Table S1 Stretching frequencies (cm^{-1}) of BiI_6^{3-} complexes

Sym	Description		Calculated [a]	PED [b]	Observed [c]			
					$n\text{-}C_3H_7NH_3$ [d]		$Cr(en)_3$ [d]	
					IR	Raman	IR	Raman
A_{1g}	ν_1	Sym. stretch	104 (0, 10)	$\nu_{EE}(100)$	-	119 (7)	-	139 (10)
E_g	ν_2	Stretching	85 (0, 2)	$\nu_{EE}(100)$	-	105 (10)	-	128 (5)
T_{1u}	ν_4	Stretching	106 (10, 0)	$\nu_{EE}(69)\delta(31)$	110 s	-	135 s	-
				Reference	1		1	

[a] Relative infrared and Raman intensities given in parentheses
[b] Potential energy distribution (applicable to all tables):
ν_{EE} : M-X stretching frequencies for external bond across from an external bond
ν_{EB} : M-X stretching frequencies for external bond across from a bridging bond
ν_B : M-X stretching frequencies for bridging bond
δ: bending and torsional motions
[c] s-strong, m-medium, w-weak, vs-very strong, br-broad, sh-shoulder
[d] cation

Table S2 Stretching frequencies (cm^{-1}) of $BiBr_6^{3-}$ complexes

Sym		Description	Calculated [a]	PED	Observed [b]							
					CH_3NH_3 [c]		$C_6H_5CH_2NH_3$ [c]		n-$C_3H_7NH_3$ [c]		$C_3H_5NH_3$ [c]	
					IR	Raman	IR	Raman	IR	Raman	IR	Raman
A_{1g}	ν_1	Sym. stretch	144 (0, 10)	$\nu_{EE}(100)$	152 sh	154 (10)	158 s	157 (10)	-	157 (10)	150 sh	158(10)
E_g	ν_2	Stretching	115 (0, 2)	$\nu_{EE}(100)$	-	135 (1)	-	129 (1)	-	138 (3)	-	142 (2)
T_{1u}	ν_4	Stretching	131 (10, 0)	$\nu_{EE}(68)\delta(32)$	126 s	-	124 vs	-	123 vs	-	130 s	-
				Reference	1		1		1		1	

[a] Relative infrared and Raman intensities given in parentheses
[b] s-strong, m-medium, w-weak, vs-very strong, br-broad, sh-shoulder; relative Raman intensities in parentheses
[c] cation

Table S3 Stretching frequencies (cm^{-1}) of $BiCl_6^{3-}$ complexes

Sym		Description	Calculated [a]	PED	Observed	
					$(C_5H_5NH)_3$ [b]	
					IR	Raman
A_{1g}	ν_1	Sym. stretch	227 (0, 10)	$\nu_{EE}(100)$	255	252
E_g	ν_2	Stretching	176 (0, 2)	$\nu_{EE}(100)$	-	212
T_{1u}	ν_4	Stretching	169 (10, 0)	$\nu_{EE}(70)\delta(30)$	169	-
				Reference	65	

[a] Relative infrared and Raman intensities given in parentheses
[b] cation

Table S4 Stretching frequencies (cm^{-1}) of SbI_6^{3-} complexes

Sym	Description	Calculated [a]	PED
A_{1g}	ν_1 Sym. stretch	104 (0, 10)	$\nu_{EE}(100)$
E_g	ν_2 Stretching	84 (0, 3)	$\nu_{EE}(100)$
T_{1u}	ν_4 Stretching	127 (10, 0)	$\nu_{EE}(63)\delta(37)$

[a] Relative infrared and Raman intensities given in parentheses; no observed data has been reported.

Table S5 Stretching frequencies (cm^{-1}) of $SbBr_6^{3-}$ complexes

Sym	Description	Calculated [a]	PED	Observed [b]				
				$(n\text{-}C_3H_7)_2NH_2$ [c]		$(C_2H_5)_2NH_2$ [c]		$(CH_3)_2NH_2$ [c]
				IR	Raman	IR	Raman	IR
A_{1g}	ν_1	Sym. stretch	$\nu_{EE}(100)$	-	150 (10)	-	178 s, br	-
E_g	ν_2	Stretching	$\nu_{EE}(100)$	-	129 (7)	-	-	-
T_{1u}	ν_4	Stretching	$\nu_{EE}(64)\delta(36)$	135 s	-	178 s, br	-	150 s, br
			Reference	23		66		67

[a] Relative infrared and Raman intensities given in parentheses
[b] s-strong, m-medium, w-weak, vs-very strong, br-broad, sh-shoulder; relative Raman intensities in parentheses
[c] cation

Table S6 Stretching frequencies (cm^{-1}) of $SbCl_6^{3-}$ complexes

Sym	Description		Calculated [a]	PED	Observed [b]	
					$(CH_3S)_3$ [c]	$(CH_3Se)_3$ [c]
					Raman	Raman
A_{1g}	ν_1	Sym. stretch	224 (0, 10)	$\nu_{EE}(100)$	282 m, br	278 m
E_g	ν_2	Stretching	164 (0, 3)	$\nu_{EE}(100)$	183 mw	174 m
T_{1u}	ν_4	Stretching	178 (10, 0)	$\nu_{EE}(64)\delta(36)$	-	-
				Reference	68	68

[a] Relative infrared and Raman intensities given in parentheses
[b] s-strong, m-medium, w-weak, vs-very strong, br-broad, sh-shoulder; relative Raman intensities in parentheses
[c] cation

Table S7 Stretching frequencies (cm^{-1}) of $Bi_2I_9^{3-}$ complexes

Sym	Description		Calculated [a]	PED	Observed [b]					
					$(CH_3)_2NH_2$[c]		piperidinium[c]		4-picolinium[c]	
					IR	Raman	IR	Raman	IR	Raman
A_1'	ν_1	BiI_3 Sym. stretch	136(0, 10)	$\nu_{EB}(43)\nu_B(28)\delta(29)$	-	138 (10)	-	135 (10)	-	134 (10)
E'	ν_6	BiI_3 Sym. stretch	135 (5, 0)	$\nu_{EB}(44)\nu_B(28)\delta(28)$	128 s	-	129 s	-	134 sh	-
A_2"	ν_{12}	BiI_3 Antisym. stretch	121(10, 0)	$\nu_{EB}(49)\nu_B(24)\delta(27)$	110 sh	-	114 sh	124 w	123 s	123 (1)
E"	ν_{15}	BiI_3 Antisym. stretch	116(0, 5)	$\nu_{EB}(54)\nu_B(14)\delta(32)$	-	112 (3)	-	112 (2)	113 sh	116 (4)
A_1'	ν_2	Sym. stretch (i.p.)	113 (0, 10)	$\nu_B(55)\nu_{EB}(11)\delta(34)$	-	-	99 (2)	99 (2)	-	92 (1)
E'	ν_7	Sym. stretch (i.p.)	100 (0, 2)	$\nu_B(44)\nu_{EB}(24)\delta(32)$	-	-	-	-	-	-
A_2"	ν_{13}	Antisym. stretch (i.p.)	103 (2, 0)	$\nu_B(55)\nu_{EB}(2)\delta(43)$	83 m	-	85 m	-	80 ms	-
E"	ν_{16}	Antisym. stretch (i.p.)	75 (0, 0)	$\nu_B(65)\nu_{EB}(8)\delta(27)$	-	-	-	-	-	-
				Reference	1		1		1	

[a] Relative infrared and Raman intensities given in parentheses

[b] s-strong, m-medium, w-weak, vs-very strong, br-broad, sh-shoulder; relative Raman intensities in parentheses

[c] cation

Table S8 Stretching frequencies (cm^{-1}) of $Bi_2Br_9^{3-}$ complexes

Sym	Description		Calculated [a]	PED	Observed [b]			
					Et_3NH [c]		i-Bu_2NH_2 [c]	
					IR	Raman	IR	Raman
A_1'	ν_1	$BiBr_3$ Sym. stretch	177 (0, 10)	$\nu_{EB}(58)\nu_B(12)\delta(30)$	-	182 (10)	-	180 (10)
E'	ν_6	$BiBr_3$ Sym. stretch	168 (9, 0)	$\nu_{EB}(43)\nu_B(22)\delta(35)$	-	-	-	-
A_2"	ν_{12}	$BiBr_3$ Antisym. stretch	161 (8, 0)	$\nu_{EB}(77)\nu_B(3)\delta(20)$	163 vs	163 w, sh	161 vs	-
E"	ν_{15}	$BiBr_3$ Antisym. stretch	152 (0, 3)	$\nu_{EB}(66)\nu_B(3)\delta(31)$	-	158 (3)	-	165 (3)
A_1'	ν_2	Sym. stretch (i.p.)	145 (0, 3)	ν_B (63)$\nu_{EB}(6)\delta(31)$	-	145 (1)	-	-
E'	ν_7	Sym. stretch (i.p.)	131 (0, 1)	ν_B (45)$\nu_{EB}(18)\delta(37)$	-	123 (1)	-	122 w
A_2"	ν_{13}	Antisym. stretch (i.p.)	130 (10, 0)	$\nu_B(48)\nu_{EB}(12)\delta(40)$	99 vs	-	103 vs	-
E"	ν_{16}	Antisym. stretch (i.p.)	88 (0, 0)	$\nu_B(61)\nu_{EB}(12)\delta(27)$	-	-	-	-
				Reference	1		1	

[a] Relative infrared and Raman intensities given in parentheses
[b] s-strong, m-medium, w-weak, vs-very strong, br-broad, sh-shoulder
[c] cation

Table S9 Stretching frequencies (cm^{-1}) of $Bi_2Cl_9^{3-}$ complexes

Sym	Description		Calculated [a]	PED	Observed [b]		
					$(CH_3)_4P$ [c]	$(CH_3)_2NH_2$ [c]	
					Raman	IR	Raman
A_1'	ν_1	$BiCl_3$ Sym. stretch	268 (0, 10)	$\nu_{EB}(59)\nu_B(12)\delta(29)$	278 s	-	288 vs
E'	ν_6	$BiCl_3$ Sym. stretch	235 (6, 0)	$\nu_{EB}(59)\nu_B(14)\delta(27)$	-	247 s	-
A_2"	ν_{12}	$BiCl_3$ Antisym. stretch	251 (3, 0)	$\nu_{EB}(60)\nu_B(18)\delta(22)$	-	281 m	-
E"	ν_{15}	$BiCl_3$ Antisym. stretch	226 (0, 2)	$\nu_{EB}(67)\nu_B(8)\delta(25)$	235 s	-	238 s
A_1'	ν_2	Sym. stretch (i.p.)	200 (0, 1)	$\nu_B(50)\nu_{EB}(15)\delta(35)$	-	-	-
E'	ν_7	Sym. stretch (i.p.)	194 (1, 1)	$\nu_B(49)\nu_{EB}(5)\delta(46)$	172 m	-	-
A_2"	ν_{13}	Antisym. stretch (i.p.)	175 (10, 0)	$\nu_B(45)\nu_{EB}(18)\delta(37)$	-	165 s	-
E"	ν_{16}	Antisym. stretch (i.p.)	113 (0, 0)	$\nu_B(57)\nu_{EB}(15)\delta(28)$	-	-	-
				Reference	58	59	

[a] Relative infrared and Raman intensities given in parentheses
[b] s-strong, m-medium, w-weak, vs-very strong, br-broad, sh-shoulder; relative Raman intensities in parentheses
[c] cation

Table S10 Stretching frequencies (cm^{-1}) of $Sb_2I_9^{3-}$ complexes

Sym	Description		Calculated [a]	PED	Observed [b]					
					CH_3NH_3 [c]		4-Picolinium [c]		$CH_3O(CH_2)_3NH_3$ [c]	
					IR [c]	Raman	IR [c]	Raman	IR [c]	Raman
A_1'	ν_1	SbI_3 Sym. stretch	160 (0, 7)	$\nu_{EB}(32)\nu_B(29)\delta(39)$	-	170 (10)	-	160 (10)	-	181 (6)
E'	ν_6	SbI_3 Sym. stretch	158 (4, 0)	$\nu_{EB}(33)\nu_B(29)\delta(38)$	160 s	-	161 s	-	150 s	-
A_2"	ν_{12}	SbI_3 Antisym. stretch	136 (10, 0)	$\nu_{EB}(32)\nu_B(30)\delta(38)$	145 sh	-	148 m	-	-	-
E"	ν_{15}	SbI_3 Antisym. stretch	123 (0, 5)	$\nu_{EB}(44)\nu_B(19)\delta(37)$	-	-	-	151 (19)	-	161 (10)
A_1'	ν_2	Sym. stretch (i.p.)	114 (0, 10)	$\nu_B(50)\nu_{EB}(21)\delta(29)$	-	125 (12)	-	129 (4)	-	129 (8)
E'	ν_7	Sym. stretch (i.p.)	100 (0, 2)	$\nu_B(39)\nu_{EB}(25)\delta(36)$	-	110 (20)	-	114(7)	-	-
A_2"	ν_{13}	Antisym. stretch (i.p.)	106 (0, 0)	$\nu_B(42)\nu_{EB}(23)\delta(35)$	-	-	-	-	-	-
E"	ν_{16}	Antisym. stretch (i.p.)	78 (0, 0)	$\nu_B(68)\delta(32)$	-	-	-	-	-	-
				Reference	23		23		23	

[a] Relative infrared and Raman intensities given in parentheses
[b] s-strong, m-medium, w-weak, vs-very strong, br-broad, sh-shoulder; relative Raman intensities in parentheses
[c] cation

Table S11 Stretching frequencies (cm^{-1}) of $Sb_2Br_9^{3-}$ complexes

Sym	Description		Calculated [a]	PED	Observed [b]					
					$N(C_2H_5)_4$ [c]		methylammonium [c]		CH_3NH_3 [c]	
					IR [c]	Raman [c]	IR [c]	Raman [c]	IR [c]	Raman [c]
A_1'	ν_1	$SbBr_3$ Sym. stretch	196 (0, 10)	ν_{EB} (40)ν_B(22)δ38)	-	201 s, br	-	176 s, br	-	215 (9)
E'	ν_6	$SbBr_3$ Sym. stretch	190 (6, 0)	ν_{EB}(36)ν_B(27)δ(37)	199 s	-	201 s, br	-	185 s	-
A_2"	ν_{12}	$SbBr_3$ Antisym. stretch	169 (10, 0)	ν_{EB}(47)ν_B(19)δ(34)	184 sh	-	185 s, br	-	-	-
E"	ν_{15}	$SbBr_3$ Antisym. stretch	160 (0, 5)	ν_{EB}(51)ν_B(13)δ(36)	-	-	-	-	-	192 (10)
A_1'	ν_2	Sym. stretch (i.p.)	146 (0, 5)	ν_B(60)ν_{EB}(5)δ(35)	-	155 s, br	-	115 s, br	-	123 (3)
E'	ν_7	Sym. stretch (i.p.)	129 (0, 2)	ν_B(42)ν_{EB}(22)δ(36)	-	-	-	-	-	-
A_2"	ν_{13}	Antisym. stretch (i.p.)	137 (3, 0)	ν_B(51)δ(49)	152 sh	-	-	-	155 w	-
E"	ν_{16}	Antisym. stretch (i.p.)	84 (0, 0)	ν_B(60)ν_{EB}(7)δ(33)	-	-	-	-	-	-
				Reference	66		66		23	

[a] Relative infrared and Raman intensities given in parentheses
[b] s-strong, m-medium, w-weak, vs-very strong, br-broad, sh-shoulder; relative Raman intensities in parentheses
[c] cation

Table S12 Stretching frequencies (cm^{-1}) of $Sb_2Cl_9^{3-}$ complexes

Sym	Description	Calculated [a]	PED	Observed [b]			
				CH_3NH_3 [c]		$(CH_3)_2NH_2$ [c]	
				IR	Raman	IR	Raman
A_1'	ν_1 $SbCl_3$ Sym. stretch	281 (0, 10)	ν_{EB} (65)δ(35)	-	323 vs	-	322 vs
E'	ν_6 $SbCl_3$ Sym. stretch	248 (7, 0.3)	ν_{EB}(47)ν_B(20)δ(33)	279 m	-	270 m	-
A_2"	ν_{12} $SbCl_3$ Antisym. stretch	253 (6, 0)	ν_{EB}(71)ν_B(8)δ(21)	263 s	-	-	-
E"	ν_{15} $SbCl_3$ Antisym. stretch	229 (0, 3)	ν_{EB}(68)δ(32)	-	278 s	-	275 s
A_1'	ν_2 Sym. stretch (i.p.)	192 (0, 1)	ν_B(53)ν_{EB}(11)δ(36)	-	-	-	-
E'	ν_7 Sym. stretch (i.p.)	189 (0.4, 1)	ν_B(46)ν_{EB}(12)δ(42)	-	-	-	-
A_2"	ν_{13} Antisym. stretch (i.p.)	175 (10, 0)	ν_B(44)ν_{EB}(15)δ(41)	168 s	-	183	-
E"	ν_{16} Antisym. stretch (i.p.)	101 (0, 0.3)	ν_B(42)ν_{EB}(28)δ(30)	-	-	-	-
			Reference	69		69	

[a] Relative infrared and Raman intensities given in parentheses
[b] s-strong, m-medium, w-weak, vs-very strong, sh-shoulder
[c] cation

Table S13 Calculated stretching frequencies (cm^{-1}) of $Bi_2I_{10}^{4-}$ complexes

Sym	Description		Calculated [a]	PED
A_g	ν_1	BiI_2 Sym. stretch	126 (0, 10)	$\nu_{EB}(51)\nu_{EE}(13)\nu_B(13)\delta(23)$
B_{3u}	ν_{26}	BiI_2 Sym. stretch	120 (2, 0)	$\nu_{EB}(52)\nu_{EE}(22)\nu_B(10)\delta(16)$
B_{2g}	ν_{10}	BiI_2 Antisym. stretch	112 (0, 3)	$\nu_{EB}(72)\nu_B(4)\delta(24)$
B_{1u}	ν_{18}	BiI_2 Antisym. stretch	118 (7, 0)	$\nu_{EB}(49)\nu_B(24)\delta(27)$
A_g	ν_2	BiI_2 Sym. stretch	107 (0, 2)	$\nu_{EE}(38)\nu_B(28)\nu_{EB}(19)\delta(15)$
B_{3u}	ν_{27}	BiI_2 Sym. stretch	105 (1, 0)	$\nu_{EE}(48)\nu_{EB}(30)\nu_B(9)\delta(13)$
B_{1g}	ν_7	BiI_2 Antisym. stretch	97 (0, 0)	$\nu_{EE}(72)\delta(28)$
B_{2u}	ν_{22}	BiI_2 Antisym. stretch	99 (10, 0)	$\nu_{EE}(72)\delta(28)$
A_g	ν_3	BiI_2 Sym. stretch	99 (0, 2)	$\nu_B(50)\nu_{EE}(21)\delta(29)$
B_{3u}	ν_{28}	BiI_2 Sym. stretch	91 (7, 0)	$\nu_B(46)\nu_{EB}(20)\nu_{EE}(6)\delta(28)$
B_{2g}	ν_{11}	BiI_2 Antisym. stretch	87 (0, 1)	$\nu_B(63)\nu_{EB}(21)\delta(16)$
B_{1u}	ν_{19}	BiI_2 Antisym. stretch	100 (1, 0)	$\nu_B(58)\nu_{EB}(8)\delta(34)$

[a] Relative infrared and Raman intensities given in parentheses; no experimental data has been reported.

Table S14 Stretching frequencies (cm^{-1}) of $Bi_2Br_{10}^{4-}$ complexes

Sym	Description		Calculated [a]	PED	Observed [b]		
					$C_2H_5N_4S$ [c]	$C_3N_2H_5$ [c]	
					IR	IR	Raman
A_g	ν_1	$BiBr_2$ Sym. stretch	171 (0, 10)	$\nu_{EB}(44)\nu_{EE}(19)\nu_B(12)\delta(25)$	-	-	164 vs
B_{3u}	ν_{26}	$BiBr_2$ Sym. stretch	162 (1, 0)	$\nu_{EB}(43)\nu_{EE}(21)\nu_B(19)\delta(17)$	-	185 vw	-
B_{2g}	ν_{10}	$BiBr_2$ Antisym. stretch	149 (0, 2)	$\nu_{EB}(65)\nu_B(2)\delta(33)$	-	-	-
B_{1u}	ν_{18}	$BiBr_2$ Antisym. stretch	159 (6, 0)	$\nu_{EB}(45)\nu_B(20)\delta(35)$	180	198 vs	-
A_g	ν_2	$BiBr_2$ Sym. stretch	143 (0, 2)	$\nu_{EE}(33)\nu_{EB}(20)\ \nu_B(27)\delta(20)$	-	-	-
B_{3u}	ν_{27}	$BiBr_2$ Sym. stretch	134 (3, 0)	$\nu_{EE}(39)\nu_{EB}(29)\ \nu_B(14)\delta(18)$	-	-	-
B_{1g}	ν_7	$BiBr_2$ Antisym. stretch	139 (0, 0)	$\nu_{EE}(72)\delta(28)$	-	-	-
B_{2u}	ν_{22}	$BiBr_2$ Antisym. stretch	148 (10, 0)	$\nu_{EE}(72)\delta(28)$	164	-	-
A_g	ν_3	$BiBr_2$ Sym. stretch	131 (0, 1)	$\nu_B(40)\nu_{EE}(20)\nu_{EB}(8)\delta(32)$	-	-	106 m
B_{3u}	ν_{28}	$BiBr_2$ Sym. stretch	119 (9, 0)	$\nu_B(41)\nu_{EB}(16)\nu_{EE}(13)\delta(30)$	150	143 vs	-
B_{2g}	ν_{11}	$BiBr_2$ Antisym. stretch	104 (0, 1)	$\nu_B(65)\nu_{EB}(19)\delta(16)$	-	-	-
B_{1u}	ν_{19}	$BiBr_2$ Antisym. stretch	125 (0.2, 0)	$\nu_B(45)\nu_{EB}(11)\delta(44)$	-	114 vw	-
				Reference	60	61	

[a] Relative infrared and Raman intensities given in parentheses
[b] s-strong, m-medium, w-weak, vs-very strong, br-broad, sh-shoulder; relative Raman intensities in parentheses
[c] cation

Table S15 Stretching frequencies (cm^{-1}) of $BiBr_5^{2-}$ complexes

Sym	Description		Calculated [a]	PED	Observed [b]			
					4-picolinium[c]		pyridinium[c]	
					IR	Raman	IR	Raman
A_g	ν_1	$BiBr_2$ Sym. stretch	171 (0, 10)	$\nu_{EB}(44)\nu_{EE}(19)\nu_B(12)\delta(25)$	-	169 (10)	-	180 (10)
B_{3u}	ν_{26}	$BiBr_2$ Sym. stretch	162 (1, 0)	$\nu_{EB}(43)\nu_{EE}(21)\nu_B(19)\delta(17)$				
B_{2g}	ν_{10}	$BiBr_2$ Antisym. stretch	149 (0, 2)	$\nu_{EB}(65)\nu_B(2)\delta(33)$	159 ms	156 (5)	157 s	166 (1)
B_{1u}	ν_{18}	$BiBr_2$ Antisym. stretch	159 (6, 0)	$\nu_{EB}(45)\nu_B(20)\delta(35)$				
A_g	ν_2	$BiBr_2$ Sym. stretch	143 (0, 2)	$\nu_{EE}(33)\nu_{EB}(20)\nu_B(27)\delta(20)$	-	142 (1)	-	-
B_{3u}	ν_{27}	$BiBr_2$ Sym. stretch	134 (3, 0)	$\nu_{EE}(39)\nu_{EB}(29)\nu_B(14)\delta(18)$				
B_{1g}	ν_7	$BiBr_2$ Antisym. stretch	139 (0, 0)	$\nu_{EE}(72)\delta(28)$	-	-	-	-
B_{2u}	ν_{22}	$BiBr_2$ Antisym. stretch	148 (10, 0)	$\nu_{EE}(72)\delta(28)$				
A_g	ν_3	$BiBr_2$ Sym. stretch	131 (0, 1)	$\nu_B(40)\nu_{EE}(20)\nu_{EB}(8)\delta(32)$	-	-	108 vs	-
B_{3u}	ν_{28}	$BiBr_2$ Sym. stretch	119 (9, 0)	$\nu_B(41)\nu_{EB}(16)\nu_{EE}(13)\delta(30)$				
B_{2g}	ν_{11}	$BiBr_2$ Antisym. stretch	104 (0, 1)	$\nu_B(65)\nu_{EB}(19)\delta(16)$	122 s, br	-	-	-
B_{1u}	ν_{19}	$BiBr_2$ Antisym. stretch	125 (0.2, 0)	$\nu_B(45)\nu_{EB}(11)\delta(44)$				
				Reference	1		1	

[a] Relative infrared and Raman intensities given in parentheses; calculated for $Bi_2Br_{10}^{4-}$

[b] s-strong, m-medium, w-weak, vs-very strong, br-broad, sh-shoulder; relative Raman intensities in parentheses

[c] cation

Table S16 Stretching frequencies (cm^{-1}) of $BiCl_5^{2-}$ complexes

Sym		Description	Calculated [a]	PED	Observed [b]		
					$bpyH_2$ [c]	$C_{12}H_{12}N$ [c]	$C_{12}H_{18}N$ [c]
					Raman	Raman	Raman
A_g	ν_1	$BiCl_2$ Sym. stretch	272 (0, 10)	$\nu_{EB}(46)\nu_{EE}(28)\nu_B(5)\delta(21)$	248	285	279
B_{3u}	ν_{26}	$BiCl_2$ Sym. stretch	259 (2, 0)	$\nu_{EB}(46)\nu_{EE}(20)\nu_B(19)\delta(15)$			
B_{2g}	ν_{10}	$BiCl_2$ Antisym. stretch	233 (0, 2)	$\nu_{EB}(64)\nu_B(15)\delta(21)$	-	-	-
B_{1u}	ν_{18}	$BiCl_2$ Antisym. stretch	230 (5, 0)	$\nu_{EB}(69)\nu_B(9)\delta(22)$			
A_g	ν_2	$BiCl_2$ Sym. stretch	222 (0, 2)	$\nu_{EE}(52)\nu_{EB}(34)\delta(14)$	208	244	246
B_{3u}	ν_{27}	$BiCl_2$ Sym. stretch	203 (1, 0)	$\nu_{EE}(55)\nu_{EB}(29)\nu_B(6)\delta(10)$			
B_{1g}	ν_7	$BiCl_2$ Antisym. stretch	164 (0, 0)	$\nu_{EE}(72)\delta(28)$	-	197	-
B_{2u}	ν_{22}	$BiCl_2$ Antisym. stretch	185 (10, 0)	$\nu_{EE}(71)\delta(29)$			
A_g	ν_3	$BiCl_2$ Sym. stretch	161 (0, 1)	$\nu_B(46)\nu_{EE}(40)\nu_{EB}(12)\delta(2)$	-	157	-
B_{3u}	ν_{28}	$BiCl_2$ Sym. stretch	153 (7, 0)	$\nu_B(60)\nu_{EB}(20)\delta(20)$			
B_{2g}	ν_{11}	$BiCl_2$ Antisym. stretch	133 (0, 2)	$\nu_B(48)\nu_{EE}(9)\nu_{EB}(18)\delta(25)$	-	147	-
B_{1u}	ν_{19}	$BiCl_2$ Antisym. stretch	155 (2, 0)	$\nu_B(28)\delta(72)$			
				Reference	62	63	64

[a] Relative infrared and Raman intensities given in parentheses; calculated for $Bi_2Cl_{10}^{4-}$

[b] s-strong, m-medium, w-weak, vs-very strong, br-broad, sh-shoulder; relative Raman intensities in parentheses

[c] cation

Table S17 Stretching frequencies (cm^{-1}) of SbI_5^{2-} complexes

Sym	Description		Calculated [a]	PED	Observed [b]					
					$C_2H_5NH_3$ [c]		$C_5H_{11}NH_3$ [c]		$H_3N(CH_2)_6NH_3$ [c]	
					IR [c]	Raman	IR [c]	Raman	IR [c]	Raman
A_g	ν_1	SbI_2 Sym. stretch	140 (0, 10)	ν_{EB} (40)ν_B(24)ν_{EE}(4)δ(32)	-	160 (10)	170 sh	169 (10)	160 sh	154
B_{3u}	ν_{26}	SbI_2 Sym. stretch	120 (2, 0)	ν_{EB}(56)ν_{EE}(20)ν_B(2)δ(22)						
B_{2g}	ν_{10}	SbI_2 Antisym. stretch	117 (0, 5)	ν_{EB}(56)ν_B(14)δ(30)	145	155 (5)	135 m	134 (1)	-	-
B_{1u}	ν_{18}	SbI_2 Antisym. stretch	132 (7, 0)	ν_{EB}(39)ν_B(28)δ(33)						
A_g	ν_2	SbI_2 Sym. stretch	110 (0, 3)	ν_{EE}(38)ν_B(36) ν_{EB}(4)δ(22)	-	100 (2)	-	100 (2)	-	100 (1)
B_{3u}	ν_{27}	SbI_2 Sym. stretch	105 (3, 0)	ν_{EE}(31)ν_{EB}(28)ν_B(21)δ(20)						
B_{1g}	ν_7	SbI_2 Antisym. stretch	108 (0, 0)	ν_{EE}(60)δ(40)	-	-	-	-	135 s	-
B_{2u}	ν_{22}	SbI_2 Antisym. stretch	107 (10, 0)	ν_{EE}(65)δ(35)						
A_g	ν_3	SbI_2 Sym. stretch	99 (0, 1)	ν_B(40)ν_{EE}(26)ν_{EB}(11)δ(23)	-	-	-	-	-	-
B_{3u}	ν_{28}	SbI_2 Sym. stretch	96 (5, 0)	ν_B(40)ν_{EB}(16)ν_{EE}(12)δ(32)						
B_{2g}	ν_{11}	SbI_2 Antisym. stretch	87 (0, 1)	ν_B(59)ν_{EB}(18)δ(23)	85 sh	-	90 m	-	-	-
B_{1u}	ν_{19}	SbI_2 Antisym. stretch	100 (0, 0)	ν_B(49)ν_{EB}(22)δ(29)						
				Reference	23		23		23	

[a] Relative infrared and Raman intensities given in parentheses; calculated for $Sb_2Cl_{10}^{4-}$

[b] s-strong, m-medium, w-weak, vs-very strong, br-broad, sh-shoulder; relative Raman intensities in parentheses

[c] cation

Table S18 Stretching frequencies (cm^{-1}) of $SbBr_5^{2-}$ complexes

Sym	Description		Calculated [a]	PED	Observed [b]			
					$C_6H_5CH_2NH_2$ [c]		$C_4H_9NH_3$ [c]	
					IR [c]	Raman	IR [c]	Raman
A_g	ν_1	$SbBr_2$ Sym. stretch	188 (0, 10)	$\nu_{EB}(38)\nu_B(18)\nu_{EE}(11)\delta(33)$	210 m	213 (10)	-	205 (10)
B_{3u}	ν_{26}	$SbBr_2$ Sym. stretch	163 (4, 0)	$\nu_{EB}(53)\nu_{EE}(19)\delta(28)$				
B_{2g}	ν_{10}	$SbBr_2$ Antisym. stretch	157 (0, 4)	$\nu_{EB}(60)\ \nu_B(9)\ \delta(31)$	187 m	164 (2)	175 s	190 (8)
B_{1u}	ν_{18}	$SbBr_2$ Antisym. stretch	180 (6, 0)	$\nu_{EB}(41)\ \nu_B(26)\ \delta(33)$				
A_g	ν_2	$SbBr_2$ Sym. stretch	144 (0, 3)	$\nu_{EE}(35)\nu_B(26)\nu_{EB}(11)\delta(28)$	-	148 (2)	-	147 (3)
B_{3u}	ν_{27}	$SbBr_2$ Sym. stretch	136 (5, 0)	$\nu_{EE}(26)\nu_B(26)\nu_{EB}(22)\delta(26)$				
B_{1g}	ν_7	$SbBr_2$ Antisym. stretch	152 (0, 0)	$\nu_{EE}(65)\delta(35)$	150 sh	-	-	-
B_{2u}	ν_{22}	$SbBr_2$ Antisym. stretch	161 (10, 0)	$\nu_{EE}(65)\delta(35)$				
A_g	ν_3	$SbBr_2$ Sym. stretch	126 (0, 2)	$\nu_B(37)\nu_{EE}(18)\nu_{EB}(10)\delta(35)$	-	-	-	-
B_{3u}	ν_{28}	$SbBr_2$ Sym. stretch	113 (5, 0)	$\nu_B(42)\nu_{EE}(19)\nu_{EB}(6)\delta(33)$				
B_{2g}	ν_{11}	$SbBr_2$ Antisym. stretch	91 (0, 1)	$\nu_B(56)\nu_{EB}(11)\delta(33)$	115 s	-	110 s	-
B_{1u}	ν_{19}	$SbBr_2$ Antisym. stretch	117 (0, 0)	$\nu_B(46)\nu_{EB}(23)\delta(31)$				
				Reference	23		23	

[a] Relative infrared and Raman intensities given in parentheses; calculated for $Sb_2Br_{10}^{4-}$

[b] s-strong, m-medium, w-weak, vs-very strong, br-broad, sh-shoulder; relative Raman intensities in parentheses

[c] cation

Table S19 Stretching frequencies (cm^{-1}) of $Sb_2Cl_{10}^{4-}$ complexes

Sym	Description		Calculated [a]	PED
A_g	ν_1	$SbCl_2$ Sym. stretch	316 (0, 10)	$\nu_{EB}(32)\nu_{EE}(22)\nu_B(11)\delta(35)$
B_{3u}	ν_{26}	$SbCl_2$ Sym. stretch	274 (4, 0)	$\nu_{EB}(60)\nu_{EE}(16)\nu_B(4)\delta(20)$
B_{2g}	ν_{10}	$SbCl_2$ Antisym. stretch	252 (0, 7)	$\nu_{EB}(75)\delta(25)$
B_{1u}	ν_{18}	$SbCl_2$ Antisym. stretch	257 (5, 0)	$\nu_{EB}(65)\nu_B(12)\delta(23)$
A_g	ν_2	$SbCl_2$ Sym. stretch [b]	258 (5, 0)	$\nu_{EB}(43)\nu_{EE}(13)\ \nu_B(21)\delta(23)$
			211 (0, 2)	$\nu_{EE}(34)\nu_{EB}(14)\nu_B(14)\delta(38)$
B_{3u}	ν_{27}	$SbCl_2$ Sym. stretch	183 (1, 0)	$\nu_{EE}(50)\nu_{EB}(20)\nu_B(18)\delta(12)$
B_{1g}	ν_7	$SbCl_2$ Antisym. stretch	161 (0, 0)	$\nu_{EE}(63)\delta(37)$
B_{2u}	ν_{22}	$SbCl_2$ Antisym. stretch	182 (10, 0)	$\nu_{EE}(68)\delta(32)$
A_g	ν_3	$SbCl_2$ Sym. stretch [b]	178 (0, 3)	$\nu_B(39)\nu_{EE}(20)\nu_{EB}(4)\delta(37)$
B_{3u}	ν_{28}	$SbCl_2$ Sym. stretch [b]	123 (4, 0)	$\nu_B(38)\delta(62)$
B_{2g}	ν_{11}	$SbCl_2$ Antisym. stretch	77 (0, 1)	$\nu_B(50)\nu_{EB}(6)\delta(44)$
B_{1u}	ν_{19}	$SbCl_2$ Antisym. stretch	181 (1, 0)	$\nu_B(67)\delta(33)$

[a] Relative infrared and Raman intensities given in parentheses
[b] Strongly coupled with bending motions