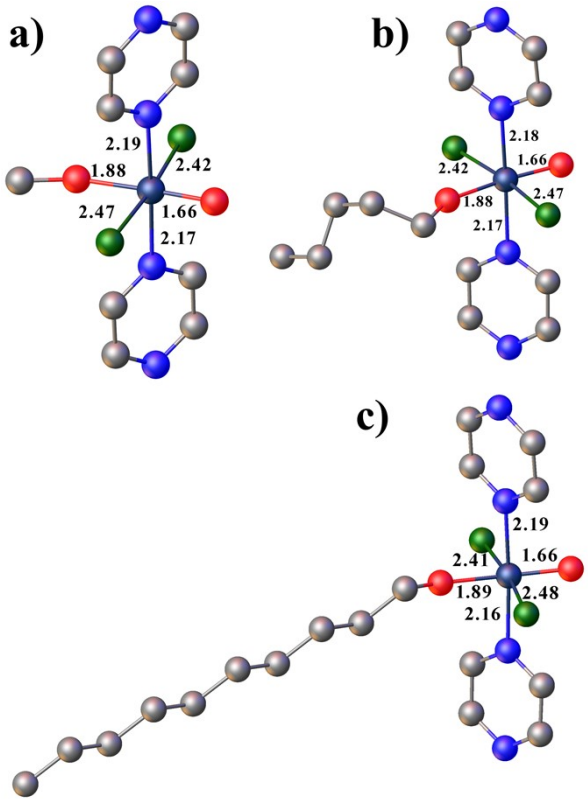

Figure S4. DFT optimized models of structures **1**(a), **5**(b) and **10**(c). Hydrogen atoms omitted for clarity. Distances are given in angstroms.

pXRD part

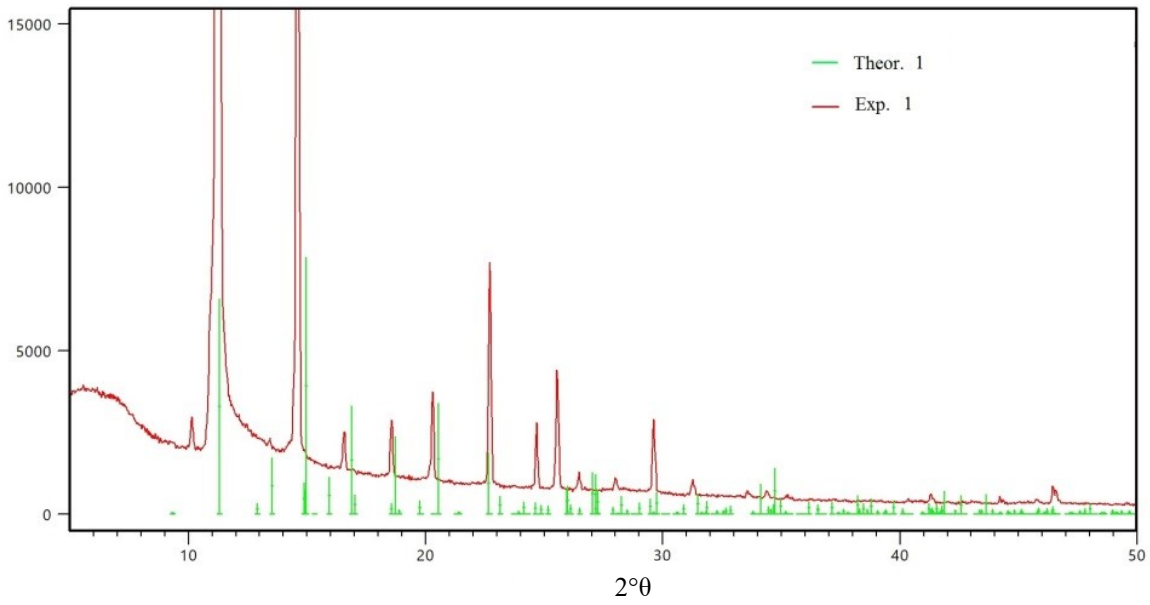

Figure S5.1. pXRD of compound **1**.

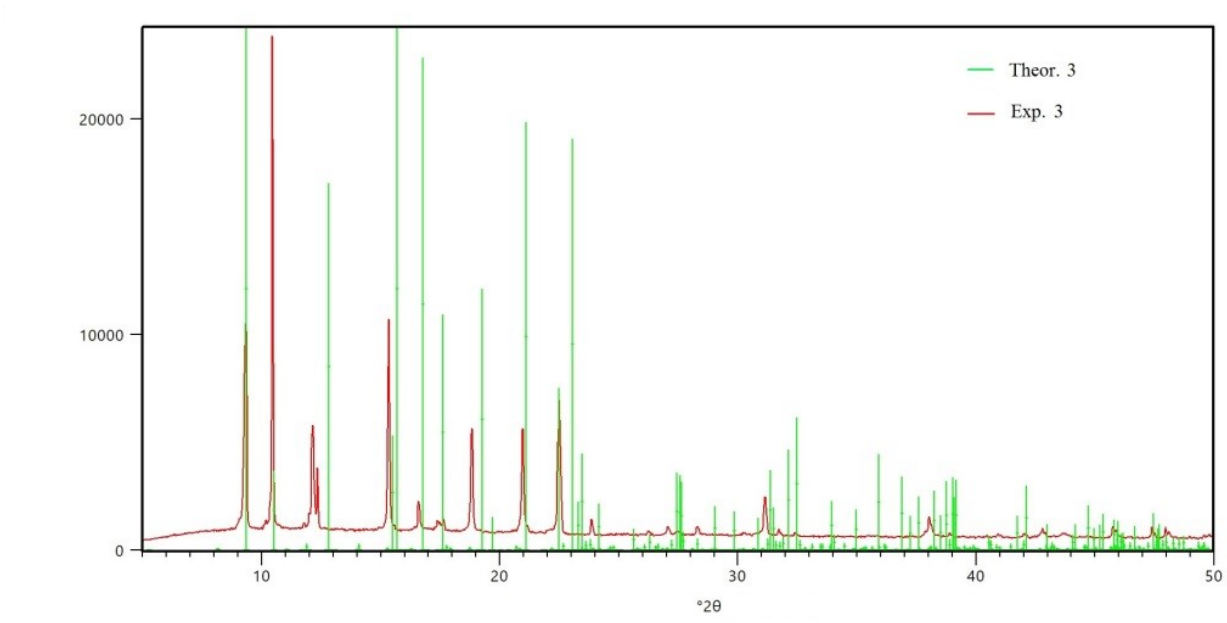

Figure S5.2. pXRD of compound **3**.

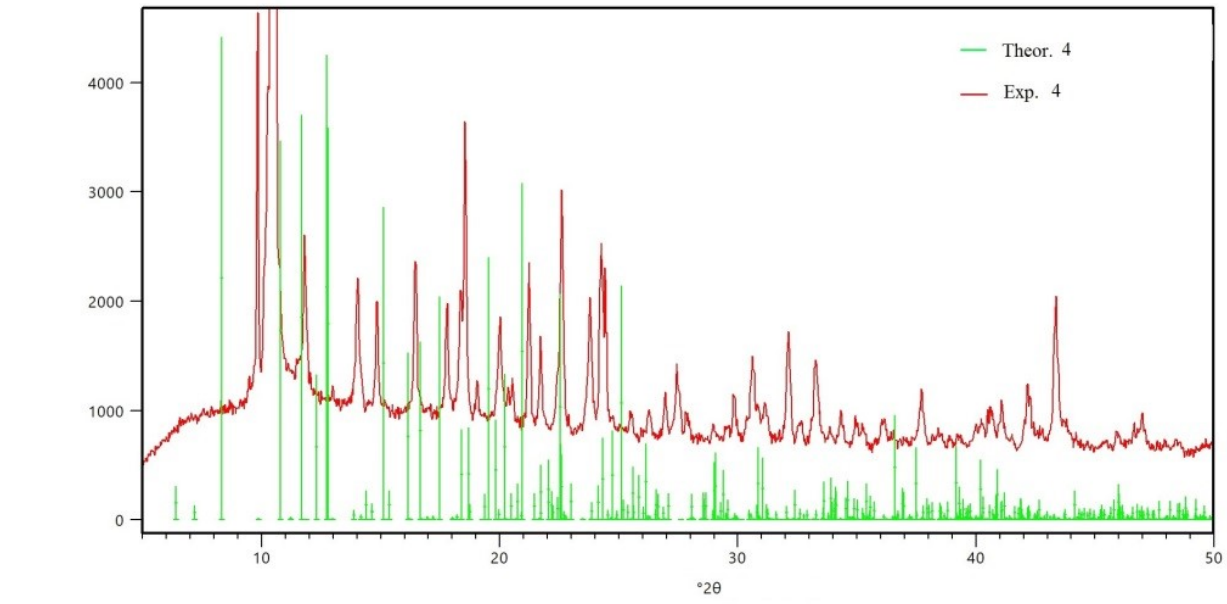

Figure S5.3. pXRD of compound **4**.

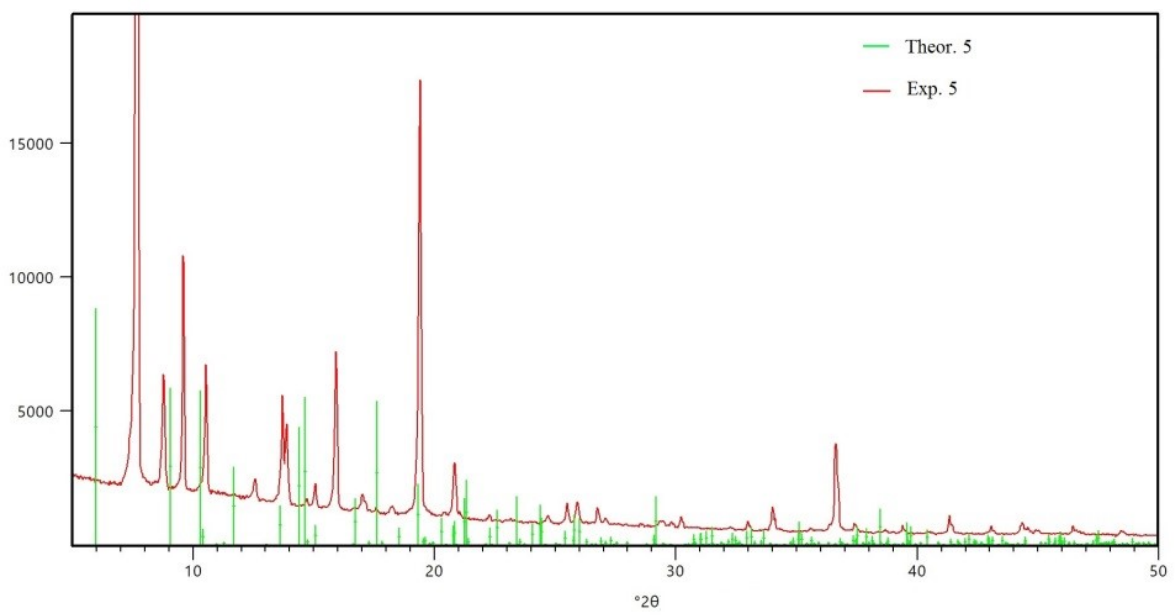

Figure S5.4. pXRD of compound **5**.

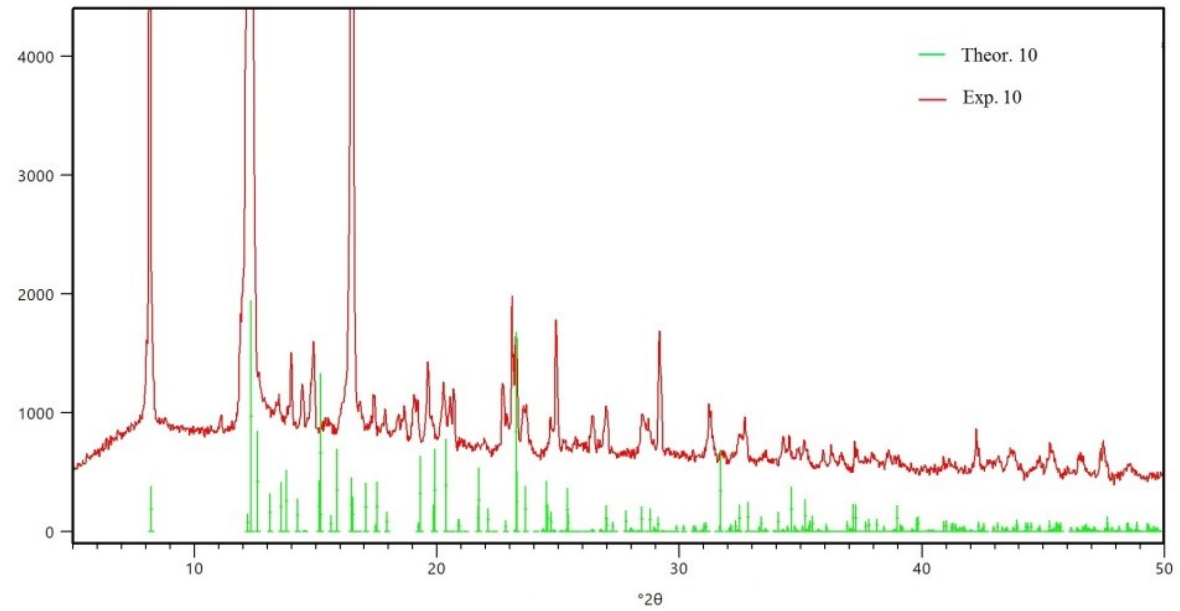

Figure S5.5. pXRD of compound **10**.

DTA and MALDI-LI mass-spectroscopy part

Heating was carried out in a reducing atmosphere (Ar + 1.5% H_2) to avoid the formation of volatile technetium compounds. The thermal decomposition of homologous complexes occurs in the temperature range 130 - 400°C and includes in at least 3 stages, the waves of which are shown in the thermolysis curves of all complexes. According to pXRD data, the final Tc-containing decomposition product is a mixture of metal and its carbide; the residual mass after heating to 1000°C does not depend on the composition of

the complex and is in the range of 47-55%. PXRD results for the non-covalent reductive thermolysis residue of **7** are shown in the figure S8 in SI.

The first stage of decomposition for all compounds corresponds to two sequential processes, as can be clearly seen in the curves of compounds **3** and **7**. For the compound **1**, apparently due to the rather high initial temperature of decomposition, both stages occur almost simultaneously and there is no noticeable response in the curves TG and DTA. The total mass loss for all compounds is about 14-16%. Presumably the first stage is the sequential elimination of one oxygen atom and one chlorine atom. The onset of decomposition is accompanied by an endothermic effect (Figure S6 and S7 in SI) and presumably occurs with a change in the oxidation state of the metal to a lower one. The first stage thermolysis temperature ranges are (°C): **1**- 158 – 188; **3**- 144 – 185; **7**- 130 – 188; **9**- 116 – 189. The second stage of thermolysis occurs with a mass loss of the order of 7-10%, which corresponds to the second chlorine atom elimination. The process is accompanied by an exothermic effect. Temperature ranges of the second stage of thermolysis are (°C): **1**- 259 – 280; **3**- 225 – 254; **7**- 198 – 230; **9**- 206 – 240. The third stage of decomposition probably corresponds to several processes occurring sequentially. The mass loss ranged from 24% for **1** and 31% for **3**, the compounds **7** and **9** continued to lose mass until the end of the experiment. The third stage probably corresponds to the decomposition of organic components, the reduction of technetium to a metallic form and is accompanied by an exothermic effect. The decomposition of pyrazine and heavy aliphatic residues under conditions of oxygen deficiency leads to the accumulation of carbon in the residue. Heating metallic technetium in the presence of carbon residues leads to the formation of a carbide phase, detected by X-ray phase analysis. The third stage of decomposition of the compounds **1** and **3** occurs in the temperature ranges (°C): **1**- 333 – 420; **3**- 316 – 560. The described temperature ranges for the thermolysis of **1** roughly coincide with the temperature ranges earlier shown in the [1].

The approximately equal loss of mass at all stages of decomposition for all complexes suggests that the cleavage of the Tc-O-R bond and the elimination of the O-R group, oddly enough, is one of the last to occur. This statement is also supported by the fact that the stages of thermolysis of the complexes differ in the temperatures at which the reaction begins and ends, which indicates differences in the composition of the decomposition products.

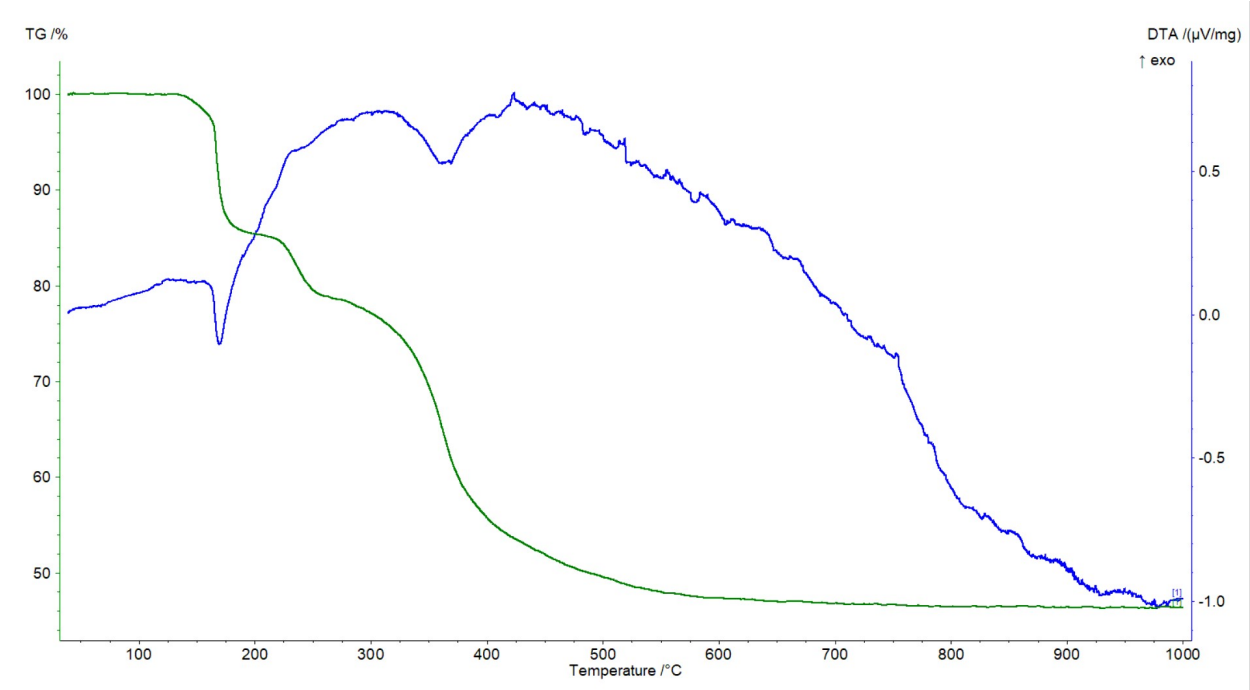

Figure S6. TG and DTA cursives of compound **3**

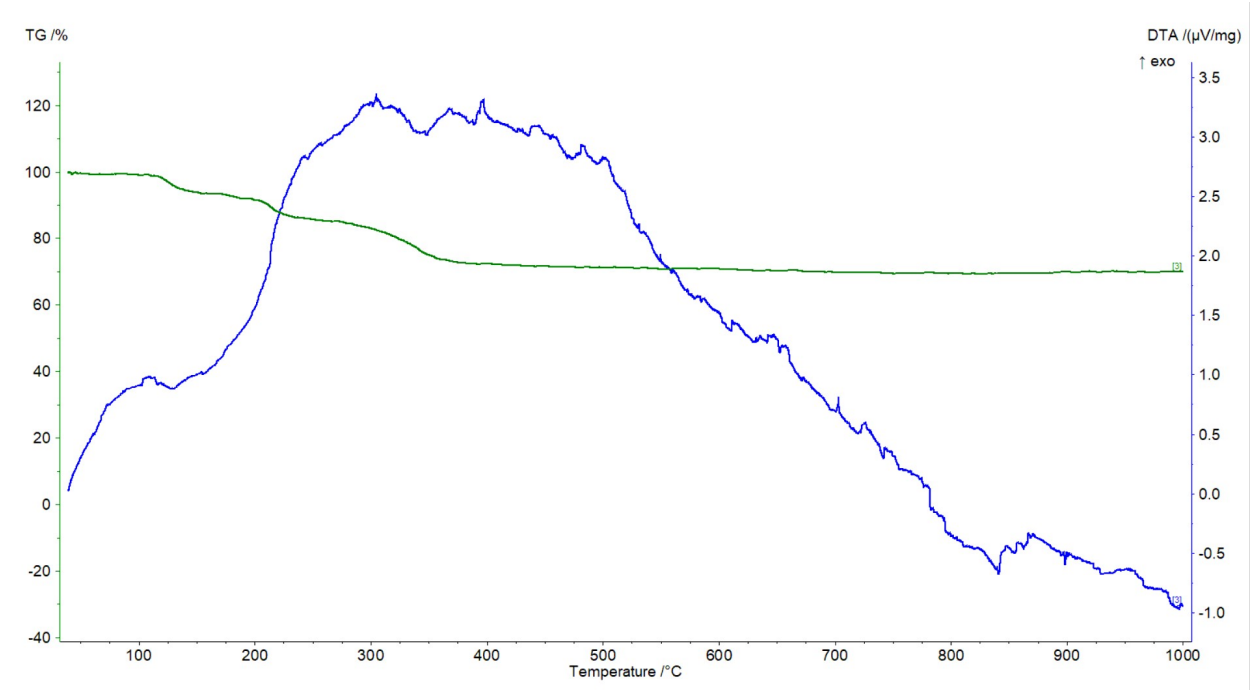

Figure S7. TG and DTA cursives of compound **9**

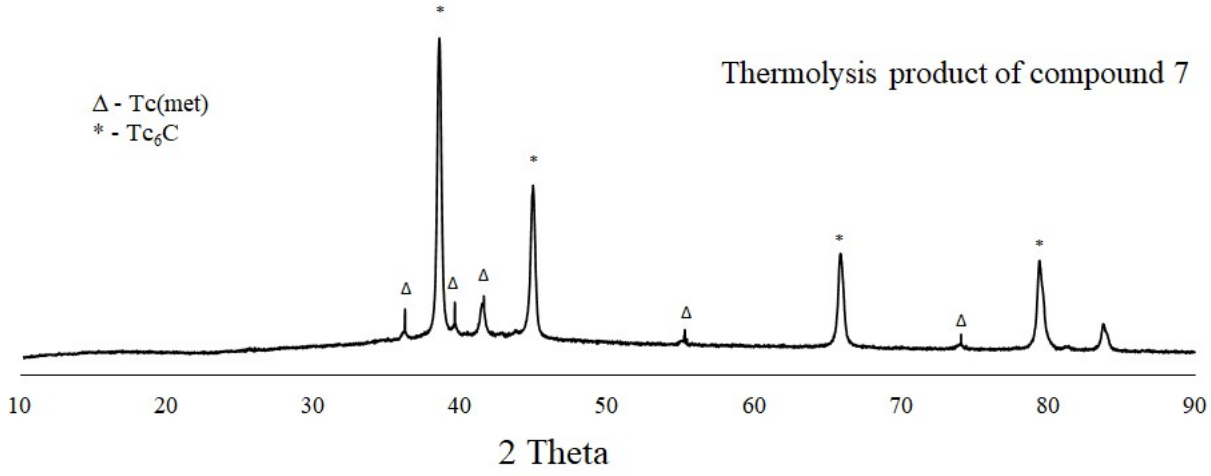

Figure S8. PXRD of product of thermolysis of **7**

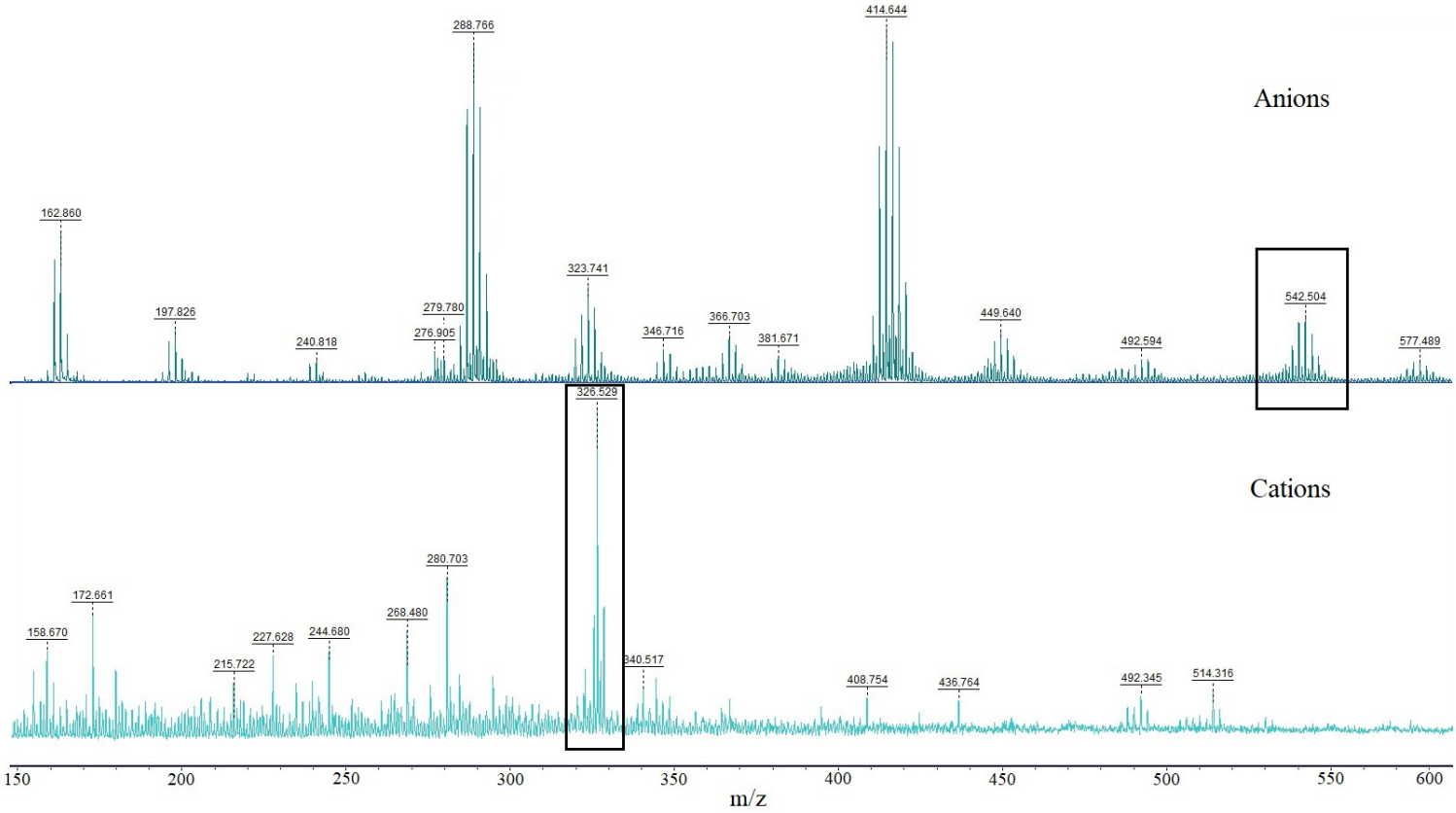

Figure S9. MALDI-LI mass-spectroscopy dried methanol solution of **1**

From residual organic signals it was possible to identify a multiplet with mass 542.504 (calc. 542.514 a.m.u.), presumably corresponding to a molecular anion $[Tc(V)OCl_3(N_2C_4H_4)\times 2Cl_2\times ClO_4]^-$ and a multiplet with mass 326.529 (Calc. 326.64 a.m.u.) of the cation $[Tc(V)O_2Cl(N_2C_4H_4)_2OH]^+$ (the proposed structural formulas are given in the table S45). In the light mass region, the ions did not contain organic fragments from either methanol or chloroform precipitates. In **1**, also no particles with a fragment O-R were detected. The LI spectra are shown in Figure S9.

Table S45. Correspondence of the peaks recorded in the cationic and anionic mass spectra (LI-MALDI) to the expected formulas of molecular ions.

	m/z, a.m.u.	possible structural formula
Found	326.529	
Calc.	326.64	
Found	542,504	
Calc.	542.514	

IR and UV-Vis spectroscopy part

Infrared spectroscopy (ATR) of **3**, **4**, **5**, **6**, **7**, **9** and **10** expectedly showed similar results (Figure S10). The list of peaks for each of the listed compounds is given in the table S46. The bulk of the peaks correspond to vibrations of organic fragments of the aliphatic substituent (cm^{-1}): CH_2 720-740 (δ), 2915-2940 (ν_{as}) 2845-2870 (νs) 1440-1480 (δ); CH_3 1370-1385 (δs), 2950-2975 (ν_{as}), 2860-2885 (νs), 1435-1470 (δ_{as}), C-O 1050-1260; pyrazine: CH 3030-3080 (νCH); aromatic ring vibrations 1575-1600, 1475-1525, 1575-1590 cm^{-1}. Pyrazine vibrations are mostly consistent with literature data 2,3. Tc=O vibrations are in ranges 920-890, 850-840 cm^{-1}. Unfortunately, the vibrations of the Tc-Cl and Tc-N bonds lie in the short-wave region up to 600 cm^{-1} and are not displayed on the spectrum. There is no shift in the absorption bands with increasing length of the hydrocarbon substituent.

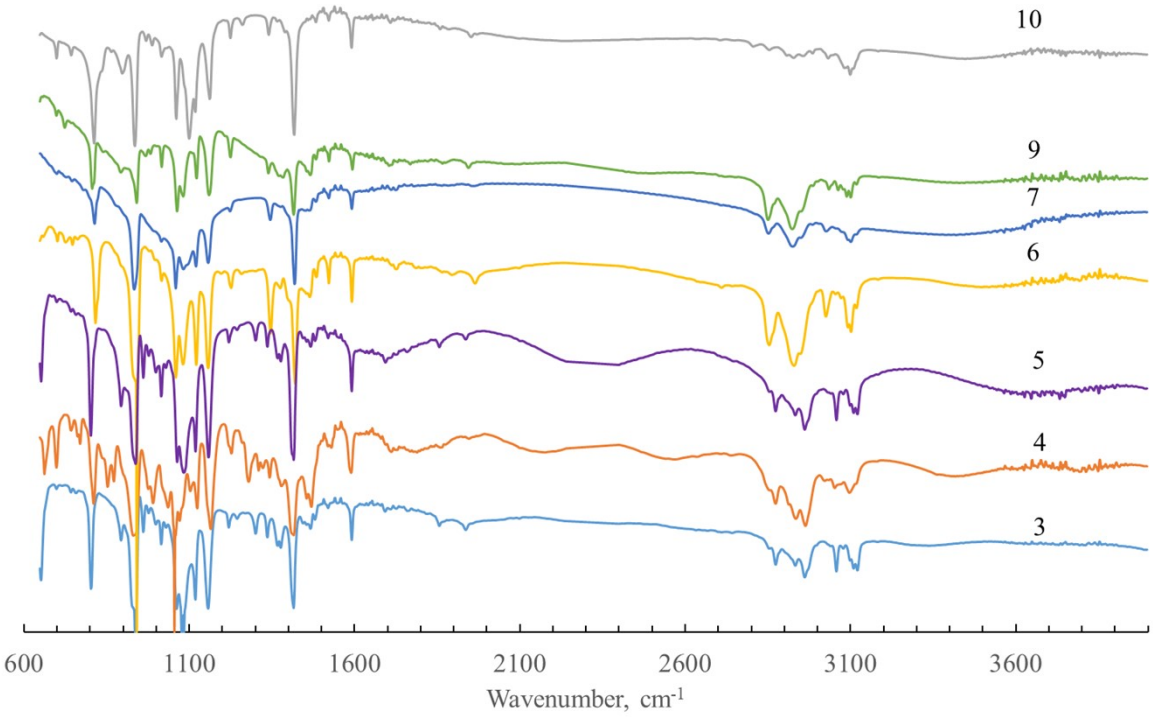

Figure S10. Infrared spectroscopy of the compounds **3**, **4**, **5**, **6**, **7**, **9**, **10**.

Table S46. The list of peaks IR-spectrum of compounds **3**, **4**, **5**, **6**, **7**, **9**, **10**

3		**4**		**5**		**6**		**7**		**9**		**10**	
cm^{-1}	Intens, a.u.	cm^{-1}	Intens, a.u.+50	cm^{-1}	Intens, a.u.+100	cm^{-1}	Intens, a.u.+150	cm^{-1}	Intens, a.u.+200	cm^{-1}	Intens, a.u.+250	cm^{-1}	Intens, a.u.+300
652	34	661	104	652	165	661	261	698	301	698	340	698	377
698	94	698	108	663	209	702	257	746	296	723	332	744	380
742	91	742	133	698	343	727	256	814	268	806	291	812	321
758	91	760	128	744	211	746	255	821	284	812	295	835	369
802	28	812	85	758	208	762	258	879	280	841	316	866	382
893	60	839	114	802	129	816	203	933	225	893	302	897	367
941	0	852	95	814	187	823	219	991	264	931	296	935	320
960	65	871	99	868	188	895	240	1016	257	941	282	968	389
978	78	893	100	893	148	935	166	1059	226	968	313	987	386
999	70	941	0	937	110	941	0	1082	238	983	315	1016	378
1014	57	960	107	960	167	976	251	1095	242	1016	306	1061	338
1030	68	976	94	978	181	993	245	1120	240	1062	277	1088	357
1057	62	991	85	999	171	1016	231	1155	243	1082	286	1099	324
1080	0	1014	95	1030	174	1053	163	1224	277	1120	299	1118	342
1118	21	1035	82	1062	112	1082	176	1344	271	1161	288	1163	351
1157	15	1055	0	1086	105	1120	175	1396	274	1224	312	1224	391
1219	68	1070	73	1118	118	1157	173	1419	229	1340	302	1259	399
1244	74	1080	82	1157	115	1196	136	1468	278	1371	300	1340	393
1302	65	1103	92	1219	190	1226	226	1483	283	1383	299	1365	402
1336	62	1124	81	1246	199	1259	235	1522	285	1415	274	1390	395
1367	56	1161	71	1300	191	1344	215	1552	291	1468	301	1417	327
1377	55	1223	121	1336	187	1375	226	1591	278	1485	312	1483	401
1415	15	1259	124	1367	180	1406	216	1726	291	1524	310	1522	402
1456	70	1280	99	1375	178	1423	166	2851	262	1552	318	1552	408
1466	68	1309	106	1415	113	1464	220	2924	523	1593	304	1591	384
1481	74	1323	108	1468	188	1485	233	2955	260	1711	307	1709	401
1520	81	1342	101	1479	191	1522	230	2984	268	1942	305	1952	391

1551	84	1371	100	1520	193	1551	247	3028	264	2851	271	2803	385
1591	60	1379	96	1551	194	1591	217	3090	258	2868	2881	2858	383
1853	70	1415	63	1591	158	1726	238	3100	256	2924	265	2907	379
1936	67	1456	88	1693	177	1965	229	3121	262	2951	277	2928	378
2853	54	1469	82	1859	189	2855	189			2984	293	2959	379
2874	44	1458	112	1934	192	2932	175			3034	291	2984	381
2912	44	1713	118	2855	158	2947	183			3059	291	3032	377
2961	35	2853	93	2872	145	2984	217			3088	286	3080	371
2972	41	2872	84	2932	142	3024	207			3100	286	3100	367
3057	39	2912	83	2961	133	3055	222			3121	295	3109	371
3076	55	2934	74	2974	141	3073	220						
3098	47	2965	70	3057	139	3102	197						
3109	41	3021	99	3076	156	3092	197						
3121	40	3051	94	3105	147	3117	213						
		3096	91	3109	144								
		3117	97	3121	143								

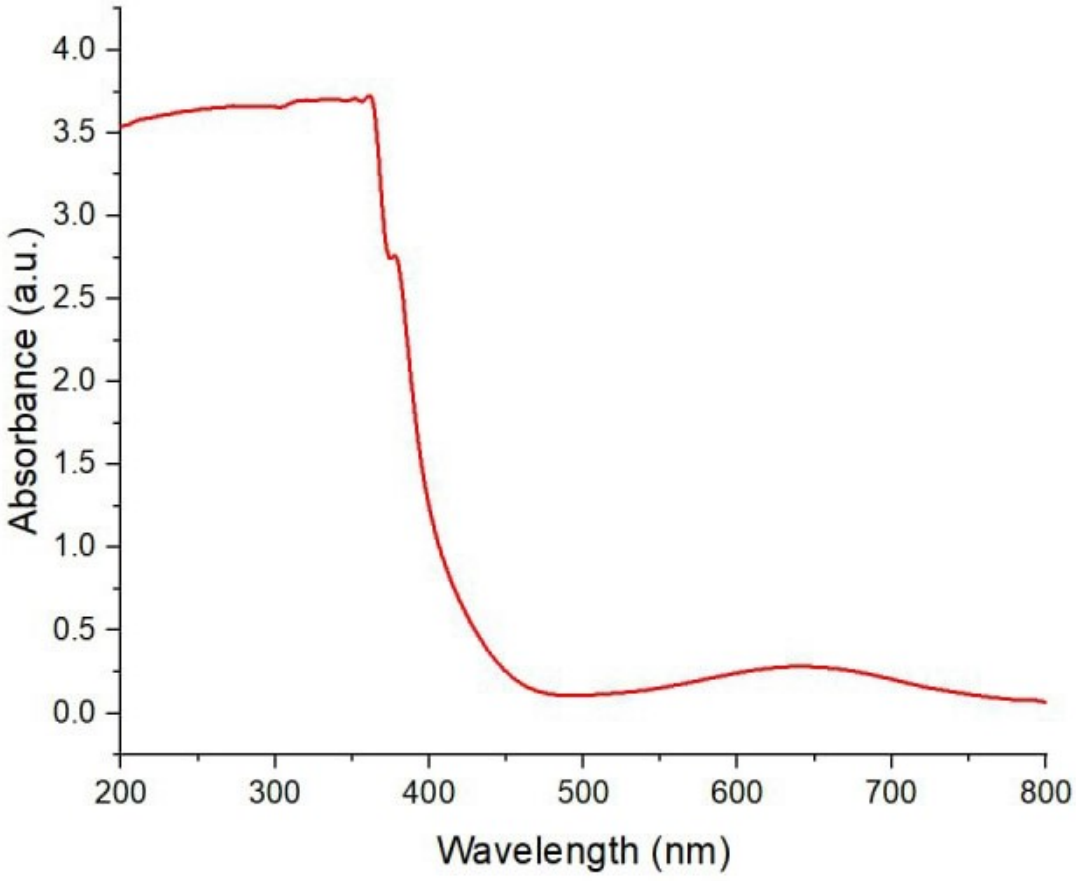

Figure S11. The full experimental spectrum of compound **3** in PrOH (*c*[Tc] = 5 mmol/l) at the moment crystal growth begins.

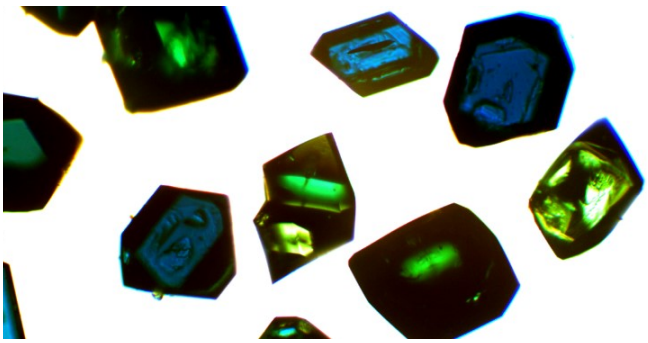

Figure S12. Photograph of crystals of compound **3**. Magnification 30x, polarized light.

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