Interaction of M^{3+} lanthanide cations with phosphoryl containing $(alkyl)_3P{=}O$ *versus* $(alkyl\text{-}O)_3P{=}O$ ligands: steric effects are more important than basicity effects †

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The concept of acid–base interactions between metallic cations and putative ligands, widely used in cation coordination and complexation chemistry, is discussed from the analysis of M^{3+} lanthanide cation binding to phosphoryl ligands in the gas phase. We report quantum mechanical calculations on the effect of alkyl *vs.* *O*-alkyl substitution in phosphoryl-containing ligands **L** interacting with M^{3+} (La^{3+}, Eu^{3+}, Yb^{3+}; **L** = Me_3PO, $Me_2(MeO)PO$, $Me(MeO)_2PO$ and $(MeO)_3PO$). In the charged 1 : 1 $\mathbf{L}M^{3+}$ complexes, *O*-alkyl substituted ligands yield lower interaction energies than the alkyl substituted ones, in agreement with the calculated gas phase basicities. However, the effect is surprisingly small (about 10 times smaller than the alkyl *vs.* aryl substituent effect). The comparison of $\mathbf{L}M^{3+}$ with neutral $\mathbf{L}MCl_3$ and $\mathbf{L}_2MCl_3$ complexes reveals an *amplification* of *O*-alkyl *vs.* alkyl weakening effect, though, due to repulsions between **L**, the counterions, and the other ligand, and to the softer character of the metal–ligand bond. Thus, in condensed phases where the first coordination shell of the cation is saturated and generally contains neutralizing counterions, the better binding of $(alkyl)_nPO$ ligands, compared to $(alkyl\text{-}O)_nPO$ ones results mostly from "steric" interactions in the first coordination sphere, rather than from the changes in oxygen "basicity". The conclusions are validated by a number of comparisons using polarization functions on the ligand and accounting for correlation effects (MP2 or DFT-B3LYP calculations). They are important in the context of designing efficient ionophores for lanthanide and actinide cations.

Introduction

The design of ligands for lanthanide or actinide cations represents a challenging task for important applications in extraction metallurgy,[1–3] in photophysics and medicine[4–7] and from a basic point of view. Following the analysis performed in host–guest supramolecular systems, it is desirable to precisely determine and analyse the intrinsic (gas phase) interactions between the cation and the binding sites of the ligand.[8–12] Unfortunately, for practical reasons, gas phase information for trivalent lanthanide or actinide ions is presently unavailable. This led us to undertake quantum mechanical (QM) studies on the interaction between lanthanide cations and typical ligands.[13–16] QM calculations provide insights into the intrinsic metal–ligand interaction energies, and into the electronic and structural changes that occur upon complexation. At a more general level, they provide a basis to analyze widely used concepts (*e.g.* donor–acceptor and HSAB interactions) in metal ion coordination chemistry.[17–21]

In this paper, we focus on lanthanide complexes of neutral phosphoryl containing molecules of $R^1R^2R^3PO$ type (R^i = alkyl/*O*-alkyl groups), with the aim of investigating the effect of the "basicity" of the phosphoryl oxygen O_P on the binding strength with trivalent lanthanide cations. The latter is expected to decrease upon alkyl→*O*-alkyl substitution, due to the electron-withdrawing effect of *O*-alkyl groups.[22,23] For instance, TBP (tributyl phosphate ($(O\text{-butyl})_3PO$), an extractant molecule used on an industrial scale for the treatment of nuclear waste, extracts less lanthanide and actinide cations than does its $(butyl)_3PO$ analogue.[1] Progressive *O*-alkyl→alkyl substitution in the series of ligands 1–4 (Fig. 1) leads to a regular increase of lanthanide cation extraction efficiency,[24] the latter being assumed to correlate with Taft's polar constants of the substituent groups at phosphorus.[25] There are, however, some problems with the interpretation of such correlations, as substitution not only perturbs the basicity of the ligand, but also modifies the interactions within the first coordination sphere of the cation, as well as solvation features of the complex.[24] We also notice that arguments concerning the basicity of these systems do not rest on direct experimental measurements, but on theoretical models and indices (*e.g.* orbital energies or atomic charges in the gas phase)[26] or on indirect evidence, like comparative hydrogen-bonding. For instance, in CCl_4 solution, the interaction energy (ΔG) between phenol and the phosphoryl system increases from −3.0 for $(MeO)_3PO$, −3.5 for $Me(MeO)_2PO$, to −4.3 kcal mol^{-1} for Me_3PO,[27] which suggests that interactions with cations follow the same sequence. However, in CCl_4 solution, Ph_3PO interacts less (by 0.3 kcal mol^{-1}) than Me_3PO with phenol, although Ph_3PO displays the *largest* interactions with M^{3+} lanthanides, due to polarization effects.[13] Polarization plays a minor role in hydrogen bonding interactions. Thus, *explicit calculations on cation complexes "in the gas phase" are crucial to investigate intrinsic binding features.*

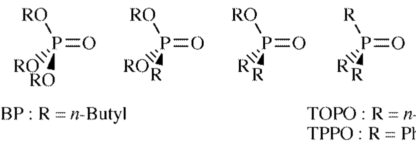

Fig. 1 Phosphoryl derivatives. R = Methyl in the calculated systems.

More specifically, we first selected a series of complexes $\mathbf{L}M^{3+}$, where the ligands model alkylphosphates, dialkyl alkyl-

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† Tables S1–S5 are available as supplementary data. For direct electronic access see http://www.rsc.org/suppdata/p2/1999/2423, otherwise available from BLDSC (SUPPL. NO. 57654, pp. 5) or the RSC Library. See Instructions for Authors available *via* the RSC web page (http://www.rsc.org/authors).

phosphonates, alkyl dialkylphosphinates and trialkylphosphine oxides, respectively (**L** = Me_3PO, $Me_2(MeO)PO$, $Me(MeO)_2PO$ and $(MeO_3)PO$; see Fig. 1). Such functionalities may be anchored to lipophilic platforms like calixarenes, leading to ionophoric molecules.[28–30] Due to computer time limitations, the alkyl group is represented by methyl. Each ligand interacts with La^{3+}, Eu^{3+} and Yb^{3+}, which represent respectively a "large", "average" and "small" ion.[31,32] We first assess the intrinsic ("gas phase") $\mathbf{L}\cdots M^{n+}$ interactions in 1 : 1 charged complexes, and determine the most important trends in geometrical and electronic structures. In relation to Monte Carlo or molecular dynamics (MD) studies of such systems in solution using a force field representation of the potential energy,[33,34] it is indeed important to test how the ligand and ion parameters (effective size, charge, *etc.*) are transferable from one complex to the other at a consistent computational level. In addition, we report the calculated gas phase protonation energies E_{prot} of all ligands **L**, in order to compare the trends in E_{prot} with those in the $\mathbf{L}\cdots M^{3+}$ interaction energies.

We then investigate the role of counterions and of stoichiometry by modeling selected $\mathbf{L}MCl_3$ 1 : 1 and $\mathbf{L}_2MCl_3$ 2 : 1 complexes (**L** = $(MeO)_3PO$ *vs.* Me_3PO; M = La *vs.* Eu *vs.* Yb), which are more representative of complexes formed in condensed phases than are $\mathbf{L}M^{3+}$ complexes. Like those involved in liquid–liquid extraction, they are neutral, and the coordination number of the cation is higher than in the $\mathbf{L}M^{3+}$ complexes. The comparison of $\mathbf{L}M^{3+}$ and $\mathbf{L}_2MCl_3$ complexes will also give insights into the effect of stoichiometry and counterions on the cation selectivities and on the *O*-alkyl *vs.* alkyl substituent effect. The Me_3PO complexes were originally described in ref. 13, but have been reoptimized in a consistent manner together with the $\mathbf{L}MCl_3$ and $\mathbf{L}_2MCl_3$ ones (**L** = Me_3PO).

Methods

The QM *ab initio* calculations were performed at the HF level using the GAUSSIAN94 package.[35] The 46 + $4f^n$ core electrons of the lanthanide cations were described by the quasi relativistic effective core potential (ECP) of Dolg *et al.*[36,37] and the valence electrons by a (7s,6p,5d)/[5s,4p,3d] gaussian basis set supplemented by one f polarization function of exponent 0.591 as optimized for La by Frenking *et al.*[38] This exponent was kept for the whole series of lanthanides. Calculations on the $H_3PO\cdots Eu^{3+}$ system, using a 28 electron small core ECP (*i.e.* including the 4s, 4p, 4d and 4f electrons in the valence space) showed that the use of large core ECP for our purpose is satisfactory.[13] The H, C, N, O, and P atoms were described by the standard "DZ" Dunning–Hay double-ζ basis set[39] adding one 3d polarization function on the P atom of exponent $\zeta_{3d} = 0.37$ (DZ-P* basis set). Additional calculations were performed on all **L**, $\mathbf{L}M^{3+}$, $\mathbf{L}MCl_3$, $\mathbf{L}_2MCl_3$ and $\mathbf{L}H^+$ species, adding polarization functions on all atoms of **L** (exponents being $\zeta_{3dC} = 0.75$, $\zeta_{3dO} = 0.85$, $\zeta_{3dN = 0.80,}$ $\zeta_{2pH} = 0.80$), leading to the DZ* basis set.

The geometries of the systems were obtained as follows. The free ligands **L** and their protonated $\mathbf{L}H^+$ forms were fully optimized at the HF level using analytical gradients and the DZ-P* and DZ* basis sets. For the complexes, all parameters have been numerically optimized at the HF level, freezing the CH_3 and OCH_3 groups at their geometry optimized in the corresponding free ligands. No symmetry constraint was imposed on the system. The conformation of **L** ligands bearing OMe groups depends on the dihedral angle(s) φ = O=P–O–Me. We initially considered all "ideal" conformers of the uncomplexed **L**, with g^+ ($\varphi = 60°$), g^- ($\varphi = -60°$), t ($\varphi = 180°$) dihedrals. Full optimizations with the 6-31G* basis set indicated that the preferred form was *ggg* (45°; 45°; 45°) for $(MeO)_3PO$, $g{+}g^-$ (27°, −27°) for $(MeO)_2MePO$, and *g* (34°) for $(MeO)Me_2PO$. The structure of $(MeO)_3PO$ is in agreement with experimental electron diffraction data[40] and with previous calculations.[41] These structures were used as starting points to optimize the free ligands. In order to get insights into the conformation of the complexed ligands, a full 6-31G* optimization of their Mg^{2+} complexes was first performed. For $(MeO)_3PO$, the two most stable conformers were *gtt* (66°, 140°, 169°) and "*ttt*" (136°, 136°, 136°) ($\Delta E = 0$ and 1.1 kcal mol^{-1}). The conformation of the $(MeO)_2MePO$ and $(OMe)(Me_2)PO$ complexes was respectively *gt* (86°, 169°) and *t* (180°). In addition, we considered the $(MeO)_3PO\cdots Eu^{3+}$ complex in the "ideal" *ttt*, *ttg*, tg^+g^-, g^+g^- and $g^+g^-g^+$ ideal conformations, and optimized the $O_P\cdots Eu^{3+}$, P=O, P–O and O–C distances (Table 1). This study confirmed the preference for the *gtt* and *ttt* forms, which are very close in energy ($\Delta\Delta E = 0$ and 0.2 kcal mol^{-1}). Thus, optimization of the $\mathbf{L}M^{3+}$ complexes started with optimized dihedrals of the corresponding $\mathbf{L}Mg^{2+}$ complexes. Note that for the Me_3PO complexes, the P–Me distances and the $P{=}O\cdots M^{3+}$ angles were optimized, while in the study of Troxler *et al.*,[13] they were kept rigid.

Table 1 $(MeO)_3P{=}O\cdots Eu^{3+}$ complex with "ideal" *g*/*t* O=P–O–C dihedral angles (°): optimized distances (Å) and relative energies (kcal mol^{-1}) from HF/DZ*//HF/DZ* calculations

Dihedral angles	*d*(O=P)	*d*(P–O)	*d*(O–C)	*d*(M–O)	ΔE^a
(300,300,300)	1.667	1.523	1.471	1.976	7.59
(300,300,180)	1.645	1.525	1.477	1.978	2.38
(300,60,180)	1.646	1.525	1.477	1.978	5.33
(300,180,180)	1.622	1.622	1.483	1.982	0.00[b]
(60,300,180)	1.644	1.643	1.528	1.977	6.02
(60,300,300)	1.667	1.526	1.470	1.977	14.75
(180,180,180)	1.601	1.538	1.485	1.986	0.19
(134,134,134)[c]	1.640	1.527	1.492	1.964	−9.29

[a] ΔE with respect to the most stable conformation (300,180,180). [b] Total energy $E = -793.0332$ hartrees. [c] Optimized complex.

In the $\mathbf{L}MCl_3$ and $\mathbf{L}_2MCl_3$ complexes (**L** = Me_3PO *vs.* $(MeO)_3PO$) we optimized the $M\cdots O$, $M\cdots Cl$, P=O, P–R distances, the $P{=}O\cdots M$, Cl–M–Cl, R–P=O bond angles and the O=P–O–C and P=O–M–Cl dihedrals. No symmetry was imposed. The initial conformation of the complexed $(MeO)_3PO$ ligand was taken from the corresponding most stable $\mathbf{L}M^{3+}$ complexes (see Table 2).

The effect of electron correlation was investigated by performing MP2/DZ*//HF/DZ-P* and B3LYP-DFT/DZ*//HF/DZ-P* calculations on all $\mathbf{L}M^{3+}$ complexes, as well as on selected $\mathbf{L}EuCl_3$ and $\mathbf{L}_2EuCl_3$ complexes. The fact that geometry optimization at the HF level was sufficient was checked on Eu^{3+} complexes, where the DFT/DZ*//DFT/DZ* interaction energies (obtained from structures optimized at the DFT level) differed by less than 3 kcal mol^{-1} from the DFT/DZ*//HF/DZ-P* energies obtained from structures optimized at the HF level (Table 3). Similar conclusions have been obtained previously with the $H_3PO\cdots UO_2^{2+}$ system.[14]

The interaction energy ΔE between the ligand **L** and the cation M^{3+} or the salt MCl_3 was calculated with respect to the optimized geometries of all species, as defined in Chart 1. The basis set superposition error ("BSSE") was estimated in typical cases using the counterpoise method.[42] The atomic charges were obtained by a Mulliken population analysis.

Results

In the following, we compare the relative binding strengths in the cation series and in the ligand series. Most of the conclusions are independent of the computational level. Therefore, the numbers cited in the text refer to the "standard" HF/DZ*//HF/DZ-P* methodology for simplicity.[43] We first analyze the most salient trends in the structural and electronic features of the charged $\mathbf{L}M^{3+}$ complexes. This is followed by the neutral $\mathbf{L}MCl_3$ and $\mathbf{L}_2MCl_3$ systems.

Table 2 Interaction energies ΔE (kcal mol^{-1}) in the **L**M^{3+} complexes at different computational levels (HF/DZ-P* optimization). BSSE is the basis set superposition energy and ΔE_{corr} is the BSSE corrected interaction energy. Total energies are given in Table S1

		HF/DZ*			DFT/DZ*			MP2/DZ*		
Ligand (L)	M	ΔE	BSSE	ΔE_{corr}	ΔE	BSSE	ΔE_{corr}	ΔE	BSSE	ΔE_{corr}
$(MeO)_3PO$	La	−206.1	3.3	−202.8	−227.0	5.2	−221.8	−217.3	7.7	−209.5
	Eu	−225.9	3.5	−222.5	−250.0	5.4	−244.6	−238.6	8.5	−230.1
	Yb	−245.2	3.7	−241.5	−270.1	5.7	−264.5	−257.9	9.0	−249.0
$(MeO)_2MePO$	La	−206.4	3.4	−203.0	−227.6	5.2	−222.4	−217.7	7.9	−209.8
	Eu	−226.3	3.6	−222.7	−250.3	5.3	−245.0	−239.0	8.6	−230.4
	Yb	−245.5	3.7	−241.7	−270.6	5.5	−265.0	−258.2	9.0	−249.2
$(MeO)Me_2PO$	La	−207.9	3.5	−204.5	−230.7	5.5	−225.3	−220.5	8.1	−212.4
	Eu	−227.9	3.6	−224.2	−253.7	5.7	−248.0	−241.9	8.8	−233.2
	Yb	−247.1	3.8	−243.3	−273.6	5.9	−267.7	−261.2	9.2	−252.0
Me_3PO	La	−210.9	3.6	−207.3	−237.6	5.7	−231.9	−225.2	8.5	−216.7
	Eu	−231.1	3.7	−227.3	−259.0	6.0	−253.0	−246.9	9.1	−237.8
	Yb	−250.5	4.0	−246.3	−279.4	6.2	−273.2	−266.3	9.6	−256.7

Table 3 Interaction energies ΔE (kcal mol^{-1}) in the **L**Eu^{3+} complexes obtained at different levels of optimization: HF/DZ*//HF/DZ-P*, HF/DZ*//HF/DZ*, DFT/DZ*//DFT/DZ* and DFT/DZ*/HF/DZ-P*

	HF/DZ*// HF/DZ-P*	HF/DZ*// HF/DZ*	DFT/DZ*// DFT/DZ*	DFT/DZ*// HF/DZ-P*
$(MeO)_3POEu^{3+}$	−225.9	−226.8	−252.8	−250.0
$(MeO)_2MePOEu^{3+}$	−226.3	−224.3		
$(MeO)Me_2POEu^{3+}$	−227.9	−226.6		
Me_3POEu^{3+}	−231.1	−230.8	−261.3	−259.0

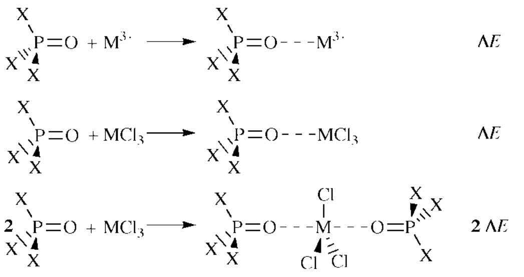

Chart 1

The charged 1 : 1 LM^{3+} complexes: relative cation–ligand binding energies

The ion–ligand interaction energies ΔE are reported in Table 2. They range from −250 (in the $Me_3PO\cdots Yb^{3+}$ complex) to −206 kcal mol^{-1} (in the $(MeO)_3PO\cdots La^{3+}$ complex). In all cases studied, the BSSE is small compared to these numbers, and nearly constant (about 5 kcal mol^{-1}). This is why we consider in the following the uncorrected ΔE's only. They reveal significant cation discrimination by a given ligand, as well as a (weaker) ligand discrimination by a given cation.

In the cation series, with any of the ligands studied, the ΔE's increase as expected with the cation hardness ($La^{3+} < Eu^{3+} < Yb^{3+}$). The range of La^{3+}/Yb^{3+} interaction energies is nearly independent of the ligand and amounts to about 40 kcal mol^{-1} for a given ligand. This value is close to the one found with the Me_3PO, Et_3PO and Ph_3PO ligands.[13] In the ligand series, however, the changes in interaction energies with a given cation are much smaller by comparison. The energy difference between Me_3PO and $(MeO)_3PO$ complexes is only about 5 kcal mol^{-1} for a given cation. This is much less than the difference calculated between the corresponding Me_3PO and Ph_3PO complexes (about 50 kcal mol^{-1}).[13] In addition, we notice that the increment per MeO→Me substitution, nearly independent of the cation size, grows with the number of MeO groups present, *i.e.* it is smallest for $(MeO)_3PO$ *vs.* $Me(MeO)_2PO$ complexes (less than one kcal mol^{-1}), and largest for $Me_2(MeO)PO$ *vs.* Me_3PO. This indicates that the substituent effects are not simply additive. We also notice that the energy increment per Me→MeO substitution is in the same order of magnitude as the conformational energies of a given complex (see Table 1). It is thus not unlikely that with other conformers of the ligands, the order might be somewhat modified.

The above conclusions are validated by computational tests concerning the role of polarization functions on the ligand (Table S4)†[44] and the role of correlation effects. Comparison of Me_3PO *vs.* $(MeO)_3PO$ complexes taking into account correlation effects (Table 2) gives differences in interaction energies $\Delta\Delta E$ somewhat larger than those obtained at the HF level (about 10 kcal mol^{-1} from DFT/DZ* calculations and 7 kcal mol^{-1} from MP2/DZ* calculations), but still much smaller than the $\Delta\Delta E$ of Me_3PO *vs.* Ph_3PO complexes. Calculations at the DFT or MP2 level also yield a smaller difference for $(MeO)_3PO$ *vs.* $Me(MeO)_2PO$ complexes than for $Me_2(MeO)PO$ *vs.* $(Me)_3PO$ complexes. In all simulations, the selectivity in the cation series remains unchanged: for any of the studied ligands, the energy difference between **L**La^{3+} and **L**Yb^{3+} complexes amounts to about 40 kcal mol^{-1} (Table 2).

2 Charged 1 : 1 LM^{3+} complexes: structural and electronic changes upon complexation

The geometries optimized with the DZ-P* basis set, which was used consistently for all systems are summarized in Table 4 and Fig. 2.[43]

Uncomplexed ligands. In the uncomplexed ligands, the three Me→MeO substitutions lead to a shortening of the P=O bond (from 1.51 to 1.49 Å) and of the P–Me and P–OMe bonds (Table 4), as expected from electronegativity effects. Contrary to expectations from "basicity effects", as the number of MeO groups increases, the charge of the phosphoryl O_P oxygen remains nearly constant (about −0.65 e with the DZ-P* basis set and −0.80 e with the DZ* basis set), while the positive charge at phosphorus markedly increases (from 0.82 to 1.26 e with the DZ-P* basis set, and from 0.99 to 1.70 e with the DZ* basis set). Thus, *in the uncomplexed ligands, the electron withdrawing MeO substituents pull most of the charge from the P atom, rather than from the O_P* atom.

Table 4 Optimized parameters in the LM^{3+} complexes

Ligand (L)	M	$d(M\cdots O)$[a]	$d(P{=}O)$[a]	$d(P–O)$[a]	$d(P–C)$[a]	a(OPO) (°)	a(POC) (°)
$(MeO)_3PO$	—		1.488	1.586		115	
	—[b]		1.466	1.585		115	
	La	2.076	1.608	1.543			
	Eu	1.985	1.616	1.541			
	[b]	1.982	1.618	1.540			
	Yb	1.904	1.621	1.539			
$(MeO)_2MePO$	—		1.494	1.603	1.793	113	126
	—[b]		1.472	1.602	1.798	113	121
	La	2.077	1.618	1.552	1.789		
	Eu	1.986	1.625	1.550	1.789		
	[b]	1.983	1.627	1.538	1.790		
	Yb	1.907	1.629	1.548	1.789		
$(MeO)Me_2PO$	—		1.500	1.618	1.808 1.813	113	126
	—[b]		1.479	1.616	1.815 1.812	114	121
	La	2.078	1.640	1.566	1.796		
	Eu	1.988	1.647	1.563	1.795		
	[b]	1.983	1.649	1.552	1.796		
Me_3PO	Yb	1.908	1.653	1.562	1.795		
	—		1.509		1.824		113
	—[b]		1.488		1.827		113
	La	2.076	1.670		1.806		
	Eu	1.984	1.677		1.806		
	[b]	1.977	1.678		1.806		
	Yb	1.905	1.683		1.806		

[a] In Å. Unless otherwise specified[b], they come from HF/DZ-P*//HF/DZ-P* calculations. See Chart 1 for definitions. [b] Optimized HF/DZ*//HF/DZ* parameters.

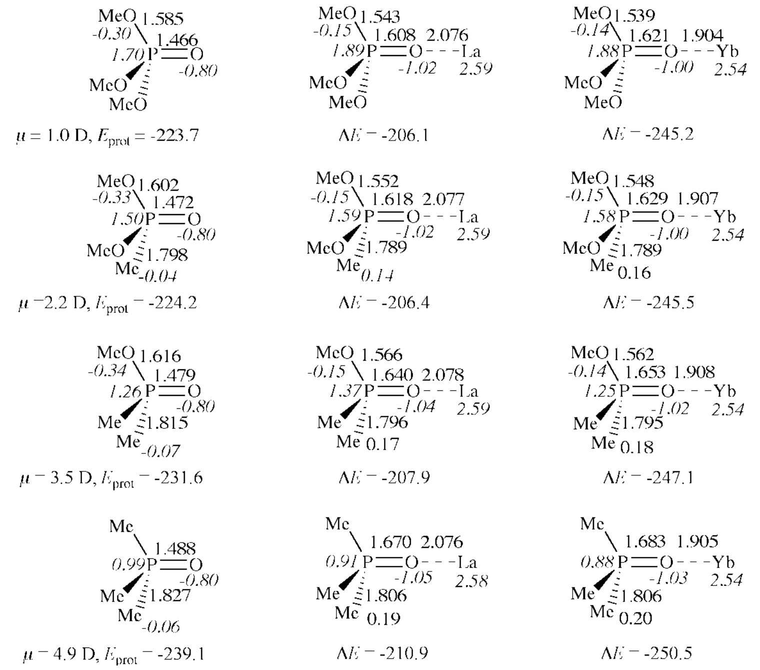

Fig. 2 Selected parameters in **L** and in the LLa^{3+} and LYb^{3+} complexes (**L** = $(MeO)_3PO$ *vs.* $(MeO)_2MePO$ *vs.* $(MeO)Me_2PO$ *vs.* Me_3PO). Optimized distances (Å) from HF/DZ* optimizations for **L** and HF/DZ-P* optimizations for LM^{3+}. Mulliken charges (*in italics*) and interaction energies ΔE (kcal mol^{-1}) from HF/DZ*//HF/DZ-P* calculations.

LM^{3+} complexes. The cation coordination to the ligands **L** induces a number of structural and electronic perturbations, related to electron transfer from **L** to the cation, and polarization of **L** (Fig. 3). These effects are largest with the hardest cation Yb^{3+}. For a given ligand, the $O_P\cdots M^{3+}$ distances follow the order of cationic radii and decrease from 2.08 Å in LLa^{3+} to 1.90 Å in LYb^{3+}. In the ligand series, however, these distances are nearly constant for a given cation (within 0.002 Å) (Table 4), in line with the weak differences in interaction energies ΔE reported above.

The P=O bond distances lengthen markedly upon complexation (by 0.13 Å for the $(MeO)_3PO\cdots Eu^{3+}$ and 0.17 Å for the $Me_3PO\cdots Eu^{3+}$ complexes) and depend more on the phosphorus substituents. For a given cation, P=O is about 0.06 Å longer with Me_3PO than with $(MeO)_3PO$ ligands. This evolution is consistent with IR spectroscopic data on related phosphoryl compounds.[45] Smaller changes are observed in the other bond distances. As the number of MeO groups increases, the Me–P and MeO–P bonds shorten in the free and complexed ligands, as expected from neighbouring electroattractive substituent effects. They also shorten upon complexation (Table 4). These trends follow those suggested by the mesomeric forms of

Table 5 Mulliken charges in the $\mathbf{L}M^{3+}$ complexes: from HF/DZ*//HF/DZ-P* calculations. See Chart 1 for definitions. Charges from HF/DZ-P*//HF/DZ-P* calculations are given in Table S5

Ligand (L)	M	q(M)	q(O=P)	q(P)	q(O–C)	q(CH_3–O)	q(CH_3–P)	q(R_3)[a]
$(MeO)_3PO$	—		−0.797	1.701	−0.624	0.322		−0.906
	La	2.594	−1.022	1.892	−0.607	0.456		−0.453
	Eu	2.557	−1.015	1.891	−0.604	0.460		−0.432
	Yb	2.539	−1.006	1.886	−0.602	0.463		−0.417
$(MeO)_2MePO$	—		−0.797	1.503	−0.650	0.319	−0.044	−0.706
	La	2.587	−1.023	1.591	−0.605	0.457	0.141	−0.155
	Eu	2.561	−1.014	1.587	−0.602	0.461	0.149	−0.133
	Yb	2.544	−1.006	1.580	−0.602	0.464	0.156	−0.120
							−0.055	
$(MeO)Me_2PO$	—		−0.794	1.260	−0.660	0.321	−0.071	−0.465
	La	2.586	−1.038	1.373	−0.607	0.457	0.165	0.180
	Eu	2.561	−1.030	1.264	−0.604	0.462	0.174	0.206
	Yb	2.545	−1.021	1.254	−0.603	0.465	0.180	0.222
Me_3PO	—		−0.800	0.995			−0.065	−0.195
	La	2.580	−1.052	0.910			0.187	0.561
	Eu	2.558	−1.042	0.893			0.190	0.570
	Yb	2.542	−1.034	0.881			0.204	0.612

[a] Total charge on the three groups (Me; OMe).

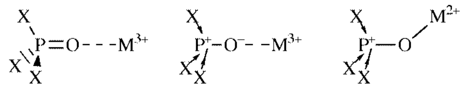

Fig. 3 Schematic representations of **L**igand metal complexes, which highlight the interactions between the cation and the unperturbed **L**igand (*left*), the polarization of **L** by the cation (*center*) and the covalent character of the **L**igand–Metal bond (*right*).

the complexes (Fig. 3), where the polar contribution increases from La^{3+} to Yb^{3+} in the cation series, and from $(MeO)_3PO$ to Me_3PO in the ligand series.

The optimized P=O···M angles are close to 180°, indicating that the linear coordination is intrinsically preferred. This is due to the "hardness" of the trivalent cations which interact with the permanent and induced dipoles of the ligand. However, bending is an easy process. For instance, bending the P=O–Eu angle from 180° to 160° uses only 2.4 kcal mol^{-1} in $Me_3PO \cdots Eu^{3+}$, 1.0 kcal mol^{-1} in the $(MeO)_3PO \cdots Eu^{3+}$ and 0.4 kcal mol^{-1} in $Ph_3PO \cdots Eu^{3+}$. In the latter complex, bending is somewhat easier (by 1.5 kcal mol^{-1}) *trans* rather than *cis* to the Ph–P bond, as anticipated from polarization effects.

Changing the conformation of the complexed ligand also strongly perturbs its structure, as seen in the $(MeO)_3PO \cdots Eu^{3+}$ complex where the P=O bond lengths vary by up to 0.07 Å (Table 1). This is more than the changes observed upon alkyl→*O*-alkyl substitution (Table 4). Interestingly, the more stable is the ligand, the less it is perturbed: the $O \cdots Eu^{3+}$ distances are longest and the P=O distances are shortest in the most stable *gtt* and *ttt* conformers. This points out the lack of general correlation between the bond properties of the complexed ligands and the interaction energies ΔE's. One also notices marked conformational ("stereoelectronic") effects on the P–OMe bond distances, as depicted in phosphoric acid and phosphate esters.[46]

The electronic reorganization induced by the cation coordination (see Table 5 and Fig. 2) also follows the trends suggested by Fig. 3: charge is transferred from the ligand to the cation, while the phosphoryl oxygen atom becomes more negative. The electron transfer to the cation increases with the interaction energy ΔE, *i.e.* from the $(MeO)_3PO \cdots La^{3+}$ complex to the $Me_3PO \cdots Yb^{3+}$ one (Table 5). For the La^{3+}–Yb^{3+} complexes, the transfer is 0.39–0.45 e with the $(MeO)_3PO$ ligand, and 0.42–0.46 e with Me_3PO (DZ* basis set). Similar numbers are found with the DZ-P* basis set (Table S4).† Electron transfer to the metal does not stem from the coordinated O_P atom, which instead becomes more negative due to the polarization effects ($\Delta q_o = -0.22$ e with both $(MeO)_3PO$ and Me_3PO ligands). As a result, the phosphorus atom becomes more positive in methoxy-substituted ligands, but (slightly) less positive in Me_3PO, as a result of electron donation from the alkyl groups. For instance, compared to the free ligands, the changes of charges are $Me^{+0.14}$–$O^{+0.01}$–$P^{+0.19}$–$O^{-0.22}$ in the $(MeO)_3PO \cdots La^{3+}$ complex and $Me^{+0.27}$–$P^{-0.11}$–$O^{-0.23}$ in the $Me_3PO \cdots Yb^{3+}$ complex.[47]

In all $\mathbf{L}M^{3+}$ complexes, the total charge on the MeO groups is negative (about −0.14 e) while the total charge of Me groups is positive (+0.14 to 0.20 e), thus leading (*ceteris paribus*) to a switch of attractive *vs.* repulsive secondary interactions with M, as well as with the added counterions when $(MeO)_3PO$ are replaced by Me_3PO ligands.

3 The 1:1 $\mathbf{L}MCl_3$ and 2:1 $\mathbf{L}_2MCl_3$ neutral complexes: energy, structural and electronic features

In the series of neutral complexes, we considered the Me_3PO and $(MeO)_3PO$ ligands only, to investigate the *O*-alkyl *vs.* alkyl substituent effect. Results are presented in Fig. 4 and Tables 6 to 7. The binding energy ΔE of a given ligand **L** drops markedly (by about a factor 5), compared to ΔE in the charged $\mathbf{L}M^{3+}$ complexes (Table 6). This is due to a change in the electrostatic interactions which are mostly of a charge–dipole type in $\mathbf{L}M^{3+}$ complexes (211 to 245 kcal mol^{-1}) and of a dipole–dipole type in the $\mathbf{L}MCl_3$ (46 to 66 kcal mol^{-1}) and $\mathbf{L}_2MCl_3$ complexes (26 to 53 kcal mol^{-1}). The metal–ligand interactions are softer in $\mathbf{L}MCl_3$ and $\mathbf{L}_2MCl_3$ than in $\mathbf{L}M^{3+}$ complexes.

The most interesting result, as far as the alkyl→*O*-alkyl substitution is concerned, is the *amplification of the interaction energy difference* $\Delta\Delta E$ *due to the presence of counterions or of other ligands in the coordination sphere of the cation*. Indeed, whatever M^{3+} is, replacement of $(MeO)_3PO$ by Me_3PO leads to a $\Delta\Delta E$ of 2–3 kcal mol^{-1} in $\mathbf{L}M^{3+}$, of 20 kcal mol^{-1} in the $\mathbf{L}MCl_3$ complexes, and of 23–30 kcal mol^{-1} in the $\mathbf{L}_2MCl_3$ complexes (Table 6), Me_3PO being more strongly bound than $(MeO)_3PO$. Amplification of the alkyl→*O*-alkyl substituent effect is also observed in calculations taking into account correlation effects (Table 6). With both DFT or MP2 calculations, $\Delta\Delta E$ is about 10 kcal mol^{-1} larger in $\mathbf{L}EuCl_3$ or $\mathbf{L}_2EuCl_3$ complexes than in the $\mathbf{L}Eu^{3+}$ complexes. This amplification may be related to the repulsions between the anions and ligands in the first coordination sphere of the cation. Upon alkyl→*O*-alkyl substitution, these repulsions increase, due to the accumulation of negatively charged atoms around the cation. Other effects, like the change of hard to soft character of the metal–ligand bond upon coordination of neutralizing counterions (*vide infra*) may also contribute to this amplification.

Table 6 Interaction energies (kcal mol^{-1}) and optimized parameters in the $\mathbf{LMCl_3}$ and $\mathbf{L_2MCl_3}$ complexes (HF/DZ*//HF/DZ-P* calculations). Total energies are given in Table S2

Complexes	M	ΔE	ΔE^a	ΔE^b	$d(M\cdots O)^c$	$d(P{=}O)^c$	$d(P{-}O)^c$	$d(P{-}C)^c$	$d(M\cdots Cl)^c$	$a(OMCl)^d$	$a(MOP)^d$
$(MeO)_3POMCl_3$	La	−39.2			2.328	1.514	1.570		2.755	96;103;104	167
	Eu	−42.9	−38.5	−46.7	2.225	1.514	1.569		2.652	97;104;105	166
	Yb	−45.9			2.132	1.513	1.568		2.547	99;104;105	165
Me_3POMCl_3	La	−60.0			2.308	1.547		1.809	2.753	98	180
	Eu	−63.0	−57.3	−62.9	2.205	1.546		1.809	2.646	100	180
	Yb	−66.4			2.115	1.545		1.808	2.549	101	180
$((MeO)_3PO)_2MCl_3$	La	−28.6			2.416	1.507	1.574		2.834		149
	Eu	−30.2	−26.9	−36.3	2.302	1.505	1.574		2.726		151
	Yb	−31.2			2.204	1.504	1.573		2.632		152
$(Me_3PO)_2MCl_3$	La	−49.4			2.382	1.535		1.811	2.815		174
	Eu	−51.7	−46.2	−52.9	2.273	1.533		1.811	2.714		174
	Yb	−53.4			2.175	1.530		1.810	2.617		174
									2.636		175

[a] DFT/DZ*//HF/DZ-P* calculations. [b] MP2/DZ*//HF/DZ-P* calculations. [c] In Å. [d] In degrees.

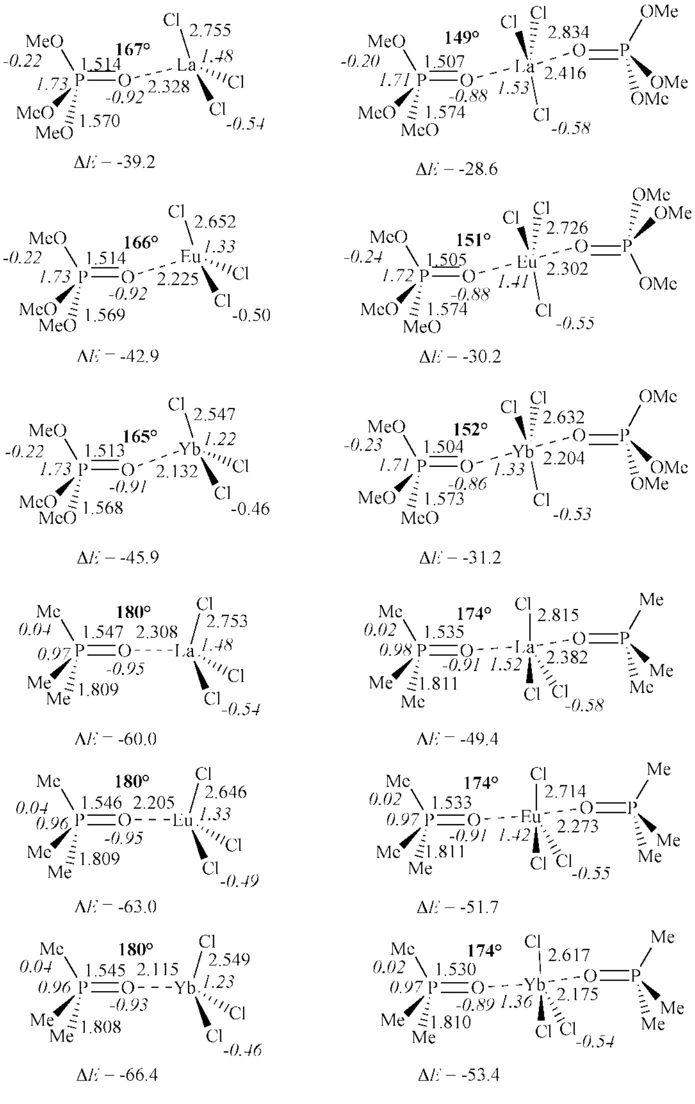

Fig. 4 Selected parameters in $\mathbf{LMCl_3}$ and $\mathbf{L_2MCl_3}$ complexes ($\mathbf{L} = (MeO)_3PO$ *vs.* Me_3PO). Optimized distances (Å) and POM angles (°) from HF/DZ*-P* optimizations. Mulliken charges (*in italics*) and interaction energies ΔE (kcal mol^{-1}) from HF/DZ*//HF/DZ-P* calculations.

The coordination of three chloride anions to $\mathbf{L}M^{3+}$ complexes leads to a lengthening of the metal–ligand bond, of about 0.2 Å for all systems. For a given ligand, these bonds are also longer by 0.2 Å in the La^{3+} than in the Yb^{3+} complexes. Around a given cation, the M···O and the M–Cl distances are somewhat larger ($\Delta = 0.01$ to 0.02 Å) in the $(MeO)_3PO$ than in the Me_3PO complexes, which may be indicative of larger ligand–anion repulsions in the former ones. An interesting difference concerns the linearity of metal coordination. The optimized P=O···M angle is linear (180°) in $Me_3PO\cdots MCl_3$, but bent (about 165°) in $(MeO)_3PO\cdots MCl_3$. Furthermore, comparison of the linear/bent (160°) $\mathbf{L}EuCl_3$ complexes shows that the Me_3PO ligand prefers the linear coordination (by 4 kcal mol^{-1}), while the $(MeO)_3PO$ ligand prefers the bent coordin-

Table 7 Mulliken charges in the $\mathbf{LMCl_3}$ and $\mathbf{L_2MCl_3}$ complexes (HF/DZ*//HF/DZ-P* calculations)

Complexes	M	q(M)	q(O=P)	q(P)	q(O–CH$_3$)	q(CH$_3$)	q(Cl)
$(MeO)_3POMCl_3$	La	1.485	−0.924	1.728	−0.590	0.370	−0.542; −0.547
	Eu	1.334	−0.922	1.731	−0.590	0.370	−0.502; −0.494
	Yb	1.225	−0.909	1.727	−0.589	0.371	−0.460; −0.470
Me_3POMCl_3	La	1.481	−0.947	0.967		0.043	−0.541
	Eu	1.331	−0.945	0.964		0.043	−0.494
	Yb	1.226	−0.932	0.960		0.044	−0.463
$((MeO)_3PO)_2MCl_3$	La	1.526	−0.880	1.711	−0.585	0.347	−0.570; −0.603
	Eu	1.408	−0.878	1.720	−0.586	0.350	−0.566; −0.546
	Yb	1.333	−0.860	1.713	−0.584	0.351	−0.550; −0.527
$(Me_3PO)_2MCl_3$	La	1.517	−0.910	0.977		0.019	−0.582; −0.588
	Eu	1.424	−0.910	0.973		0.017	−0.558; −0.550
	Yb	1.359	−0.892	0.966		0.017	−0.530; −0.550

Table 8 Calculated protonation energies (in kcal mol^{-1}) of **L**, structural parameters and Mulliken charges of $\mathbf{LH^+}$ (HF/DZ*//HF/DZ* calculations). Total energies are given in Table S3

Ligand (L)	E_{prot}	d(P=O)^a	d(O···H)^a	a(POH) (°)	q(H)	q(P)	q(O=P)
$(MeO)_3PO$	−223.7	1.568	0.950	120	0.371	1.766	−0.606
$(MeO)_2MePO$	−224.2	1.557	0.953	118	0.381	1.511	−0.572
$(MeO)Me_2PO$	−231.6	1.573	0.952	118	0.380	1.245	−0.593
Me_3PO	−239.1	1.593	0.950	120	0.371	0.911	−0.605

^{a} In Å.

ation (by 0.3 kcal mol^{-1}). These features are consistent with the fact that polarization effects are smaller in $(MeO)_3PO$ than in Me_3PO complexes, and that the metal–ligand bonds therefore become softer.

Coordination of a second ligand to the $\mathbf{LMCl_3}$ complexes leads to an additional lengthening of the M···O bonds (about 0.05 Å), and shortening of the P=O bonds (about 0.01 Å; Table 6). The M–Cl bonds also lengthen, as expected from repulsion effects between the ligands and the anions, and reduced attractions with the metal. As in the 1 : 1 complexes, the P=O···Eu angles of the $\mathbf{L_2MCl_3}$ complexes are almost linear (about 175°) with Me_3PO as ligand, but markedly bent (about 150°) with $(MeO)_3PO$ as ligand (Table 6).

Upon coordination of counterions to $\mathbf{LM^{3+}}$ (Table 7), the cationic charge drops markedly (about 1.0 e), mostly due to the electron donation from the counterions (about 0.5 e each). The cationic charge is somewhat more positive in the lanthanum than in the ytterbium complexes ($\Delta q = 0.2$ e), but nearly the same in a given $(MeO)_3POMCl_3$ complex as in the corresponding Me_3PO one. Coordination of a second ligand **L** to $\mathbf{LMCl_3}$ leads to smaller electronic perturbations. The cation becomes more positive (by 0.1 e, or less), while the chlorides become more negative (by about 0.05 e each), probably because the MCl_3 moiety evolves from a pyramidal structure in the $\mathbf{LMCl_3}$ to a planar one in $\mathbf{L_2MCl_3}$, where its dipole moment becomes zero. It thus polarizes **L** somewhat less in the 2 : 1 than in the 1 : 1 complex (Table 8).

Discussion and conclusion

We report a QM study of the binding of "large", "average" or "small" trivalent lanthanide cations to phosphoryl containing ligands, which represent an important class of ligands used to extract actinides or lanthanides from nuclear waste. The calculations provide insights into energy and structural features of these complexes "in the gas phase".

First, as generally anticipated from "basicity effects", the ligand binding energy ΔE decreases in the charged $\mathbf{LM^{3+}}$ complexes upon alkyl→*O*-alkyl substitution. At a quantitative level, however, the effect is surprisingly small (a few kcal mol^{-1}), compared to the Me→Et or Me→Ph substitutions at the phosphoryl group (about 15 and 50 kcal mol^{-1}, respectively).[13] This is the result of two antagonist contributions. The decrease of dipole moments[48] and of polarizabilities upon Me→OMe substitution favors the alkyl-substituted ligands. However, secondary electrostatic interactions between the cation and phosphorus substituents give the opposite trend: they are attractive with *O*-alkyl groups, but repulsive with alkyl ones. Other more subtle effects, like the covalent character of the metal–ligand bond also favor *O*-alkyl substituted ligands.

Correlation between basicities (protonation energies) of the phosphoryl ligands and interactions with lanthanide cations

The protonation energies E_{prot} of the ligands calculated in the gas phase (Table 8) are remarkably close to the corresponding interaction energies calculated in the $\mathbf{LM^{3+}}$ complexes (Table 2 and Fig. 2). They increase from 223.7 to 239.1 kcal mol^{-1} from $(MeO)_3PO$ to Me_3PO, and are again very close for the $(MeO)_3PO$ and $Me(MeO)_2PO$ ligands. For $(MeO)_3PO$, the calculated protonation energy (223.7 kcal mol^{-1}) is in qualitative agreement with the experimental value (212.2 kcal mol^{-1}).[49] To our knowledge, there are no experimental data for the other calculated ligands. Replacement of Me by larger (and more polarizable) alkyl groups should further enhance the preference of the alkyl over *O*-alkyl substituted phosphoryl binding sites. Indeed, experimental protonation energies are 5.5 kcal mol^{-1} larger for $(EtO)_3PO$ than for $(MeO)_3PO$.[49] We notice that this number is close to the complexation energy difference between Me_3POM^{3+} and $(MeO)_3POM^{3+}$ complexes, which confirms that, *in the absence of competing interactions, the basicity effect of alkyl→O-alkyl substitution is weak*, and that alkylphosphate ligands like TBP build strong complexes with lanthanide cations. However, (*vide infra*) accumulation of ligands and counterions *amplifies* this intrinsically weak effect.

Protonation of the phosphoryl oxygen leads to a marked lengthening of the P=O bond (Table 8), as upon coordination of M^{3+} cations to **L**. An important difference concerns the P–O–H$^+$ angle which is bent (about 120°; Table 8), due to the soft covalent-like coordination of the proton. This contrasts with the P=O···M^{3+} coordination which is linear. As expected from the conservation of total bond order at phosphorus, the Me–P and MeO–P bonds shrink upon protonation. The

Mulliken population analysis shows that upon protonation the P atom becomes more positively charged, while the O_P atom becomes less negative (Table 8). These trends are opposite to those found in $\mathbf{L}M^{3+}$ complexes, due to the softer and more covalent character of the bond with the proton.

Importance of counterions and of "steric effects" in the first coordination sphere of the cation

The comparison of charged $\mathbf{L}M^{3+}$ to neutral $\mathbf{L}MCl_3$ and $\mathbf{L}_2MCl_3$ complexes demonstrates the *importance of counterions and ligand stoichiometry on the alkyl/O-alkyl substituent effects, as the preference for alkyl substituted ligands increases in the presence of counterions and of other ligands*. In condensed phases (*e.g.* solid state or in solution), the first coordination sphere is saturated, and generally involves three counterions and three phosphoryl ligands.[24] Their mutual repulsion is still larger than in the model $\mathbf{L}_2MCl_3$ species, especially when chlorides are replaced by bidendate nitrate or carboxylate anions, leading to enhanced "*electrostatic strain*" in the first coordination sphere, and therefore, to enhanced alkyl *vs.* *O*-alkyl preference in substituted ligands.

Interestingly, this counterion effect is the inverse of that found with amide or pyridine ligands, where the counterions and additional ligands lead to levelling and reduction of the energy impact of H→Me substitution.[15] In that case, the substituted center is more remote from the cation, and changes in permanent dipole moment of the ligands have less energy consequence than changes in the ligand polarizabilities. A still different counterion effect has been found in methyl compared to phenyl derivatives of R_3PO ligands. Intrinsically, Ph_3PO was found to form stronger complexes than Me_3PO with lanthanide or uranyl cations, as expected from polarization effects. However, when counterions were added to the system, the reverse order was found: Me_3PO binds slightly better than Ph_3PO to $UO_2(NO_3)_2$[14] or to MCl_3.[13] Thus, *effective substituent effects depend on multiple interactions in the first coordination sphere of the cation, as well as intrinsic cation–ligand interactions*.

The large structural changes in the $\mathbf{L}M^{3+}$, compared to the $\mathbf{L}MCl_3$ and $\mathbf{L}_2MCl_3$ complexes also make clear that the structures of the former should not be directly compared with those in condensed phases, while the latter should be more amenable to such comparisons. We searched the Cambridge Crystallographic Database for lanthanide complexes with the $O{=}PC_3$ fragment, and found no data allowing for a comparison of alkyl *vs.* *O*-alkyl substituted phosphoryl ligands. The retrieved structures have been discussed in ref. 13. As most of them contain Ph_3PO as ligand, they are less relevant to the questions addressed in this paper. One point of interest concerns the linearity of metal–phosphoryl coordination. Intrinsically (in $\mathbf{L}M^{3+}$ complexes) we find that the preferred arrangement is linear, which seems in contradiction with the observation of $P{=}O\cdots M$ angles (M = La, Eu, Yb) ranging from 144° to 175° in the solid state structures. Our comparison of $\mathbf{L}M^{3+}$ with $\mathbf{L}MCl_3$ and $\mathbf{L}_2MCl_3$ complexes shows that *bending results in fact from multiple coordination of anions and ligands to the metal*, which leads to softer metal–ligand interactions and to important steric interactions (mostly of electrostatic origin) around the metal. Thus, structures in condensed phases cannot be analyzed solely on the basis of metal–ligand bond properties.

Recently, an EXAFS study of holmium complexes with TBP and bidentate CMPO or diphosphine oxide ligands has been reported in ethanol solution,[50] where $Ho–O_P$ distances were found to be about 0.2 Å longer with TBP than with the other ligands. This was attributed to the lower basicity of the phosphoryl oxygen in TBP. Based on our calculations, we offer an alternative view. For a given metal, changes in "basicity" should have minor effects on the metal–ligand bond distances, since in our optimized series of complexes, the $M\cdots O_P$ distances differ only by about 0.001 Å for a given metal. We suggest that *the dominant effects are the repulsions in the first coordination sphere* of the $\mathbf{L}_3HoCl_3$ complex, which are largest for $\mathbf{L}$ = TBP, leading to the longer and "weaker" $Ho–O_{TBP}$ bond. Generally speaking, the role of steric strain in complex metal formation is well recognized, but mostly in terms of deformation of the ligands upon complexation, or in terms of steric crowding in bulky ligands.[18] To our knowledge, strain related to electrostatic repulsions has not been considered so far.

Relevance of the calculated data for ion separation and extraction

Selective cation binding in solution is a complex process, which depends on the ion : ligand stoichiometry, and on the dynamic competition with counterions and solvent molecules. Its thermodynamics depend on enthalpic and entropic components.

Our study demonstrates the *importance of counterions and environment effects for the effectiveness of substituent effects in the ligands*. In addition, a number of related features may be expected, concerning the complexation and liquid–liquid extraction of lanthanides. The first one concerns the anchoring of phosphoryl binding sites to a molecular lipophilic platform (*e.g.* calixarenes or resorcinarenes), generally leading to preorganized ligands and enhanced cation extraction.[51,52] We suggest that an important feature of such ligands is to wrap sufficiently around the cation to prevent (or reduce) the binding of counterions in its first coordination sphere. As pointed out above, removal of counterions from the cation has different consequences, concerning substituent effects: this should decrease the preference of alkyl over *O*-alkyl substituents, but increase the preference of aryl over alkyl substituents. Another question is related to the water affinity of the complex. Intrinsically, the *O*-alkyl substituted ligands are more hydrophilic than the corresponding alkyl ones. However, in their complexed states, the former are expected to prevent water coordination in the first coordination sphere of the extracted cation (repulsion effects), which facilitates their migration from the water–organic interface to the organic phase. According to similar arguments, the lifetime of water molecules coordinated to the complexed cation is also expected to decrease due to "electrostatic strain effects". To our knowledge, these questions have not been addressed experimentally so far.

To conclude, we emphasize the importance of computational approaches to compare the intrinsic (gas phase) binding features of various classes of ligands used in the complexation and liquid–liquid extraction of lanthanide and actinide cations. Such computations should contribute to a better understanding of the basis of efficient complexation and separation of lanthanides and actinides by known ligands, and to the design of new ones.

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43 The comparison of the DZ-P* geometries with those obtained with the larger DZ* basis set has been performed for the **L** and **L**Eu^{3+} species (Table 4). In the free ligands, the P=O bond is about 0.02 Å longer than with the DZ* basis set, while the P–OMe and P–Me bonds differ by less than 0.005 Å. In the corresponding **L**Eu^{3+} complexes, the P=O bond is about 0.005 Å shorter, compared to the DZ* values and the M–O$_P$ distances are about 0.005 Å longer. However, the corresponding changes in interaction energies ΔE between **L** and Eu^{3+} are small (less than 2 kcal mol^{-1}; Table 3).

44 Table S4 shows the effect of polarization functions (pf's) in the HF calculations. For a given **LM**$^{3+}$ complex, one observes a systematic decrease of the interaction energies ΔE upon addition of pf's: compare the D95 results (no polarization functions on **L**) with the DZ-P* (pf's on the P atom only) and DZ* results (pf's on all atoms of **L**). One also sees that pf's on the phosphorus atom have a larger effect on ΔE than the pf's on the other atoms of **L.** The comparison of ΔE's in the ligand series shows that the effect of pf's is larger for the Me–O than for the Me substituted ligands. As a result, the difference $\Delta\Delta E$ between (MeO)$_3$PO and Me$_3$PO complexes increases from 2–3 kcal mol^{-1} (DZ-P* basis set) to about 5 kcal mol^{-1} (DZ* basis set). In the absence of pf's (D95 basis set), $\Delta\Delta E$ is exaggerated ($\Delta\Delta E$ is about 22 kcal mol^{-1} for any M^{3+} cation), but still remains smaller than the change in ΔE related to the Me$\rightarrow$Ph substitution.[13]

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48 The calculated dipole moments of Me$_3$PO, Me$_2$(MeO)PO, Me(MeO)$_2$PO and (MeO)$_3$PO are respectively 4.9, 3.5, 2.2, 1.0 Debye with the DZ* basis set and 5.3, 3.5, 2.4, 1.1 Debye with the DZ-P* basis set.

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