Supplementary Material (ESI) for New Journal of Chemistry

DFT modeling of the relative affinity of nitrogen ligands for trivalent f elements: an energetic point of view

Laurence Petit, Claude Daul, Carlo Adamo and Pascale Maldivi

SUPPLEMENTARY INFORMATION

Supplementary information 1. Detailed results for $[La(MeBTP)_3]^{3+}$ in a vacuum and in pyridine solvent (COSMO). Experimental values[23] are mentioned in parentheses.

	$[La(MeBTP)_3]^{3+}$, vacuum	**$[La(MeBTP)_3]^{3+}$, pyridine Cosmo**
Optimized geometries		
d(M-N_c), Å	2.68 (2.67)	2.68 (2.67)
d(M-N_l), Å	2.66 (2.63)	2.66 (2.63)
Mulliken charges		
q(M), $\|e^-\|$	2.00	1.98
q(MeBTP), $\|e^-\|$	0.33	0.34
Energetic analysis		
ΔE_{Pauli}, eV	8.74	8.90
ΔE_{elec}, eV	-17.84	-19.70
ΔE_{steric}, eV	-9.11	-10.79
ΔE_{orb}, eV	-20.54	-18.98
ΔE_{solv} (el)*, eV	-	16.76
ΔE_{solv} (cd)*, eV	-	0.18
ΔE_{tot}, eV	-29.64	-12.84
Orbital analysis		
	No backdonation	**No backdonation**
	Donation 0.18 $\|e^-\|$ on d(La) orbitals	**Donation** 0.18 $\|e^-\|$ on d(La) orbitals

* el : electrostatic term in the solvation energy – cd : cavitation and dispersion terms in the solvation energy

Supplementary information 2. Energetic decomposition of the different contributions involved in the complexation process of M^{3+} by 3 ligands. Details relative to cerium complexes in the optimized geometry of uranium systems and of uranium complexes in the optimized geometry of cerium systems is also given. For comparison, the evolution of back-bonding effects is shown.

	M=Ce	M=U	M=Ce in U geometry	M=U in Ce geometry
[M(Terpy)$_3$]$^{3+}$				
ΔE_{Pauli}, eV	48.61	63.46	57.21	53.63
ΔE_{elec}, eV	-20.37	-23.76	-23.48	-20.36
ΔE_{steric}, eV	28.24	39.70	33.72	33.27
ΔE_{orb}, eV	-57.56	-70.31	-63.33	-63.22
$\Delta E_{bonding}$, eV	-29.32	-30.62	-29.60	-29.94
Back-bonding, $\|e^-\|$	0.08	0.48	0.16	0.30
[M(MeBTP)$_3$]$^{3+}$				
ΔE_{Pauli}, eV	52.24	68.79	61.79	57.84
ΔE_{elec}, eV	-21.64	-25.50	-25.03	-21.77
ΔE_{steric}, eV	30.60	43.29	36.76	36.08
ΔE_{orb}, eV	-61.52	-75.23	-67.45	-67.88
$\Delta E_{bonding}$, eV	-30.91	-31.94	-30.69	-31.80
Back-bonding, $\|e^-\|$	0.16	0.59	0.25	0.47
[M(HBTP)$_3$]$^{3+}$				
ΔE_{Pauli}, eV	51.35	67.30		
ΔE_{elec}, eV	-21.29	-24.95		
ΔE_{steric}, eV	30.06	42.35		
ΔE_{orb}, eV	-58.86	-72.27		
$\Delta E_{bonding}$, eV	-28.79	-29.92		

Supplementary information 3. Percentage contributions of the electrostatic and orbital terms to the metal-ligand bond.

	$[Ce(terpy)_3]^{3+}$	$[U(terpy)_3]^{3+}$	$[Ce(MeBTP)_3]^{3+}$	$[U(MeBTP)_3]^{3+}$	$[Ce(HBTP)_3]^{3+}$	$[U(HBTP)_3]^{3+}$
%elec	26.1	25.3	26.0	25.3	26.6	25.7
%orb	73.9	74.7	74.0	74.7	73.4	74.3