Supporting Information for "Geometries, interaction energies and bonding in $[Po(H_2O)_n]^{4+}$ and $[PoCl_n]^{4-n}$ complexes", by Zhutova *et al.*

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Table S1 Interaction energies (kcal mol^{-1}) with BSSE correction obtained at various levels of theory for polonium(IV) complexes with water, computed according to Eqs. 1 and 2 (see main text).

$n(H_2O)$	CCSD(T) / aug-cc-pVDZ	MP2 / aug-cc-pVDZ	MP2 / aug-cc-pVTZ	MP2 / aug-cc-pVQZ*	MP2 / def2-TZVP	MP2 / def2-QZVP
1	−236.2	−249.2	−257.9	−262.7	−262.0	−263.8
2	−409.5	−439.0	−454.7	−462.9	−461.4	−464.9
3	−541.1	−586.4	−607.7	−618.5	−616.1	−621.4
4		−694.9	−718.8		−728.9	
5		−791.8	−817.6		−829.4	
6		−875.8	−903.1		−918.2	
7		−941.2	−971.1		−987.8	
8		−1004.4	−1035.9		−1054.0	
9		−1052.7	−1085.5		−1104.4	

*Geometries for these calculations were taken from the MP2/aug-cc-pVTZ structures (single points).

Table S2 Interaction energies (kcal mol^{-1}) without BSSE correction obtained at various levels of theory for polonium(IV) complexes with water, computed according to Eq. 1 (see main text).

$n(H_2O)$	CCSD(T) / aug-cc-pVDZ	CCSD(T) / aug-cc-pVTZ	CCSD(T) / def2-TZVP	MP2 / aug-cc-pVDZ	MP2 / aug-cc-pVTZ	MP2 / aug-cc-pVQZ*	MP2 / def2-TZVP	MP2 / def2-QZVP
1	−238.6	−254.6	−247.4	−251.7	−261.0	−267.8	−264.7	−262.5
2	−414.3	−446.2	−431.0	−443.7	−460.8	−472.4	−466.8	−462.3
3	−548.2			−593.1	−616.6	−632.0	−624.6	−617.6
4				−703.0	−730.0		−739.9	
5				−801.1	−830.9		−843.1	
6				−886.1	−917.9		−934.9	
7				−952.4	−987.6		−1006.2	
8				−1016.4	−1054.6		−1074.0	
9				−1065.4	−1106.5		−1126.0	

*Geometries for these calculations were taken from the MP2/aug-cc-pVTZ structures (single points).

Table S3 Interaction energies (kcal mol^{-1}) with BSSE correction obtained at the MP2 level of theory with various basis sets for polonium(IV) complexes with chlorides, computed according to Eqs. 1 and 2 (see main text).

$n(Cl^-)$	aug-cc-pVDZ	aug-cc-pVTZ	aug-cc-pVQZ*	def2-TZVP	def2-QZVP*
1	−859.8	−877.4	−884.4	−883.7	−885.5
2	−1371.5	−1403.4	−1414.8	−1415.0	−1416.7
3	−1693.1	−1734.0	−1748.4	−1749.2	−1750.1
4	−1847.0	−1889.0	−1905.6	−1911.4	−1909.3
5	−1897.8			−1974.3	−1972.5
6	−1886.5			−1947.8	−1949.5
7	−1749.1			−1861.4	−1809.6
8	−1546.5			−1650.3	−1601.8

*Geometries for these calculations were taken from the MP2/aug-cc-pVTZ and MP2/def2-TZVP structures, respectively (single points).

Table S4 Interaction energies (kcal mol^{-1}) without BSSE correction obtained at the MP2 level of theory with various basis sets for polonium(IV) complexes with chlorides, computed according to Eq. 1 (see main text).

$n(Cl^-)$	aug-cc-pVDZ	aug-cc-pVTZ	aug-cc-pVQZ*	def2-TZVP	def2-QZVP*
1	−862.0	−880.0	−887.7	−888.9	−887.8
2	−1376.1	−1408.6	−1421.2	−1425.2	−1421.9
3	−1700.3	−1742.3	−1758.0	−1765.4	−1759.0
4	−1857.6	−1899.5	−1916.8	−1933.0	−1923.2
5	−1923.0			−2003.0	−1990.9
6	−1905.1			−1986.1	−1972.7
7	−1772.9			−1904.5	−1837.9
8	−1575.7			−1696.8	−1634.1

*Geometries for these calculations were taken from the MP2/aug-cc-pVTZ and MP2/def2-TZVP structures, respectively (single points).

Table S5 Mean MP2 Po−O bond lengths (Å), obtained for polonium(IV) complexes with water for various basis sets.

$n(H_2O)$	aug-cc-pVDZ	aug-cc-pVTZ	def2-TZVP	def2-QZVP
1	2.08	2.04	2.03	2.02
2	2.11	2.08	2.07	2.06
3	2.15	2.11	2.11	2.10
4	2.20	2.17	2.17	2.16
5	2.25	2.22	2.22	2.21
6	2.30	2.27	2.27	2.26
7	2.34	2.31	2.31	2.30
8	2.37	2.34	2.34	2.34
9	2.41	2.38	2.39	2.37

Table S6 Mean MP2 Po−O bond lengths (Å), obtained for polonium(IV) complexes with chlorides for various basis sets

$n(Cl^-)$	aug-cc-pVDZ	aug-cc-pVTZ	def2-TZVP
1	2.30	2.25	2.25
2	2.33	2.29	2.28
3	2.40	2.35	2.34
4	2.52	2.48	2.47
5	2.59		2.54
6	2.66		2.60
7	2.77		2.72
8	2.88		2.83

Table S7 MP2/def2-TZVP atomic charges for polonium(IV) complexes with chlorides derived from different charge schemes.

Molecule	QTAIM			Mulliken			Hirshfeld		
	q(Po)	q(Cl)		q(Po)	q(Cl)		q(Po)	q(Cl)	
$[PoCl]^{3+}$	2.52	0.48		2.23	0.77		2.15	0.85	
$[PoCl_2]^{2+}$	2.06	−0.03		1.52	0.24		1.34	0.33	
$[PoCl_3]^{+}$	1.94	−0.31		1.25	−0.08		0.93	0.02	
$PoCl_4$	1.98	−0.50		1.25	−0.31		0.77	−0.19	
$[PoCl_5]^{-}$	2.06	−0.64	(x2)	1.29	−0.49	(x2)	0.71	−0.40	(x2)
		−0.59	(x3)		−0.43	(x3)		−0.34	(x3)
$[PoCl_6]^{2-}$	2.13	−0.69		1.43	−0.57		0.67	−0.44	
$[PoCl_7]^{3-}$	2.13	−0.74	(x5)	1.84	−0.70	(x5)	0.92	−0.58	(x5)
		−0.71	(x2)		−0.67	(x2)		−0.50	(x2)
$[PoCl_8]^{4-}$	2.12	−0.76		1.96	−0.74		1.02	−0.63	