

Supporting Information for

Crystallographic Insights into (ImHR)₂[TcBr₆] (Im = imidazole, R = H, Me, Et): Non-Covalent Interactions and Mass Spectrometry

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Table S1. Bond Lengths for **I** at 100K.

Atom	Atom	Length/Å		Atom	Atom	Length/Å
Tc1	Br1 ¹	2.5287(4)		N1	C5	1.379(5)
Tc1	Br1	2.5287(4)		N1	C2	1.319(5)
Tc1	Br2	2.5210(4)		N3	C4	1.380(5)
Tc1	Br2 ¹	2.5210(4)		N3	C2	1.325(6)
Tc1	Br3 ¹	2.5568(4)		C5	C4	1.357(6)
Tc1	Br3	2.5568(4)				

¹1-X,1-Y,1-Z

Table S2. Bond Angles for **I** at 100K.

Atom	Atom	Atom	Angle/°		Atom	Atom	Atom	Angle/°
Br1 ¹	Tc1	Br1	180.0		Br2	Tc1	Br3	89.150(12)
Br1	Tc1	Br3	91.005(12)		Br2	Tc1	Br3 ¹	90.850(12)
Br1	Tc1	Br3 ¹	88.995(12)		Br2 ¹	Tc1	Br3 ¹	89.151(12)
Br1 ¹	Tc1	Br3	88.995(13)		Br2 ¹	Tc1	Br3	90.849(12)
Br1 ¹	Tc1	Br3 ¹	91.005(12)		Br3	Tc1	Br3 ¹	180.0
Br2	Tc1	Br1 ¹	89.746(12)		C2	N1	C5	109.5(3)
Br2 ¹	Tc1	Br1 ¹	90.254(12)		C2	N3	C4	109.8(4)
Br2 ¹	Tc1	Br1	89.745(12)		C4	C5	N1	106.8(3)
Br2	Tc1	Br1	90.255(12)		C5	C4	N3	106.0(4)
Br2	Tc1	Br2 ¹	180.0		N1	C2	N3	107.9(4)

¹1-X,1-Y,1-Z

Table S3. Hydrogen Bonds for **I** at 100K.

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
N1	H1	Br2 ¹	0.88	2.75	3.420(3)	133.6
N3	H3	Br2 ²	0.88	2.95	3.483(4)	120.4
N3	H3	Br3	0.88	2.73	3.447(3)	139.0

$^11+X,1/2-Y,1/2+Z; ^2+X,1/2-Y,1/2+Z$

Table S4. Torsion Angles for **I** at 100K.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
N1	C5	C4	N3	0.8(4)	C2	N1	C5	C4	-0.2(4)
C5	N1	C2	N3	-0.5(4)	C2	N3	C4	C5	-1.1(4)
C4	N3	C2	N1	1.0(4)					

Table S5. Bond Lengths for **II**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Tc1	Br1	2.5032(3)	N1	C1	1.330(3)
Tc1	Br1 ¹	2.5032(3)	N1	C3	1.328(3)
Tc1	Br2 ¹	2.5150(3)	N2	C1	1.382(3)
Tc1	Br2	2.5150(3)	N2	C4	1.352(3)
Tc1	Br3 ¹	2.5207(3)	C1	C2	1.464(3)
Tc1	Br3	2.5207(3)	C3	C4	1.382(3)

$^1-X,-Y,1-Z$

Table S6. Bond Angles for **II**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
Br1	Tc1	Br1 ¹	180.0	Br2 ¹	Tc1	Br3	88.590(9)
Br1 ¹	Tc1	Br2	90.361(10)	Br2 ¹	Tc1	Br3 ¹	91.410(9)
Br1	Tc1	Br2	89.640(9)	Br2	Tc1	Br3 ¹	88.591(8)
Br1 ¹	Tc1	Br2 ¹	89.639(9)	Br3	Tc1	Br3 ¹	180.0
Br1	Tc1	Br2 ¹	90.360(9)	C3	N1	C1	108.12(19)
Br1	Tc1	Br3	90.069(11)	C4	N2	C1	107.15(18)
Br1	Tc1	Br3 ¹	89.931(11)	N1	C1	N2	108.91(18)
Br1 ¹	Tc1	Br3 ¹	90.069(11)	N1	C1	C2	125.46(19)
Br1 ¹	Tc1	Br3	89.931(11)	N2	C1	C2	125.63(18)
Br2 ¹	Tc1	Br2	180.0	N1	C3	C4	109.35(19)
Br2	Tc1	Br3	91.409(9)	N2	C4	C3	106.48(19)

$^1-X,-Y,1-Z$

Table S7. Hydrogen Bonds for **II**.

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
N1	H1	Br1 ¹	0.88	3.01	3.476(2)	115.4
N1	H1	Br3	0.88	2.96	3.677(2)	139.7
N2	H2	Br1 ²	0.88	2.92	3.675(2)	144.6
C3	H3	Br3 ³	0.95	2.79	3.451(2)	127.6

$^11+X,+Y,+Z; ^2-X,1-Y,-Z; ^31-X,-Y,1-Z$

Table S8. Torsion Angles for **II**.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
N1	C3	C4	N2	0.3(3)	C3	N1	C1	C2	-179.91(19)
C1	N1	C3	C4	-0.1(3)	C4	N2	C1	N1	0.4(2)
C1	N2	C4	C3	-0.4(2)	C4	N2	C1	C2	-179.9(2)
C3	N1	C1	N2	-0.2(2)					

Table S9. Bond Lengths for **III**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Tc1	Br1 ¹	2.5060(12)	N1	C1	1.330(9)
Tc1	Br1	2.5060(12)	N1	C3	1.372(9)
Tc1	Br2 ¹	2.5190(7)	N2	C1	1.324(8)
Tc1	Br2	2.5190(7)	N2	C4	1.374(10)
Tc1	Br3 ¹	2.4978(12)	C1	C2	1.479(10)
Tc1	Br3	2.4978(12)	C3	C4	1.328(11)

¹1-X,1-Y,+Z

Table S10. Bond Angles for **III**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
Br1 ¹	Tc1	Br1	89.85(6)	Br3	Tc1	Br2 ¹	90.29(4)
Br1 ¹	Tc1	Br2 ¹	91.23(4)	Br3	Tc1	Br2	89.23(4)
Br1	Tc1	Br2 ¹	89.25(4)	Br3 ¹	Tc1	Br2 ¹	89.23(4)
Br1	Tc1	Br2	91.23(4)	Br3 ¹	Tc1	Br3	91.12(6)
Br1 ¹	Tc1	Br2	89.25(4)	C1	N1	C3	109.9(6)
Br2	Tc1	Br2 ¹	179.32(7)	C1	N2	C4	110.6(6)
Br3 ¹	Tc1	Br1	89.52(3)	N1	C1	C2	126.8(6)
Br3 ¹	Tc1	Br1 ¹	179.21(5)	N2	C1	N1	106.0(6)
Br3	Tc1	Br1 ¹	89.52(3)	N2	C1	C2	127.3(7)
Br3	Tc1	Br1	179.21(5)	C4	C3	N1	107.3(7)
Br3 ¹	Tc1	Br2	90.29(4)	C3	C4	N2	106.2(7)

¹1-X,1-Y,+Z

Table S11. Hydrogen Bonds for **III**.

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
N1	H1A	Br1 ¹	0.88	2.95	3.653(7)	138.6
N1	H1A	Br1 ²	0.88	2.95	3.506(7)	122.6
N2	H2A	Br2	0.88	2.57	3.400(6)	156.8
N2	H2A	Br3 ³	0.88	3.02	3.591(7)	124.1

¹3/2-X,1/2+Y,1-Z; ²1/2+X,3/2-Y,1-Z; ³1-X,1-Y,+Z

Table S12. Bond Lengths for **IV**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Tc1	Br1	2.5058(6)	N1	C4	1.368(6)
Tc1	Br1 ¹	2.5058(6)	N2	C1	1.325(5)
Tc1	Br2	2.5059(6)	N2	C5	1.362(6)

Tc1	Br2 ¹	2.5060(6)		C1	C2	1.478(6)
Tc1	Br3 ¹	2.5063(7)		C2	C3	1.506(6)
Tc1	Br3	2.5063(7)		C4	C5	1.322(6)
N1	C1	1.324(5)				

¹1-X,1-Y,1-Z

Table S13. Bond Angles for **IV**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
Br1	Tc1	Br1 ¹	179.999(19)	Br2 ¹	Tc1	Br3	89.94(2)
Br1 ¹	Tc1	Br2 ¹	90.07(2)	Br2 ¹	Tc1	Br3 ¹	90.06(2)
Br1	Tc1	Br2	90.07(2)	Br3	Tc1	Br3 ¹	180.00(2)
Br1 ¹	Tc1	Br2	89.93(2)	C1	N1	C4	110.3(4)
Br1	Tc1	Br2 ¹	89.93(2)	C1	N2	C5	110.7(4)
Br1 ¹	Tc1	Br3	90.09(2)	N1	C1	N2	105.5(4)
Br1	Tc1	Br3 ¹	90.09(2)	N1	C1	C2	127.3(4)
Br1	Tc1	Br3	89.91(2)	N2	C1	C2	127.1(4)
Br1 ¹	Tc1	Br3 ¹	89.91(2)	C1	C2	C3	114.2(4)
Br2	Tc1	Br2 ¹	180.0	C5	C4	N1	106.8(4)
Br2	Tc1	Br3	90.06(2)	C4	C5	N2	106.7(4)
Br2	Tc1	Br3 ¹	89.94(2)				

¹1-X,1-Y,1-Z

Table S14. Hydrogen Bonds for **IV**.

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
N1	H1	Br2 ¹	0.88	2.55	3.417(4)	168.2
N2	H2	Br1 ²	0.88	2.99	3.559(4)	124.5
N2	H2	Br3 ²	0.88	2.73	3.425(4)	137.3

¹1-X,1-Y,2-Z; ²-1+X,+Y,+Z

Table S15. Torsion Angles for **IV**.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
N1	C1	C2	C3	-60.0(6)	C4	N1	C1	N2	-1.1(5)
N1	C4	C5	N2	-0.6(5)	C4	N1	C1	C2	-178.9(4)
N2	C1	C2	C3	122.6(5)	C5	N2	C1	N1	0.7(5)
C1	N1	C4	C5	1.1(5)	C5	N2	C1	C2	178.5(4)
C1	N2	C5	C4	-0.1(5)					

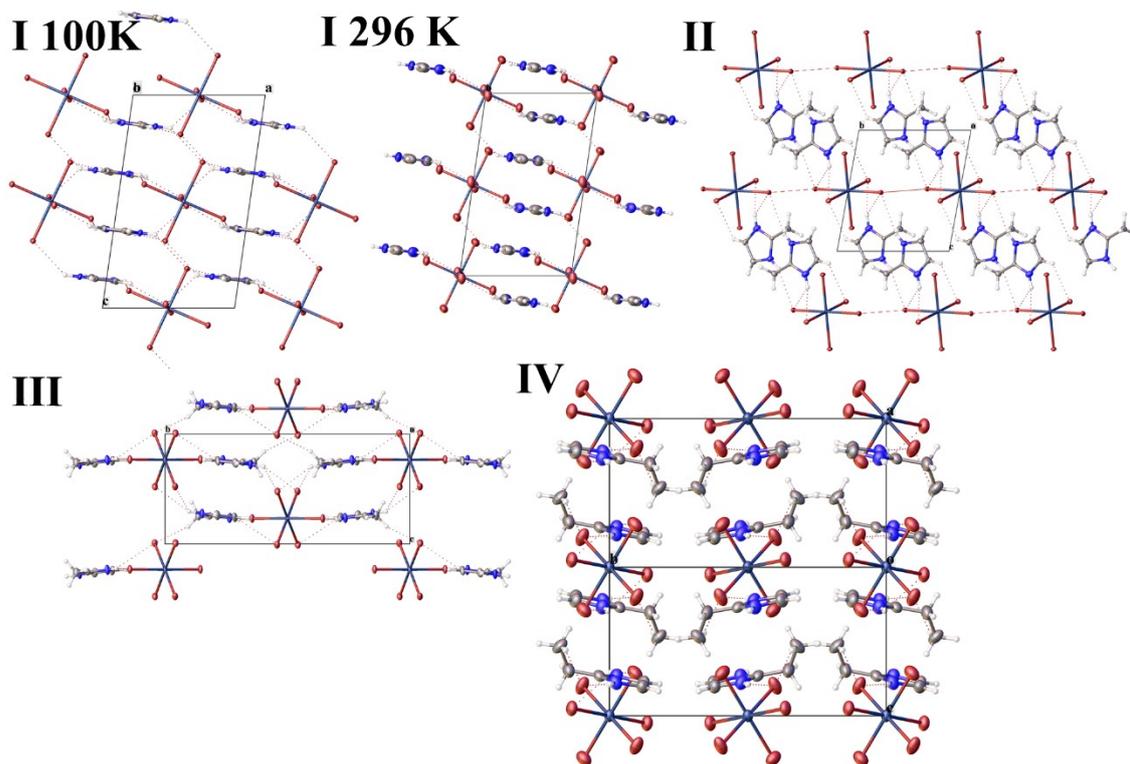


Figure S1. Crystal packing of structures I-IV.