

Ab-initio calculations of heavy-actinide hexahalide compounds: Do these heavy actinides behave as their isoelectronic lanthanide analogues?

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Electronic Supporting Information

Basis set performance in MOLCAS and ORCA

Firstly, this study aims not only to reproduce accurately the scant experimental data available but also seeks to serve as a benchmark study by means of evaluating two different software platforms, namely MOLCAS and ORCA, in combination of different basis sets. Regrettably, MOLCAS has only one all-electron basis set available for metals heavier than curium called ANO-DK3, which is equivalent to a single- ζ basis set (see Computational Details). In spite of this limitation we tried a combination of this basis set with other ones for halogens such as ANO-MB, ANO-DZ and ANO-TZP. In the case of ORCA, the all-electron relativistic basis sets (SARC) were used at TZPP level in order to compare these results with those obtained by MOLCAS. In this way an insight on the scope and limitations of the available basis set for heavy actinides can be obtained.

Our results show that all CAS calculations yield a similar energy arrangement of the low-lying states according to the minimum active space (only 5f orbitals), which is remarkably for the minimal basis set ANO-DK3 due to the computational cost implications (Table S1). If combinations ANO-DK3/ANO-X (X = DK3, MB, DZ, TZP) are compared, it is possible to observe that the best combination is in between ANO-DK3/ANO-DK3 and ANO-DK3/ANO-MB, resulting in a balanced relationship. On the other hand, an unbalanced combination of basis sets results in complications of convergence and unrealistic broken degeneracies; CASPT2 calculations fails to include properly the dynamical correlation energy as well as spin-orbit coupling (Table S1). If ORCA calculations are taken as baseline values, then the combination of simple- ζ (DK3 and MB) are the closest to these values. However, their limited number of functions results in a poor or impossible description of larger actives spaces including virtual orbitals such as the 6d orbitals of the actinide. Thus, transitions such as f→d cannot be described properly due to this limitation. In general, systems which present ionic bonds can be accurately described in an over-simplified way by these small basis sets, but if covalent character begins to appear in bonding, these basis sets may fail in describing them properly, especially for unbalanced combinations of basis set.

Based on the above discussion, the results described in the manuscript are derived from calculations carried out with ORCA and a triple- ζ basis functions (more details are given in the Theoretical Considerations and Computational Details sections).

Additional Tables

$[B_k X_6]^{3-}$		X = F						X = Cl						X = Br		
Basis set		ANO-DK3	ANO-MB	ANO-DZ	ANO-TZP	ANO-DK3	ANO-MB	ANO-DZ	ANO-TZP	ANO-DK3	ANO-MB	ANO-DZ	ANO-TZP			
E_{CAS}	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	1341.5	1295.2	1077.0	1159.0	700.4	682.1	604.7	637.3	377.8	372.2	328.9	385.2	385.2	-	-	-
	1341.5	1295.2	1077.0	1159.0	700.4	682.1	604.7	637.3	377.8	372.2	328.9	386.6	386.6	-	-	-
	1341.6	1295.2	1077.0	1159.0	700.4	682.1	604.7	637.4	378.0	372.2	328.9	386.8	386.8	-	-	-
	3713.8	3593.4	2879.6	3024.5	2093.4	2058.1	1758.4	1797.7	1122.8	1111.3	961.5	1072.6	1072.6	-	-	-
	3713.9	3593.4	2879.6	3024.5	2093.4	2058.1	1758.4	1797.7	1122.8	1111.3	961.5	1072.6	1072.6	-	-	-
E_{PT2}	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	1073.0	1144.7	6389.7	990.4	684.6	696.7	451.0	230.6	-	397.5	-	2536.0	2536.0	-	-	-
	1104.1	1158.7	6689.0	995.9	686.9	700.4	574.7	360.1	-	399.8	-	2601.7	2601.7	-	-	-
	1111.2	1166.6	6820.7	1023.1	687.2	717.6	613.4	472.4	-	401.7	-	2832.5	2832.5	-	-	-
	3526.4	3508.0	11538.5	2873.6	2114.6	2125.5	1763.8	1433.9	-	1185.4	-	2833.9	2833.9	-	-	-
	3538.5	3521.1	11850.7	2879.9	2117.1	2127.7	1779.5	1521.6	-	1189.1	-	2839.6	2839.6	-	-	-
	3545.8	3560.9	14585.8	2890.3	2118.3	2141.0	1793.0	1521.8	-	1191.2	-	3462.0	3462.0	-	-	-

Table 1: Spin-Free states obtained by means of CASSCF and CASPT2 using MOLCAS software. The active space used was CAS(8,7) which includes only the 5f shell. The basis set ANO-DK3 and MB correspond to a single- ζ basis while ANO-DZ and ANO-TZP correspond to double and triple- ζ basis sets. Energies are in cm⁻¹. Dash lines indicate that the calculation could not be obtained for convergence problems.

$[BkX_6]^{3-}$		X = F						X = Cl						X = Br	
Basis set		ANO-DK3	ANO-MB	ANO-DZ	ANO-TZP	ANO-DK3	ANO-MB	ANO-DZ	ANO-TZP	ANO-DK3	ANO-MB	ANO-DZ	ANO-TZP		
	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
104.7	103.7	95.2	97.2	82.1	81.3	73.8	75.0	53.3	53.0	47.0	50.9				
104.7	103.7	95.2	97.2	82.1	81.3	73.8	75.0	53.3	53.0	47.0	51.1				
104.7	103.7	95.2	97.2	82.1	81.3	73.8	75.0	53.3	53.0	47.0	51.2				
221.8	220.3	204.9	208.6	179.8	178.2	162.4	164.8	118.0	117.1	104.0	112.1				
221.8	220.3	204.9	208.6	179.8	178.2	162.4	164.8	118.0	117.1	104.0	112.8				
$ESO-CAS$	221.8	220.3	204.9	208.6	179.8	178.2	162.4	164.8	118.0	117.1	104.0	113.2			
1270.9	1228.4	975.9	1030.6	708.3	695.8	594.6	613.3	383.2	379.3	326.3	364.7				
1511.3	1464.5	1180.2	1240.6	880.9	866.7	746.2	766.5	486.2	481.6	416.0	460.4				
1511.3	1464.5	1180.2	1240.6	880.9	866.7	746.2	766.5	486.2	481.6	416.0	460.4				
1511.3	1464.5	1180.2	1240.6	880.9	866.7	746.2	766.5	486.2	481.6	416.0	460.4				
1629.2	1578.8	1270.9	1335.6	949.4	934.1	803.3	824.9	521.4	516.5	445.8	493.3				
1629.2	1578.8	1270.9	1335.6	949.4	934.1	803.3	824.9	521.4	516.5	445.8	493.3				
	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	-	0.0	-	-	0.0	0.0
98.2	102.8	56.9	94.4	82.6	81.3	62.3	29.7	-	55.3	-	65.7				
106.3	103.6	285.5	95.5	82.8	82.6	77.1	91.4	-	55.7	-	155.3				
110.7	106.3	599.6	98.9	83.1	84.9	83.9	128.6	-	56.0	-	399.4				
222.1	218.9	678.6	203.0	181.2	178.1	150.3	146.9	-	122.5	-	464.3				
224.0	224.4	1471.6	209.8	181.7	182.4	161.5	179.2	-	122.9	-	914.1				
$ESO-PT2$	228.9	224.9	1481.5	211.9	182.1	184.7	191.3	197.4	-	123.6	-	947.5			
1181.4	1188.2	5001.4	968.3	714.3	720.2	596.2	522.4	-	405.1	-	1353.7				
1426.3	1423.5	5005.0	1177.6	889.9	894.0	747.4	657.4	-	511.9	-	1360.1				
1427.7	1432.2	6022.2	1182.3	890.8	895.1	752.5	667.8	-	513.3	-	1432.8				
1431.4	1435.7	6061.1	1183.3	890.8	897.6	776.9	687.9	-	513.9	-	1437.5				
1544.9	1540.2	6596.4	1273.8	960.0	963.9	817.3	729.7	-	549.6	-	1605.6				
1547.6	1552.0	6697.0	1276.1	960.9	967.1	821.9	732.7	-	551.1	-	1608.5				

Table 2: Spin-Orbit states obtained by means of RASSI using MOLCAS software. The active space used was CAS(8,7) which includes only the 5f shell. The basis set ANO-DK3 and MB correspond to a single- ζ basis while ANO-DZ and ANO-TZP correspond to double and triple- ζ basis sets. Energies are in cm⁻¹. Dash lines indicate that the calculation could not be obtained for convergence problems.

Table 3: Low lying SF and SO states for $[\text{BkX}_6]^{3-}$ derived from a CAS(8,7) calculation performed in ORCA.

$[\text{BkX}_6]^{3-}$	X = F		X = Cl		X = Br	
	CASSCF	NEVPT2	CASSCF	NEVPT2	CASSCF	NEVPT2
$^7A_{2u}$	0.0	0.0	0.0	0.0	0.0	0.0
E_{SF-CAS}	1314.0	1424.0	729.4	756.6	424.0	449.6
	1314.0	1424.0	729.4	757.6	424.0	452.6
	1314.0	1424.0	729.4	757.6	424.0	452.7
E_{SO-CAS}	3349.7	3668.1	2034.9	2205.3	1177.2	1311.2
	3349.7	3670.1	2034.9	2205.4	1177.2	1312.2
	3349.7	3683.3	2034.9	2205.6	1177.3	1323.7
A_{1g}	0.0	0.0	0.0	0.0	0.0	0.0
T_{1g}	99.0	99.3	79.9	83.8	54.6	58.6
	99.0	102.4	79.9	83.9	54.6	59.9
	99.0	103.5	79.9	83.9	54.6	59.9
T_{2g}	210.9	213.2	175.0	183.4	120.4	130.5
	210.9	213.3	175.0	183.4	120.4	130.7
	210.9	219.2	175.0	183.7	120.4	132.9
A_{2g}	1137.1	1251.8	690.8	745.8	398.8	444.6
T_{2g}	1357.2	1481.8	857.6	925.1	503.5	560.2
	1357.2	1482.1	857.6	925.1	503.5	562.4
	1357.2	1485.6	857.6	925.4	503.5	562.4
E_g	1461.3	1595.9	923.8	997.9	539.9	601.7
	1461.3	1597.6	923.8	998.1	539.9	604.5

Table 4: Low lying SF and SO states for $[\text{CfX}_6]^{3-}$ derived from a CAS(9,7) calculation performed in ORCA.

$[\text{CfX}_6]^{3-}$	X = F		X = Cl		X = Br	
	CASSCF	NEVPT2	CASSCF	NEVPT2	CASSCF	NEVPT2
	0.0	0.0	0.0	0.0	0.0	0.0
$^6T_{2u}$	0.0	0.4	0.0	0.0	0.1	0.9
	0.0	0.8	0.0	1.6	0.1	2.1
	1027.2	1158.5	520.3	610.8	408.8	501.3
$^6T_{1u}$	1027.2	1158.5	520.3	610.8	408.9	501.3
	1027.2	1165.2	520.3	615.1	408.9	501.4
	1679.3	1644.6	884.2	1020.1	690.7	821.8
$^6E_u^*$	1679.3	1644.6	884.2	1021.2	690.8	822.2
	1679.3	1644.6	951.5	1047.6	765.0	881.2
	1856.6	2090.1	951.5	1049.7	765.2	882.4
$^6T_{1u}$	1856.6	2090.1	951.5	1049.7	765.3	883.9
	0.0	0.0	0.0	0.0	0.0	0.0
	0.0	0.0	0.0	0.0	0.0	0.0
E_{SF-CAS}	118.4	127.3	62.3	70.3	49.9	26.4
	118.4	127.3	62.3	70.3	49.9	26.4
	118.4	127.3	62.3	71.3	50.0	
	118.4	127.3	62.3	71.3	50.0	51.5
						51.5
$E_{1/2u}$	522.2	548.5	280.8	307.6	223.7	63.2
	533.2	548.5	280.8	307.6	223.7	63.2
	1200.8	1256.1	596.6	666.5	470.9	456.2
$F_{3/2u}$	1200.8	1256.1	596.6	666.5	470.9	456.2
	1200.8	1256.1	596.6	667.4	471.0	489.0
	1200.8	1256.1	596.6	667.4	471.0	489.0
	1413.1	1406.4	716.0	784.5	566.7	548.5
$F_{3/2u}$	1413.1	1406.4	716.0	784.5	566.7	548.5
	1413.1	1407.2	716.0	785.2	566.9	564.7
	1413.1	1407.2	716.0	785.2	566.9	564.7

*In the case of F ligand the order between SF states 6E_u and $^6T_{1u}$ change.

Table 5: Low lying SF and SO states for $[\text{BkX}_6]^{3-}$ derived from a CAS(8,12) (5f+6d shell) calculation performed in ORCA.

$[\text{BkX}_6]^{3-}$	X = F		X = Cl		X = Br	
	CASSCF	NEVPT2	CASSCF	NEVPT2	CASSCF	NEVPT2
$^7A_{2g}$	0.0	0.0	0.0	0.0	0.0	0.0
E_{SF-CAS}	1440.0	1643.3	877.6	1007.0	466.0	515.4
	1440.0	1643.7	877.6	1007.9	467.0	517.1
	1440.0	1643.1	878.0	1008.8	467.3	517.6
	3142.2	4370.6	2398.1	2753.0	1029.8	1590.0
	3148.1	4383.3	2398.5	2754.2	1030.9	1592.6
	3148.1	4390.3	2400.4	2756.8	1031.9	1593.2
A_{1g}	0.0	0.0	0.0	0.0	0.0	0.0
T_{1g}	100.9	109.5	79.9	83.8	43.0	63.9
	103.0	110.6	79.9	83.8	48.9	68.0
	103.0	111.6	79.9	83.9	48.9	70.7
T_{2g}	209.1	233.2	175.0	183.4	104.4	150.1
	213.2	233.9	175.0	183.4	107.0	155.6
	213.3	234.6	175.0	183.6	110.0	157.4
E_{SO-CAS}	A_{2g}	1110.4	1505.3	690.8	745.8	351.7
T_{2g}	1314.7	1770.2	857.6	925.1	434.8	678.7
	1315.0	1773.2	857.6	925.1	438.0	679.4
	1315.6	1773.9	857.6	925.5	438.0	680.4
E_g	1409.6	1910.9	923.9	997.9	466.1	730.9
	1409.9	1910.4	923.8	998.1	467.2	730.2

Table 6: SF and SO states for $[\text{CfX}_6]^{3-}$ derived from a CAS(9,12) (5f+6d shell) calculation performed in ORCA.

$[\text{CfX}_6]^{3-}$	X = F		X = Cl		X = Br	
	CASSCF	NEVPT2	CASSCF	NEVPT2	CASSCF	NEVPT2
$^6T_{2u}$	0.0	0.0	0.0	0.0	0.0	0.0
	0.0	0.0	0.0	0.1	1.4	1.2
	0.0	0.0	0.0	0.6	3.1	3.5
$^6T_{1u}$	944.9	1341.0	391.7	741.9	284.6	640.8
	952.9	1341.0	391.7	743.2	287.1	640.5
	953.0	1355.2	391.7	750.6	288.8	640.1
E_{SF-CAS}						
$^6E_u^*$	1688.0	1820.7	763.5	1170.3	565.7	977.6
	1688.0	1828.2	763.5	1173.1	567.8	981.8
	1695.0	1828.3				
$^6T_{1u}$			835.3	1284.4	634.5	1151.9
	1820.4	2348.3	835.3	1285.9	635.5	1153.8
	1824.9	2348.5	835.3	1288.4	636.1	1154.5
$E_{5/2u}$	0.0	0.0	0.0	0.0	0.0	0.0
	0.0	0.0	0.0	0.0	0.0	0.0
$F_{3/2u}$	118.8	145.3	54.4	83.1	40.5	74.4
	118.8	145.3	54.4	83.1	40.5	74.4
	118.8	145.3	54.4	83.1	42.8	76.8
	118.8	145.3	54.4	83.1	42.8	76.8
$E_{1/2u}$	544.4	594.5	264.6	349.7	200.4	306.4
	544.4	594.5	264.6	349.7	200.4	306.4
E_{SO-CAS}						
$F_{3/2u}$	1173.6	1398.9	523.4	784.6	392.5	685.4
	1173.6	1398.9	523.4	784.6	392.5	685.4
	1180.3	1409.6	523.4	784.6	395.4	686.5
	1180.3	1409.6	523.4	784.6	395.4	686.5
$F_{3/2u}$	1394.8	1534.9	636.2	926.1	478.5	818.2
	1394.8	1534.9	636.2	926.1	478.5	818.2
	1398.2	1540.3	636.2	926.1	481.0	823.0
	1398.2	1540.3	636.2	926.1	481.0	823.0

*In the case of F ligand the order between SF states 6E_u and $^6T_{1u}$ change.

Table 7: Low-lying SF and SO states for $[\text{EsX}_6]^{3-}$ derived from a CAS(10,7) calculation performed in ORCA.

$[\text{EsX}_6]^{3-}$	X = F		X = Cl		X = Br	
	CASSCF	NEVPT2	CASSCF	NEVPT2	CASSCF	NEVPT2
$^5A_{1g}$	0.0	0.0	0.0	0.0	0.0	0.0
$^5T_{1g}$	302.4	420.3	142.7	234.9	114.3	196.5
	302.4	428.9	142.7	242.1	114.3	205.8
	302.9	431.1	143.4	254.1	115.0	207.3
5E_g	531.4	746.1	253.8	416.4	204.2	355.0
	531.5	746.4	254.1	416.4	204.3	355.4
E_{SF-CAS}	1096.5	1456.0	495.3	746.8	395.2	629.3
	1100.3	1468.3	498.9	755.3	399.5	638.8
	1100.4	1468.3	499.7	759.1	399.5	640.0
5A_g	1157.3	1550.8	528.6	814.8	423.4	694.0
$^5T_{2g}$	1232.6	1623.1	569.1	824.2	456.5	702.6
	1233.1	1625.1	569.5	836.1	457.0	704.1
	1233.2	1630.1	570.0	839.2	457.0	713.2
E_g	0.0	0.0	0.0	0.0	0.0	0.0
	0.1	0.4	0.3	2.4	0.0	0.2
T_{1g}	26.5	36.2	11.6	19.2	9.2	16.3
	26.9	36.5	11.8	19.4	9.3	16.3
	26.9	38.4	11.9	24.0	9.3	18.4
A_{1g}	99.9	144.8	44.1	81.0	34.9	68.8
T_{2g}	457.0	588.1	214.5	302.7	175.2	259.0
	461.2	591.8	216.1	303.6	176.5	260.7
	461.2	591.8	216.2	304.4	176.5	260.8
E_{SO-CAS}	535.8	700.6	253.9	362.8	207.4	313.2
	535.9	700.7	254.3	365.1	207.4	313.5
	540.9	707.1	255.3	366.7	208.3	314.4
E_g	621.0	803.5	290.3	415.1	236.9	357.2
	621.1	803.6	290.6	415.6	237.0	357.2
T_{2g}	624.2	807.8	291.8	416.3	238.3	359.0
	624.8	808.0	292.0	418.6	238.3	359.3
	624.8	808.4	292.9	419.9	238.5	361.6

Table 8: Low-lying SF and SO states for $[FmX_6]^{3-}$ derived from a CAS(11,7) calculation performed in ORCA.

$[FmX_6]^{3-}$	X = F		X = Cl		X = Br	
	CASSCF	NEVPT2	CASSCF	NEVPT2	CASSCF	NEVPT2
$^4A_{1u}$	0.0	0.0	0.0	0.0	0.0	0.0
$^4T_{1u}$	135.0	130.8	31.6	13.9	23.0	4.2
	135.0	143.4	31.6	14.0	23.0	9.2
	135.0	143.4	31.6	22.9	23.0	23.8
$^4T_{2u}$	157.6	215.6	58.8	80.7	46.6	62.6
	157.6	215.7	58.8	81.9	46.6	67.9
	157.6	216.7	58.8	101.2	46.6	73.7
E_{SF-CAS}						
4E_u	940.5	1123.3	413.4	531.7	337.3	455.1
	940.6	1123.6	413.4	532.1	337.3	456.1
$^4T_{2u}$	1062.3	1304.2	484.7	628.1	396.9	538.1
	1062.3	1304.2	484.7	638.5	396.9	551.2
	1062.3	1304.5	484.8	640.3	396.9	557.8
$^4A_{2u}$	1227.7	1453.6	586.9	762.7	483.0	637.1
	0.0	0.0	0.0	0.0	0.0	0.0
$F_{3/2u}$	0.0	0.0	0.0	0.0	0.0	0.0
	0.0	0.5	0.0	1.4	0.0	3.1
	0.0	0.5	0.0	1.4	0.0	3.1
$F_{3/2u}$	1496.7	1555.6	1743.6	1844.6	1759.2	1866.5
	1496.7	1555.6	1743.6	1844.6	1759.2	1866.5
	1496.7	1556.9	1744.7	1845.9	1760.6	1868.8
	1496.7	1556.9	1744.7	1845.9	1760.6	1868.8
E_{SO-CAS}						
$E_{1/2u}$	2557.8	2705.8	2529.0	2660.6	2524.0	2661.2
	2557.8	2705.8	2529.0	2660.6	2524.0	2661.2
$F_{3/2u}$	3178.2	3469.9	2848.6	3104.1	2791.6	3051.5
	3178.2	3469.9	2848.6	3104.1	2791.6	3051.5
	3178.2	3470.1	2848.6	3108.3	2791.6	3052.6
	3178.2	3470.1	2848.6	3108.3	2791.6	3052.6
$E_{5/2u}$	3271.4	3586.4	2860.0	3118.0	2792.1	3056.8
	3271.4	3586.4	2860.0	3118.0	2792.1	3056.8

Table 9: Low-lying SF and SO states for $[\text{TbX}_6]^{3-}$ derived from a CAS(8,7) calculation performed in ORCA.

$[\text{TbX}_6]^{3-}$	X = F		X = Cl		X = Br	
	CASSCF	NEVPT2	CASSCF	NEVPT2	CASSCF	NEVPT2
	0.0	0.0	0.0	0.0	0.0	0.0
	396.8	449.9	166.2	164.5	135.3	120.6
	397.0	453.2	166.5	168.4	135.7	123.7
E_{SF-CAS}	397.1	454.8	166.5	168.7	135.7	125.2
	1040.7	1122.0	450.2	432.9	367.7	335.0
	1041.3	1122.1	451.2	436.1	369.2	338.2
	1041.8	1127.6	451.2	439.2	369.2	340.7
	0.0	0.0	0.0	0.0	0.0	0.0
	40.3	41.1	21.5	20.0	18.2	16.1
	40.5	42.0	21.5	21.0	18.2	17.0
	40.6	43.0	21.5	21.7	18.2	17.8
	87.7	90.4	47.0	45.3	39.7	36.9
	87.9	90.9	47.5	45.7	40.3	37.3
E_{SO-CAS}	87.9	91.0	47.5	46.5	40.3	38.0
	358.9	389.5	151.3	146.4	123.9	113.6
	437.5	469.3	189.1	181.9	155.4	113.6
	437.9	470.6	190.0	183.0	156.4	143.8
	438.1	471.7	190.0	183.6	156.5	144.3
	469.8	503.5	202.6	194.9	166.7	153.0
	469.9	505.1	202.6	195.4	166.7	153.4

Table 10: Low-lying SF and SO states for $[\text{DyX}_6]^{3-}$ derived from a CAS(9,7) calculation performed in ORCA.

$[\text{DyX}_6]^{3-}$	X = F		X = Cl		X = Br	
	CASSCF	NEVPT2	CASSCF	NEVPT2	CASSCF	NEVPT2
	0.0	0.0	0.0	0.0	0.0	0.0
	0.4	0.2	0.4	0.1	4.4	0.7
	1.6	7.2	0.5	6.2	6.9	1.2
	388.0	486.8	178.0	227.9	136.6	178.0
	388.1	486.9	178.1	228.1	140.8	179.7
	389.6	490.3	178.4	232.8	142.0	180.2
E_{SF-CAS}	648.8	812.1	282.2	369.7	216.6	288.9
	650.4	813.8	282.6	371.1	222.7	289.8
	731.7	901.6	332.2	435.8	257.8	340.0
	732.0	904.5	332.8	439.4	260.6	344.8
	733.4	905.3	333.6	440.3	261.6	347.4
	0.0	0.0	0.0	0.0	0.0	0.0
	0.0	0.0	0.0	0.0	0.0	0.0
	39.5	48.8	19.1	24.2	9.5	9.8
	39.5	48.8	19.1	24.2	9.5	9.8
	41.0	51.4	19.3	25.9	29.6	30.3
	41.0	51.4	19.3	25.9	29.6	30.3
E_{SO-CAS}	194.8	241.0	89.4	122.2	89.2	114.7
	194.8	241.0	89.4	122.2	89.2	114.7
	418.6	525.4	183.4	245.0	157.5	207.1
	418.6	525.4	183.4	245.0	157.5	207.1
	420.0	527.5	184.2	246.9	161.7	209.8
	420.0	527.5	184.2	246.9	161.7	209.8
	521.8	654.1	235.8	315.0	194.1	255.6
	521.8	654.1	235.8	315.0	194.1	255.6
	545.8	680.3	260.5	342.3	197.3	258.7
	545.8	680.3	260.5	342.3	197.3	258.7

Table 11: Energies of f-f transitions of $[\text{BkX}_6]^{3-}$ ($\text{X} = \text{F}, \text{Cl}, \text{Br}$). The number in parenthesis corresponds to the degeneracy of the states (the calculations were performed with SO-coupling). Energies are in cm^{-1} .

$[\text{BkX}_6]^{3-}$	$\text{X} = \text{F}$		$\text{X} = \text{Cl}$		$\text{X} = \text{Br}$	
Transition	CASSCF	NEVPT2	CASSCF	NEVPT2	CASSCF	NEVPT2
$^7\text{F}_6 \rightarrow ^7\text{F}_5$	5024(3)	4994(3)	4906(3)	4905(3)	4915(3)	4969(3)
	5870(3)	5885(3)	5444(3)	5480(3)	5190(3)	5275(3)
	6246(2)	5902(2)	5700(2)	5776(2)	5393(2)	5490(2)
	6335(3)	6392(3)	5800(3)	5857(3)	5454(3)	5560(3)
$^7\text{F}_6 \rightarrow ^7\text{F}_4$	7187(1)	6940(1)	7142(1)	6936(1)	7139(1)	6956(1)
	7403(3)	7130(3)	7249(3)	7014(3)	7195(3)	7004(3)
	7830(2)	7575(2)	7390(2)	7145(2)	7257(2)	7068(3)
	8626(3)	8365(3)	8027(3)	7800(3)	7658(3)	7489(3)
$^7\text{F}_6 \rightarrow ^7\text{F}_3$	9972(3)	9805(3)	9456(3)	9315(3)	9297(3)	9202(3)
	9985(3)	9840(3)	9528(3)	9372(3)	9387(3)	9289(3)
	10671(1)	10536(1)	9941(1)	9810(1)	9582(1)	9504(1)
$^7\text{F}_6 \rightarrow ^7\text{F}_2$	11801(3)	11722(3)	11022(3)	10938(3)	10714(3)	10670(3)
	12277(2)	12236(2)	11428(2)	11372(2)	11017(2)	11000(2)
$^7\text{F}_6 \rightarrow ^7\text{F}_1$	12665(3)	12604(3)	11925(3)	11859(3)	11619(3)	11599(3)
$^7\text{F}_6 \rightarrow ^7\text{F}_0$	12961(1)	12877(1)	12259(1)	12187(1)	11976(1)	11956(1)

Table 12: Energies of f-f transitions of $[\text{CfX}_6]^{3-}$ ($\text{X} = \text{F}, \text{Cl}, \text{Br}$). The number in parenthesis corresponds to the degeneracy of the states (the calculations were performed with SO-coupling). Energies are in cm^{-1} .

$[\text{CfX}_6]^{3-}$		$\text{X} = \text{F}$		$\text{X} = \text{Cl}$		$\text{X} = \text{Br}$	
Transition		CASSCF	NEVPT2	CASSCF	NEVPT2	CASSCF	NEVPT2
${}^6\text{H}_{15/2} \rightarrow {}^6\text{H}_{13/2}$	7915(4)	7980(4)	7677(2)	7752(2)	7637(2)	7715(2)	
	7936(2)	8026(2)	7723(4)	7822(4)	7687(4)	7788(4)	
	7950(4)	8045(4)	7755(4)	7876(4)	7714(2)	7850(2)	
	7965(2)	8059(2)	7768(2)	7881(2)	7728(4)	7858(4)	
	8125(2)	8318(2)	7793(2)	7968(2)	7740(2)	7919(2)	
${}^6\text{H}_{15/2} \rightarrow {}^6\text{H}_{11/2}$	10882(4)	10211(4)	10950(4)	10075(4)	10970(4)	9997(4)	
	11219(2)	10527(2)	11077(2)	10120(4)	11058(2)	10108(4)	
	11965(4)	10799(4)	11477(4)	10352(2)	11380(4)	10310(2)	
	12406(2)	12314(2)	12266(2)	12081(2)	12233(2)	12031(2)	
${}^6\text{H}_{15/2} \rightarrow {}^6\text{H}_{9/2}$	12680(4)	12416(4)	12338(4)	12085(2)	12283(2)	12036(2)	
	12728(4)	12641(2)	12340(2)	12176(4)	12285(4)	12103(4)	
	12737(2)	12698(4)	12372(4)	12197(4)	12312(4)	12109(4)	
${}^6\text{H}_{15/2} \rightarrow {}^6\text{H}_{7/2}$	13929(4)	13045(4)	13660(4)	12525(2)	13645(4)	12109(4)	
	14218(2)	13272(2)	13755(2)	12541(4)	13712(2)	12503(4)	
	14432(2)	13483(2)	14073(2)	12904(2)	13983(2)	12802(2)	
${}^6\text{H}_{15/2} \rightarrow {}^6\text{H}_{5/2}$	14595(4)	13586(4)	14088(4)	12906(4)	13986(4)	12805(4)	
	15728(2)	15180(2)	15603(2)	14849(2)	15606(2)	14825(2)	

Table 13: Energies and oscillator strengths (f) of f-d transitions of $[\text{BkX}_6]^{3-}$. Energies are given in cm^{-1} .

X = F				X = Cl				X = Br			
CASSCF	f^*	NEVPT2	f^*	CASSCF	f^*	NEVPT2	f^*	CASSCF	f^*	NEVPT2	f^*
20468.2	0.640	56136.8	1.323	26348.9	0.014	38381.3	0.065	28220.7	0.000	39837.5	0.017
20468.2	0.570	56136.8	1.019	26348.9	5.598	38381.3	0.918	28221.4	0.052	39839.8	0.000
20474.8	0.300	56138.4	1.358	26571.7	7.713	38597.3	13.421	28241.8	4.910	39857.5	7.265
20476.8	0.200	56138.5	0.771	26571.7	7.780	38597.3	13.501	28242.0	4.515	39858.0	8.302
20479.6	0.810	56140.8	0.953	26679.7	0.017	38723.4	0.000	28243.5	4.190	39858.0	7.825
20528.6	0.002	56141.2	1.450	26683.6	0.001	38724.9	0.008	28782.2	0.000	39859.9	0.000
20530.2	0.0817	56142.2	0.871	26699.5	0.121	38772.0	0.272	28922.2	0.449	40412.9	0.794
20541.6	0.116	56143.0	0.638	26703.7	0.324	38772.7	0.289	28927.6	0.431	40546.3	0.765
20548.1	0.007	56143.9	0.420	26704.4	0.219	38781.4	0.002	28932.0	0.399	40546.9	0.848
20550.0	0.001	56144.5	0.159	27185.5	0.572	39203.3	1.432	29054.8	0.002	40551.5	0.001
20561.1	0.058	56144.9	0.419	27185.9	0.591	39206.2	0.545	29055.4	0.000	40666.0	0.008
20561.2	0.021	56216.3	0.001	27192.8	1.443	39207.9	0.766	29058.1	0.003	40667.6	0.002
20631.0	0.003	56216.5	0.002	27202.1	0.029	39240.7	0.001	29865.7	0.000	40671.4	0.000
20631.0	0.001	56217.2	0.001	27202.7	0.001	39240.7	0.017	29946.1	0.000	41503.3	0.000
20648.1	0.007	56238.2	0.001					29946.6	0.000	41576.8	0.000
20648.2	0.002	56240.0	0.008					29948.9	0.000	41579.5	0.000
20659.1	0.010	56242.8	0.048					29990.0	0.002	41582.2	0.003
20660.3	0.003	56244.1	0.754					29991.1	0.000	41620.2	0.000
20664.9	0.010	56245.0	0.056					30172.2	0.000	41622.4	0.000
20669.4	0.007	56319.9	0.066					30173.2	0.000	41789.9	0.000
20670.2	0.025	56324.1	0.075					30174.0	0.000	41790.9	0.000
21547.1	0.016	56326.2	0.091								
21548.1	0.059	56336.7	0.002								
21553.2	0.038	56338.9	0.005								
21559.6	0.119	56340.5	0.000								
21562.5	0.003	56357.3	0.001								
21569.0	0.163	56409.2	0.000								
21570.1	0.044	56413.3	1.700								
21579.9	0.095	56415.9	2.530								
21580.7	0.014	56418.9	0.001								
21591.0	0.017	56420.0	0.001								
21598.7	0.001	56470.0	0.006								
21603.4	0.014	56470.6	0.012								
21604.6	0.065	56473.6	0.033								

* The oscillator strengths are scaled by a 1e-4 factor. All the values were obtained from an SO-coupling calculation. All reported transitions occurs from the ground state (configurations in Table 7 of the main manuscript) to an excited states which implies an electron promotion between 5f and 6d subshells.

Table 14: Energies and oscillator strengths (f) of f-d transitions of $[\text{CfX}_6]^{3-}$ (X = F, Cl, Br). Energies are given in cm^{-1} .

X = F				X = Cl				X = Br			
CASSCF	f^*	NEVPT2	f^*	CASSCF	f^*	NEVPT2	f^*	CASSCF	f^*	NEVPT2	f^*
50371.4	0.073	64572.5	0.002	47820.4	0.001	50066.8	0.00258	47602.1	0.000	49624.1	0.014
50371.4	0.074	64572.5	0.002	47820.4	0.001	50066.8	0.00072	47602.1	0.000	49624.1	0.029
50375.0	0.044	64597.2	0.026	47820.4	0.001	50069.9	0.00029	47606.4	0.000	49674.6	1.558
50375.0	0.098	64597.2	0.046	47820.4	0.001	50069.9	0.00066	47606.4	0.000	49674.6	0.923
50610.4	1.219	64746.2	0.918	48161.3	0.001	50301.0	0.00203	47930.4	0.078	49680.3	1.395
50610.4	1.218	64746.2	0.787	48161.3	0.001	50301.0	0.01087	47930.4	0.512	49680.3	0.954
50617.6	1.115	64747.7	0.931	48164.5	0.590	50375.1	2.38447	47934.1	0.206	49861.6	0.025
50617.6	0.542	64973.6	0.039	48164.5	0.574	50375.1	0.77627	47934.1	0.460	49861.6	0.203
50699.3	0.000	64973.6	0.040	48164.7	0.386	50382.1	0.86747	47964.2	0.021	50178.8	2.671
50699.3	0.006	65130.1	0.041	48164.7	0.744	50382.1	2.30598	47964.2	0.009	50178.8	7.595
50916.8	0.063	65130.1	0.058	48305.3	0.188	50571.0	0.27577	48079.9	0.173	50201.3	1.448
50916.8	0.049	65192.0	0.032	48305.3	0.180	50571.0	0.18592	48079.9	0.165	50201.3	8.913
51178.6	0.010	65192.0	0.032	48670.4	5.260	50969.0	9.29247	48388.5	6.0816	50880.5	0.055
51178.6	0.025	65215.7	0.094	48670.4	2.203	50969.0	1.70078	48388.5	2.532	50880.5	0.409
51186.7	0.048	65215.7	0.094	48672.0	6.761	50970.9	3.84513	48421.3	7.055	50893.3	0.249
51186.7	0.046	65252.0	0.099	48672.0	2.631	50970.9	6.47925	48421.3	1.080	50893.3	0.262
51373.1	0.017	65252.0	0.047	48776.0	0.001	51139.2	0.00262	48447.0	0.043	51982.6	0.514
51373.1	0.015	65331.5	0.109	48776.0	0.000	51139.2	0.00321	48447.0	0.010	51982.6	0.454
51886.9	0.519	65331.5	0.294	49315.4	0.297	51580.6	0.20275	49114.5	0.020	51985.2	0.873
51886.9	0.139	65431.5	0.140	49315.4	0.129	51580.6	0.22682	49114.5	0.354	52807.7	0.033
51888.5	0.249	65431.5	0.140	49315.8	0.346	51587.3	0.45579	49127.2	0.209	52807.7	0.134
51888.5	0.273	65500.4	0.073	49315.8	0.084	51587.3	0.07798	49127.2	0.228	52813.8	0.033
51965.6	0.107	65500.4	0.114					50171.9	0.078	52813.8	0.122
51965.6	0.071	65899.5	0.002					50171.9	0.882	52863.7	0.215
52002.9	0.498	65899.5	0.008					50175.8	0.440	52863.7	0.012
52002.9	0.499	65901.3	0.000					50175.8	0.574	52899.7	0.219
52032.9	0.000	65901.3	0.000					50318.1	0.058	52899.7	0.248
52209.6	4.600	66256.5	0.435					50318.1	0.052	53163.3	0.210
52239.1	1.657	66256.5	1.101					50848.0	0.041	53163.3	3.103
								50848.0	0.359	53169.7	1.148
										53169.7	2.012
										53286.2	0.195
										53286.2	0.115
										53402.8	0.014
										53592.5	0.312
										53592.5	0.286

* The oscillator strengths are scaled by a 1e-4 factor. All the values were obtained from an SO-coupling calculation.

Table 15: QTAIM parameters for $[BkX_6]^{3-}$ and $[CfX_6]^{3-}$ ($X = F, Cl, Br$) with at Bk-X distance corresponding to the Cf-X distance and *viceversa*. This variation in distance was used to compare Bk(III) with Cf(III) covalency independently of the bond distance. In parenthesis are given the values at the optimized bond distances from Table 3 in the main article.

	ρ	δ	O.S.
$[BkF_6]^{3-}$ (Cf-F dist)	0.068 (0.066)	0.302 (0.296)	3.456 (3.445)
$[BkCl_6]^{3-}$ (Cf-Cl dist)	0.047 (0.046)	0.330 (0.326)	3.323 (3.317)
$[BkBr_6]^{3-}$ (Cf-Br dist)	0.041 (0.041)	0.337 (0.335)	3.263 (3.260)
$[CfF_6]^{3-}$ (Bk-F dist)	0.064 (0.066)	0.291 (0.296)	3.423 (3.434)
$[CfCl_6]^{3-}$ (Bk-Cl dist)	0.061 (0.046)	0.377 (0.324)	3.400 (3.300)
$[CfBr_6]^{3-}$ (Bk-Br dist)	0.040 (0.040)	0.329 (0.332)	3.243 (3.369)

Table 16: Calculated and experimental M-X bond distances (M=Tb, Dy, Bk, Cf, Es, Fm ; X = F, Cl, Br) for trivalent metals. The only experimental distance reported for berkelium hexachloride corresponds to the solid state distance. All distances are given in Angstroms.

$[MX_6]^{3-}$		Calculated ^a	Calculated elsewhere ^b	Experimental
Tb	F	2.22	-	2.25 ^c
	Cl	2.69	-	2.69 ^d
	Br	2.85	-	2.82 ^e
Dy	F	2.20	-	-
	Cl	2.68	-	2.62 ^f
	Br	2.84	-	-
Bk	F	2.27	-	-
	Cl	2.72	2.72	2.58 ^g
	Br	2.88	-	-
Cf	F	2.26	-	-
	Cl	2.71	2.71	2.65 ^f
	Br	2.87	-	-
Es	F	2.25	-	-
	Cl	2.70	2.70	-
	Br	2.86	-	-
Fm	F	2.24	-	-
	Cl	2.69	2.69	-
	Br	2.85	-	-

^aDistances optimized at BP86/TZVP level of theory

^bDistances optimized at NEVPT2 level of theory, extracted from reference 48 in the main manuscript

^cDistance extracted from reference 71 in the main manuscript

^dDistance extracted from reference 72 in the main manuscript

^eDistance extracted from reference 74 in the main manuscript

^fDistance extracted from reference 73 in the main manuscript

^gDistance extracted from reference 8 in the main manuscript

Table 17: Calculated Bk-Cl bond distance for tetravalent berkelium. All distances are given in Angstroms.

$[BkCl_6]^{2-}$		Calculated ^a	Calculated elsewhere ^b
Bk	Cl	2.61	2.56

^aDistance optimized at BP86/TZVP level of theory

^bDistance optimized at NEVPT2 level of theory, extracted from reference 48 in the main manuscript