Supporting Information for:

"Excited states of polonium(IV): Electron correlation and spin-orbit coupling in the Po^{4+} free ion and in the bare and solvated $[PoCl_5]^-$ and $[PoCl_6]^{2-}$ complexes"

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1 Molecular structures

All the structures have been obtained at the MP2/def2-TZVP level of theory (see main text for more details).

1.1 Gas phase structures

1. $[PoCl_5]^-$:

6

Po 0.00000 0.00000 0.00000
Cl 0.00000 2.52599 0.00000
Cl 0.00000 0.00000 2.55781
Cl 2.18757 -1.26300 0.00000
Cl 0.00000 0.00000 -2.55781
Cl -2.18757 -1.26300 0.00000

2. $[PoCl_6]^{2-}$:

7

Po 0.00000 0.00000 0.00000
Cl 0.00000 0.00000 2.60400
Cl 0.00000 2.60400 0.00000
Cl 2.60400 0.00000 0.00000
Cl 0.00000 0.00000 -2.60400
Cl -2.60400 0.00000 0.00000
Cl 0.00000 -2.60400 0.00000

3. $[PoCl_5(H_2O)]^-$:

9

Po -0.06000 -0.00000 0.01300
Cl -1.62200 1.79100 -0.84800
Cl -1.62200 -1.79100 -0.84800
Cl -0.85200 -0.00000 2.37400
Cl 1.81200 1.84600 0.23400
Cl 1.81200 -1.84600 0.23400
O 1.20700 0.00000 -2.09800
H 1.68900 -0.76800 -1.90300
H 1.68900 0.76800 -1.90300

4. $[PoCl_5(H_2O)_2]^-$:

12

Po 0.22448 -0.02103 -0.02614
Cl 1.21980 2.14485 0.91823
O -1.23055 0.39504 1.95667
H -2.17313 0.30679 1.64945
H -1.05685 1.33640 2.11044
O -3.56325 -0.06500 0.71412
H -3.24727 -0.93499 0.41369
H -3.30254 0.50556 -0.03347
Cl -1.30851 -2.09078 -0.40216
Cl 1.63513 -0.22515 -2.05509
Cl -1.59506 1.45125 -1.24523
Cl 1.77060 -1.40296 1.41302

5. $[PoCl_6(H_2O)]^{2-}$:

10

Po 0.23500 0.00000 -0.00000
Cl 2.05000 1.82600 -0.00000
Cl 0.23000 0.00000 2.59300
O -4.31900 -0.00000 0.00000
Cl -1.62400 -1.87900 0.00000
Cl 0.23000 -0.00000 -2.59300
Cl -1.62400 1.87900 -0.00000
Cl 2.05000 -1.82600 0.00000
H -3.76600 -0.72800 0.00000
H -3.76600 0.72800 -0.00000

1.2 Solvated structures (polarisable continuum model)

1. $[PoCl_5]^-$:

6

Po 0.00000 0.00000 0.20719
Cl -0.00000 2.55845 0.29454
Cl 0.00000 0.00000 -2.20194
Cl -2.55845 0.00000 0.29454
Cl -0.00000 -2.55845 0.29454
Cl 2.55845 -0.00000 0.29454

2. $[PoCl_6]^{2-}$:

7

Po 0.00000 0.00000 0.00000
Cl -0.00000 0.00000 2.58932
Cl -0.00000 2.58932 -0.00000
Cl 2.58932 0.00000 0.00000
Cl -0.00000 -0.00000 -2.58932
Cl -2.58932 0.00000 -0.00000
Cl -0.00000 -2.58932 0.00000

3. $[PoCl_5(H_2O)]^-$:

9

Po -0.00082 -0.00000 -0.03248
Cl -2.57448 -0.00027 -0.11770
Cl 0.00269 -2.55349 -0.33109
Cl -0.02789 0.00005 2.47370
Cl 0.00216 2.55347 -0.33116
Cl 2.57505 0.00026 -0.06290
O 0.02637 -0.00002 -2.40170
H 0.11994 -0.78585 -2.89143
H 0.11986 0.78584 -2.89141

4. $[PoCl_5(H_2O)_2]^-$:

12

Po -0.20000 -0.00800 0.00900
Cl -0.95800 2.29200 -0.86000
O 1.34400 0.05600 -1.86400
H 2.29600 0.03300 -1.54800
H 1.24200 0.86400 -2.39200
O 3.73500 0.05400 -0.78400
H 4.19200 -0.79400 -0.69800
H 3.48800 0.30800 0.12100
Cl 0.89500 -2.27100 0.52400
Cl -1.78900 -0.06600 1.93500
Cl 1.64800 1.15500 1.43300
Cl -1.85900 -1.14700 -1.56200

5. $[PoCl_6(H_2O)]^{2-}$:

10

Po -0.22200 -0.00000 -0.00400
Cl -1.90300 1.81700 -0.68200
Cl 0.76400 0.00000 -2.39000
Cl 1.48200 -1.86400 0.68800
Cl -1.17400 -0.00000 2.39700
Cl 1.48200 1.86400 0.68900
Cl -1.90300 -1.81700 -0.68300
O 4.09600 -0.00000 -0.02600
H 3.58500 -0.74500 0.11700
H 3.58500 0.74400 0.11700

2 Supplemantary tables

Table S1 Numerical compositions the excited energy levels expressed in terms of the spin-orbit free states, for the bare $[PoCl_5]^-$ and $[PoCl_6]^{2-}$ complexes in the gas phase, obtained at the c-SOCI/SC-NEVPT2 level.

System	SPG	Symmetry	Composition
$[PoCl_5]^-$	D_{3h}	A_1''	$81.3\% *^3 E' + 18.7\% *^3 A_2''$
		A_2''	$86.9\% *^3 E' + 13.1\% *^1 A_2''$
		E'	$48.2\% *^3 E' + 20.8\% *^3 A_2'' + 31.0\% *^1 E'$
		E''	$^3E'$
		E'	$46.9\%' *^3 E' + 3.3\%' *^3 A_2'' + 49.8\% *^1 E'$
		A_1''	$18.7\% *^3 E' + 81.3\% *^3 A_2''$
		E'	$4.9\% *^3 E' + 75.9\% *^3 A_2'' + 19.2\% *^1 E'$
		A_2''	$13.1\% *^3 E' + 86.9\% *^1 A_2''$
$[PoCl_6]^{2-}$	O_h	A_{1u}	$^3T_{1u}$
		T_{1u}	$73.8\% *^3 T_{1u} + 26.2\% *^1 T_{1u}$
		$T_{2u} \oplus E_u$	$^3T_{1u}$
		T_{1u}	$26.2\% *^3 T_{1u} + 73.8\% *^1 T_{1u}$

Table S2 Numerical compositions the excited energy levels expressed in terms of the spin-orbit free states, for the bare $[PoCl_5]^-$ and $[PoCl_6]^{2-}$ complexes at the solvated geometries (polarisable continuum model), obtained at the c-SOCI/SC-NEVPT2 level.

System	SPG	Symmetry	Composition
$[PoCl_5]^-$	C_{4v}	A_2	$68.6\%^3A_1 + 31.3\% *^3 E$
		E	$74.8\% *^3 A_1 + 15.5\% *^3 E + 9.6\% *^1 E$
		A_1	$36.3\% *^3 E + 63.1\% *^1 A_1$
		A_2	$31.3\% *^3 A_1 + 68.7\% *^3 E$
		A_1	$62.9\% *^3 E + 36.7\% *^1 A_1$
		E	$24.4\% *^3 A_1 + 59.3\% *^3 E + 16.3\% *^1 E$
		$B_1 \oplus B_2$	^3E
		E	$0.6\% *^3 A_1 + 25.2\% *^3 E + 74.0\% *^1 E$
$[PoCl_6]^{2-}$	O_h	A_{1u}	$^3T_{1u}$
		T_{1u}	$73.9\% *^3 T_{1u} + 26.1\% *^1 T_{1u}$
		$T_{2u} \oplus E_u$	$^3T_{1u}$
		T_{1u}	$26.1\% *^3 T_{1u} + 73.9\% *^1 T_{1u}$

Table S3 Spin character of the excited energy levels and excitation energies (in eV), for the $[PoCl_5(H_2O)]^-$ complex at the solvated geometry (polarisable continuum model), obtained at the c-SOCI/SC-NEVPT2 level.

System	SPG	Composition	Energy
$[PoCl_5(H_2O)]^-$	C_1	triplet	3.21
		triplet/singlet	3.28
		triplet/singlet	3.36
		triplet/singlet	3.37
		triplet	5.14
		triplet/singlet	5.17
		triplet/singlet	5.20
		triplet/singlet	5.32
		triplet	5.40
		triplet/singlet[a]	5.41
		triplet/singlet	5.70
		triplet/singlet	5.84

[a] This energy level correlates with a pure spin-triplet energy level in the reference C_{4v} structure of the $[PoCl_5]^-$ complex. Because of the symmetry lowering to C_1, some little spin-singlet character has emerged. This is not the case of the energy levels that are here indicated as "triplet" (for which no spin-singlet character was numerically observed).