Interaction of M^{3+} Lanthanide Cations with Amide, Pyridine, and Phosphoryl $O{=}PPh_3$ Ligands: A Quantum Mechanics Study

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We report an ab initio quantum mechanical study on the interaction of M^{n+} cations ($M^{n+} = La^{3+}$, Eu^{3+}, Yb^{3+}, Sr^{2+}, and Na^+) with model ligands **L** for lanthanide or actinide cations: several substituted amides, pyridines, and the phosphoryl-containing $OPPh_3$ ligand. The interaction energies ΔE follow trends expected from the cation hardness and ligand basicity or softness in the amide series (primary < secondary-cis < secondary-trans < tertiary) as well as in the pyridine series (*para*-NO_2 < H < Me < NMe_2). Among all ligands studied, $OPPh_3$ is clearly the best, while the (best) tertiary amide binds lanthanides slightly less than the (best) pyridine-NMe_2 ligand. In the lanthanide 1:1 complexes, the energy differences $\Delta\Delta E$ as a function of M^{3+} (about 40 kcal/mol for all ligands) are less than $\Delta\Delta E$ in the pyridine series (up to about 90 kcal/mol) where marked polarization effects are found. The conclusions are validated by a number of methodological investigations. In addition to optimal binding features, we also investigate the directionality of ion coordination to the ligands and the effect of counterions and stoichiometry on the structural, electronic and energetic features of the complexes. The results are discussed in the context of modeling complexes of lanthanide and actinide cations and compared to those obtained with analogous Na^+ and Sr^{2+} complexes.

Introduction

The search for complexant molecules which specifically bind lanthanides and actinides and separate them from other cations represents a challenging task in the context of separation techniques of nuclear wastes and from a basic point of view.[1−3] For this purpose, it is fundamental to precisely assess the intrinsic energetic and stereochemical features of the elementary interactions between the putative cationic guests and the binding sites of the ligand in the gas phase.[4−8] Gas-phase data, as determined for small molecules[9,10] or real ionophores[11] interacting with alkali metal cations or Lewis acids, allow one to better understand, by comparison, what happens in solution. In the case of trivalent lanthanide or actinide ions, such data are not available. Quantum mechanical (QM) computations offer an alternative source of valuable information on structural, electronic, and energy features of noncovalent interactions in the gas phase.[12,13] In contrast with the large amount of theoretical and experimental data on alkali metal cations,[14] those dealing with actinides and lanthanides are rather scarce.[15] Some computations on the uranyl cation dealt with the cation alone[16] and its salts.[17] Others concerning lanthanide cations focused on their hydrates,[18] on their trihalide salts,[19−26] or on complexes with organic ligands.[27] We recently reported QM ab initio studies on the interaction between the uranyl[28] and trivalent lanthanide cations[29] with phosphoryl-containing OPR_3 ligands

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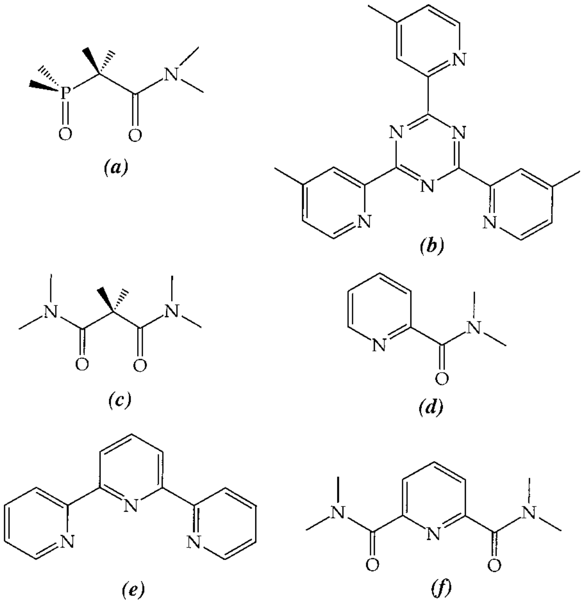

Figure 1. Schematic representation of amide-, pyridine-, and phosphoryl-containing ligands for lanthanide cations complexation: CMPO (a); TPTZ (b); malonamide (c); picolinamide (d); terpyridine (e); pyridine-2,6-dicarboxamide (f).

(R = H/Me/Et/Ph). It was found that triphenylphosphine oxide $OPPh_3$ interacts better than the alkyl analogues with lanthanide and uranyl ions. Two other important classes of ligands for lanthanides use amide and/or pyridine functionalities, either in single monodentate ligands or in fragments of polydentate ones. Representative examples involve CMPO,[30-33] picolinamide,[34] malonamide,[35] pyridinedicarboxamide,[36] oligopyridine,[37,38] and TPTZ[39] ligands (see Figure 1). The intrinsic interaction energies of such binding sites with a given cation are presently unknown.

The present paper focuses on the interaction of amide vs pyridine vs phosphoryl type ligands with lanthanide L^{3+}, Sr^{2+}, and Na^+ cations (Figure 2). Within a series of ligands, the binding strength with a given cation is expected to increase with the basicity of the ligand and with the hardness of the cation.[40-43] However, there has been so far no comparative assessment of the intrinsic (gas phase) basicities of such ligands or of their interaction energies with lanthanide cations. For instance, the gas-phase proton affinity of *p*-substituted X-pyridines increases by 25 kcal/mol upon OMe → NO_2 substitution,[44] but how this quantitatively modifies the interactions with another M^{n+} cation is presently unknown. Hydrogen bonding interactions in apolar solution, generally assumed to relate to the basicity of the ligand, increase in the order pyridine < acetamide < phosphoryl-containing ligands, but the corresponding energies are quite small (for instance, in CCl_4 solution, with $4F\text{-}C_6H_4OH$ as acid, ΔG ranges from -2.6 to -3.8 kcal/mol).[45] Interaction energies with Lewis acids (such as $SbCl_5$), used to compare the ligand's basicities in weakly polar media, are also small.[46] It is unknown whether the intrinsic interactions with hard cations follow the same order or to what extend this order is subtituent dependent. Generally speaking, "it is unreasonable to expect a single order of reaction strengths for donors that would be applicable to all acidic solutes".[42] Our aim here is to assess the energetic impact of substitution in the amide and pyridine series and to compare these two series with the phosphoryl-containing $OPPh_3$ ligand. In the amide series (noted in short as Amid-XY), we consider primary, secondary, and tertiary acetamides, where XY = HH/HMe/HPh/MeMe. The cis and trans isomers of Amid-MeH are compared. In the pyridine series (noted as Pyr-X, X = NO_2/H/Me/NMe_2) we consider *para*-substituents of attractive/electroneutral/donating type. As lanthanides, we selected La^{3+}, Eu^{3+}, and Yb^{3+}, which represent respectively a "large", "average", and "small" ion (their ionic radius is 1.032, 0.947, and 0.868 Å, respectively).[47,48] The complexes of Sr^{2+} and Na^+ cations are calculated to investigate whether the trends observed in the ligand series are all similar or cation dependent. Furthermore, it is of interest to determine whether the interactions of Eu^{3+} vs Na^+, two cations of similar radius, are close to a 3 to 1 ratio. We therefore compare the intrinsic ("gas phase") $\mathbf{L}\cdots M^{n+}$ interactions in 1:1

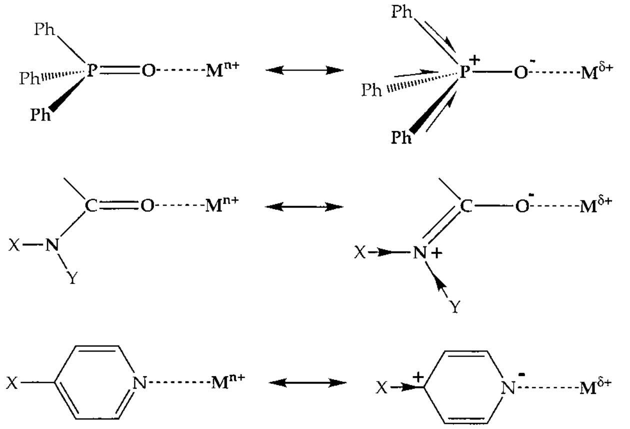

Figure 2. Schematic representation of $M^{3+}\cdots\mathbf{L}$ complexes and of mesomeric forms which highlight trends in structural and electronic reorganizations upon complexation. $\mathbf{L}$ = $OPPh_3$, Amid-XY (XY = HH/HMe/MeH/MeMe/HPh), and Pyr-X (X = H/Me/NO_2/NMe_2).

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complexes and determine the most important trends in geometrical and electronic structures. In relation with force field representations of the potential energy,[49−51] it is indeed important to assess the transferability of the ligand and ion parameters (effective size, charge, etc.) from one complex to the other at a consistent computational level. In addition, we investigate in selected $OPPh_3$, pyridine, and amide 1:1 complexes the "directionality" of M^{n+} cation binding, i.e. the energy cost to deviate from the optimal angle of binding. We also consider typical 2:1 complexes of $\mathbf{L}_2MCl_3$ type, to assess the effect of counterions and of the stoichiometry on the coordination properties of lanthanide cations (**L** = Pyr-H/AmidMe$_2$/OPMe$_3$). For computer time saving purposes, a limited combination of ions and ligands has been investigated, with a particular focus on the "best ligands". For the same reasons, the $\mathbf{L}_2MCl_3$ complex with phosphoryl-containing ligands was studied with $OPMe_3$ instead of $OPPh_3$ as ligand and the effect of substituents on **L** was investigated on 1:1 complexes only. Some results concerning the $M^{3+}\cdots OPPh_3$ and $M^{3+}\cdots OPMe_3$ 1:1 systems have been described in ref 29 at the HF level. Additional methodological tests are reported here, to allow for consistent comparisons with the other complexes. Hereafter, we generically note as **L** the ligands studied ($OPPh_3$, amides, pyridines), M^{3+} the lanthanide ions (M = La, Eu, or Yb), and M^{n+} any of the cation studied (M^{3+}, Sr^{2+}, or Na^+).

Methods

The QM ab initio calculations were performed at the HF level using the Gaussian-94 package.[52] The 46 + 4f^n core electrons of the lanthanide cations were described by the quasi relativistic pseudopotential of Dolg et al.,[53,54] 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.[55] This exponent was kept for the whole series of lanthanides. Calculations on the $Eu^{3+}\cdots OPH_3$ system, using a smaller core of 28 electrons for the pseudopotential (i.e. including the 4s, 4p, 4d, and 4f electrons in the valence space), showed that the use of a large core pseudopotential for our purpose is satisfactory.[29] The Sr^{2+} cation was described by a relativistic pseudopotential for the 28 core electrons, and the (6s,6p,5d)/[4s,4p,2d] basis set from ref 56 was used for the valence electrons. For Na^+ we used the 6-31G* basis set.[52] The H, C, N, O, and P atoms were described by the standard Dunning−Hay double-ζ basis set[57] adding one 3d polarization function on the P atom of exponent $\zeta_{3d} = 0.37$ (referred to hereafter as "DZ" basis set). In some additional test calculations, polarization functions on the atoms of **L** were also added (exponents being $\zeta_{3dC} = 0.75$, $\zeta_{3dO} = 0.85$, $\zeta_{3dN} = 0.80$, and $\zeta_{2pH} = 0.80$), leading to the DZ* basis set.

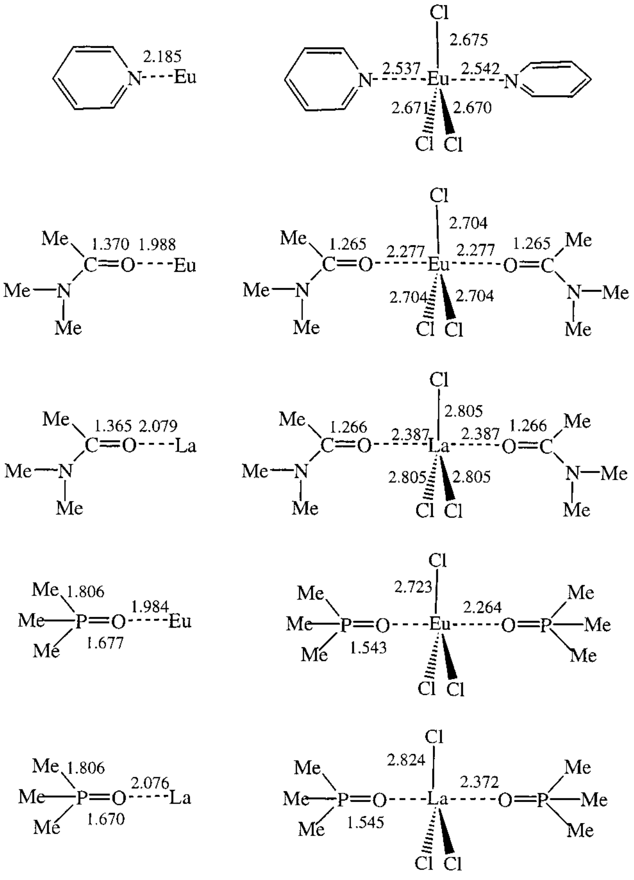

Figure 3. Optimized distances (Å) in $\mathbf{L}M^{3+}$ and $\mathbf{L}_2MCl_3$ complexes.

The geometries of the systems were obtained as follows. The free ligands were fully optimized at the HF level using analytical gradients and the DZ basis. For the $M^{n+}\cdots\mathbf{L}$ and $\mathbf{L}_2MCl_3$ complexes, all parameters have been numerically optimized at the HF level, freezing the CH_3 and Ph groups in the same geometry as in the corresponding free ligand. For the $M^{n+}\cdots OPPh_3$ complexes, unless otherwise specified, a pseudo-C_{3v} symmetry was assumed, which implies a collinear arrangement of the M···O=P atoms. Details are given in ref 29. For the $M^{n+}\cdots$Amid-XY complexes, no symmetry constraint was imposed, but the non-hydrogen atoms of the ligand were kept coplanar. The $M^{n+}\cdots$Pyr-X complexes were optimized under a C_{2v} symmetry constraint for the non-hydrogen atoms. Among the Amid-XY complexes, only those with Sr^{2+} and Eu^{3+} were investigated systematically as a function of XY substituents. A more extensive comparison of all cations was performed on $M^{n+}\cdots$Amid-Me$_2$ complexes, as this ligand is the best among the amides we considered. In the $\mathbf{L}_2MCl_3$ complexes, a planar arrangement of the MCl_3 moiety was assumed. The two pyridine fragments of (Pyr-H)$_2$MCl$_3$ were constrained to a D_{2d} symmetry, using the Pyr-H geometry optimized in the 1:1 complex, while the two amides of the (Amid-Me$_2$)$_2$MCl$_3$ complexes were related by a C_{2v} symmetry (see Figure 3).

On the methodological side, the effect of electron correlation was investigated by performing MP2/DZ//HF/DZ and B3LYP-DFT/DZ//HF/DZ calculations on selected $OPPh_3$, Amid-XY, and Pyr-X complexes. The fact that geometry optimization at the HF level was sufficient was checked on the five $M^{n+}\cdots$Amid-Me$_2$ complexes, where the DFT/DZ//DFT/DZ interaction energies (obtained from structures optimized at the B3LYP-DFT level) were, within 0.5 kcal/mol, identical to the DFT/DZ//HF/DZ energies (obtained from structures optimized at the HF level). Similar conclusions have been obtained previously with the $UO_2^{2+}\cdots OPH_3$ complex.[28]

The interaction energies ΔE of the ligands with M^{n+} were calculated with respect to the optimized geometries of **L**, as $\Delta E = E(\mathbf{L}M^{n+}) - E(\mathbf{L}) - E(M^{n+})$ for the $\mathbf{L}M^{n+}$ complexes, and as $2\Delta E = E(\mathbf{L}_2MCl_3) - 2E(\mathbf{L}) - E(MCl_3)$ for the $\mathbf{L}_2MCl_3$ complexes. The basis set superposi-

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Table 1. Interaction Energies ΔE (kcal/mol) in the **L**M^{n+} and **L**$_2$MCl$_3$ (**L** = OPPh$_3$, Amid-Me$_2$, Pyr-X) Complexes[a]

complex	method	O=PPh$_3$	Amid-Me$_2$	Pyr-NO$_2$	Pyr-H	Pyr-Me	Pyr-NMe$_2$
LLa^{3+}	HF/DZ//HF/DZ	−257.4	−203.2	−118.3	−154.3	−166.4	−204.4
	DFT/DZ//HF/DZ	−287.7	−225.9	−148.7	−177.4	−203.5	−237.3
	MP2/DZ//HF/DZ	−274.8	−218.8	−144.4	−171.0	−183.7	−231.8
LEu^{3+}	HF/DZ//HF/DZ	−279.5	−222.8	−135.2	−172.3	−185.3	−225.5
	HF/DZ*//HF/DZ	−273.0	−209.0	−132.8	−164.4	−173.6	−217.8
	DFT/DZ//HF/DZ	−314.7	−248.8	−169.4	−198.5	−225.7	−261.8
	MP2/DZ//HF/DZ	−299.3	−240.7	−163.3	−190.7	−204.2	−255.1
LYb^{3+}	HF/DZ//HF/DZ	−300.3	−241.7		−189.8	−203.4	−244.9
	DFT/DZ//HF/DZ	−341.7	−268.8		−217.0	−245.0	−282.3
	MP2/DZ//HF/DZ	−320.7	−260.5		−208.9	−223.2	−275.3
LSr^{2+}	HF/DZ//HF/DZ	−126.1	−104.1				−93.9
	DFT/DZ//HF/DZ	−133.0	−110.2				−106.4
	MP2/DZ//HF/DZ	−125.8	−105.5				−102.0
LNa^{+}	HF/DZ//HF/DZ	−55.7	−50.0				−44.1
	DFT/DZ//HF/DZ	−55.2	−49.9				−47.4
	MP2/DZ//HF/DZ	−59.3	−47.4				−46.3
L$_2$LaCl$_3$[b]	HF/DZ//HF/DZ	−54.8[c]	−45.7		−33.3		
L$_2$EuCl$_3$[b]	HF/DZ//HF/DZ	−57.5[c]	−48.1		−35.8		
L$_2$YbCl$_3$[b]	HF/DZ//HF/DZ	−60.1	−49.7				

[a] The full version of the table, including the BSSE-corrected interaction energies, is given as Supporting Information (Table S2). [b] Interaction energies between the MCl$_3$ salt and one of the two **L** ligands within the **L**$_2$MCl$_3$ complex. [c] Value calculated for the (Me$_3$PO)$_2$ MCl$_3$ complex.

tion error ("BSSE") was estimated in typical cases using the counterpoise method.[58] The atomic charges were obtained by a Mulliken population analysis.

Results

In this section, we compare the relative binding strengths in the cation series and in the ligand series, with a particular focus on lanthanide 1:1 complexes. 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 methodology for simplicity. The comparison of HF to MP2 or DFT calculations and the role of polarization functions will be addressed in the Discussion and Conclusion section. We also analyze the most salient trends in the structural and electronic features of the complexes. The total energies of the optimized systems are summarized in Table S1 (Supporting Information). Tables 1 and 2 contain the complexation energies ΔE obtained at different computational levels. Full versions of these tables, including the BSSE-corrected ΔE's, are given in Tables S2 and S3. Optimized structural parameters and Mulliken charges are given in Tables 3−5 and in Tables S4 and S5.

1. Relative Cation−Ligand Binding Energies from HF Calculations. We first consider the 1:1 M$^{n+}\cdots$**L** complexes. Tables 1 and S2 reveal large differences in ion−ligand interaction energies ΔE, which range, for the lanthanide systems, from −300 (in the Yb$^{3+}\cdots$OPPh$_3$ complex) to −118 kcal/mol (in the La$^{3+}\cdots$Pyr-NO$_2$ complex). In all cases studied, the BSSE is small compared to these numbers and nearly constant (from −2 to −4 kcal/mol; see Tables S2 and S3). As the BSSE-corrected interaction energies closely follow the uncorrected interaction energies ΔE, we will base the following discussion on the ΔE's only. They reveal significant cation discrimination by a given ligand, as well as ligand discrimination by a given cation.

In the cation series, with any of the ligands studied, the interactions increase in the expected order Na$^{+} \ll$ Sr$^{2+} \ll$ La^{3+} < Eu^{3+} < Yb^{3+}. For a given ligand, the interaction of the trivalent Eu^{3+} cation is about four to five times larger than with the monovalent Na^{+} cation, of similar ionic radius, due mostly to polarization effects. The difference in La^{3+}/Yb^{3+} interaction energies is nearly constant and amounts to about 40 kcal/mol for a given ligand. This energy range is smaller, however, than the one observed in the ligand series. Among the Pyr-X complexes, ΔE increases markedly as X becomes more electron donating: X = NO$_2$ < H < Me < NMe$_2$. For the Eu$^{3+}\cdots$Pyr-X complexes ΔE ranges from −135 to −225 kcal/mol, showing that the X substituent modulates ΔE by 90 kcal/mol! The comparison of the Pyr-Me to Pyr-H complexes of La^{3+}, Eu^{3+}, and Yb^{3+} reveals increased interactions (from 12 to 13 kcal/mol, respectively) upon *para*-alkyl substitution of the ligand.

Table 2. Interaction Energies in the M$^{n+}\cdots$Amid-XY Complexes (kcal/mol; from HF/DZ//HF/DZ Calculations)[a]

	X, Y				
	Me, Me	Me, H	H, Me	H, H	Ph, H
La^{3+}	−203.2			−182.6	−202.6
Eu^{3+}	−222.8	−214.8	−209.4	−200.9	−222.7
Yb^{3+}	−241.7			−218.8	−241.7
Sr^{2+}	−104.1	−101.7	−98.9	−95.5	−100.5
Na^{+}	−50.0				−46.8

[a] The full version of the table, including the BSSE-corrected interaction energies, is given as Supporting Information (Table S3).

In the series of amide complexes (Table 2) where only the Eu^{3+} and Sr^{2+} cations have been compared for all ligands, the substituent effect is smaller (21 kcal/mol for Eu^{3+} and 9 kcal/mol for Sr^{2+}). This is not surprising in regard to the fact that electronic perturbations induced by H/Me/Ph substitutions are weaker than those induced by the H/NO$_2$/Me/NMe$_2$ substitutions on pyridine. Table 2 shows that, with both Eu^{3+} and Sr^{2+} ions, the binding strength increases in the series primary < secondary-cis < secondary-trans ≤ tertiary amide. Among the two secondary amides, the phenyl-substituted Amid-HPh interacts better than the alkyl-substituted Amid-HMe (as expected from polarization effects) and as much as the tertiary Amid-Me$_2$ ligand. This suggests that tertiary Amid-Ph$_2$ amides (and their aryl derivatives with polarizable and/or electron-donating substituents) should still be better ligands. We did not calculate them, however, because of computer time limitations in the geometry optimization process. As a result, we focus in the following on the tertiary amide (Amid-Me$_2$) which is, together with Amid-NHPh-*trans*, "the best" amide ligand considered here.

Among the three types of ligands, the phosphoryl OPPh$_3$ ligand displays the largest interactions in the gas phase with any cation studied. This conclusion should remain valid if the Amid-Ph$_2$ were also considered. Indeed, extrapolating from

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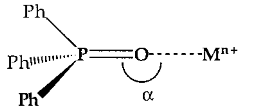
Table 3. Optimized Parameters and Mulliken Charges in the $M^{n+}\cdots OPPh_3$ Complexes (HF/DZP*//HF/DZP* Calculations)[a]

	optimized params		Mulliken charges			
M^{n+}	$d(O\cdots M^{n+})$	$d(P{=}O)$	$q(M)$	$q(O)$	$q(P)$	$q(Ph)$
none		1.510		−0.647	0.604	0.014
La^{3+}	2.025	1.686	2.493	−1.018	0.663	0.287
Eu^{3+}	1.939	1.694	2.460	−1.007	0.650	0.299
Yb^{3+}	1.871	1.697	2.435	−0.998	0.643	0.307
Sr^{2+}	2.166	1.586	1.788	−0.997	0.588	0.207
Na^{+}	2.025	1.551	0.863	−0.792	0.665	0.088

[a] See Chart 1 for definitions.

Chart 1. Definition of Atoms and Parameters in the $M^{n+}\cdots OPPh_3$ Complexes



Amid-H_2 to Amid-HPh-*trans* ($\Delta\Delta E = 22$ kcal/mol in the Eu^{3+} complex) and considering that cis is less stabilizing than the trans substitution would lead to a rough prediction of $\Delta E = -240$ kcal/mol for the $Eu^{3+}\cdots$Amid-Ph_2 complex, i.e., still about 40 kcal/mol less than in $Eu^{3+}\cdots OPPh_3$ or 10 kcal/mol less than in $Eu^{3+}\cdots OPMe_3$.[29]

The competition between Amid-Me_2 and the different Pyr-X ligands depends on the nature of the X substituent: Pyr-NMe_2 > Amid-Me_2 > Pyr-Me > Pyr-H > Pyr-NO_2. Thus, the unsubstituted or alkyl-substituted pyridine fragments of extractant molecules[1,2] interact somewhat less than the amide with a given cation.[59] We also notice that the preference for the best pyridine Pyr-NMe_2, relative to the best amide Amid-Me_2 ligand, is modest (less than 5 kcal/mol).

As 2:1 complexes of $\mathbf{L}_2MCl_3$ type, we considered those with $\mathbf{L}$ = Pyr-H vs Amid-Me_2 vs Me_3PO and $M^{3+} = Eu^{3+}$ vs La^{3+} in order to mimic structures where the cation is direcly coordinated to three anions and to (at least) two identical ligands.[60−62] In these complexes, the two ligands bind formally to a neutral MCl_3 salt and repulse each other. As a result, the interaction energy between each ligand and MCl_3 drops markedly, compared to the interaction energy in the 1:1 $\mathbf{L}M^{3+}$ complexes (with Eu^{3+}, these interactions are 35.2 vs 172.3 kcal/mol for Pyr-H, 48.1 vs 222.8 kcal/mol for Amid-Me_2, and 55.1 vs 230.9 kcal/mol for Me_3PO). However, the trends are the same as in the 1:1 $\mathbf{L}M^{3+}$ complexes: with respect to a given cation (Eu^{3+} or La^{3+}) the binding sequence remains Pyr-H <Amid-Me_2 < $OPMe_3$ (and presumably < $OPPh_3$). Each of these ligands interacts less with La^{3+} than with Eu^{3+} or Yb^{3+}, but the difference is much smaller in the $\mathbf{L}_2MCl_3$ than in the $\mathbf{L}M^{3+}$ complexes: about 2 kcal/mol instead of 22 kcal/mol (Table 1).

2. Trends in Structural and Electronic Changes upon Complexation. Complexation of the cation by a given ligand $\mathbf{L}$ induces a number of structural and electronic perturbations, related to electron transfer from $\mathbf{L}$ to the cation and polarization of $\mathbf{L}$.[46] In the lanthanide series, the smallest (and hardest) Yb^{3+} ion induces the largest polarization and charge-transfer effects.

We first consider the 1:1 $M^{n+}\cdots\mathbf{L}$ complexes. To a given ligand $\mathbf{L}$, one finds that the stronger the interaction with the cation is ($La^{3+} < Eu^{3+} < Yb^{3+}$), the shorter is the cation$\cdots\mathbf{L}$ distance, as expected from the sequence of ionic radii. For instance, in the Pyr-X series, the $M^{3+}\cdots N_{pyr}$ distance decreases from 2.33 (for the weakest complex $La^{3+}\cdots$Pyr-NO_2) to 2.03 Å (for the strongest complex $Yb^{3+}\cdots$Pyr-NMe_2). In the La^{3+}/Yb^{3+} complexes of Amid-Me_2 and $OPPh_3$, the $M^{3+}\cdots O$ distances decrease from 2.08 to 1.91 Å and from 2.02 to 1.87 Å, respectively (Tables 3−5).

In all lanthanide complexes, there is significant electron transfer to the cation, which increases from La^{3+} to Yb^{3+}: from 0.51 to 0.56 e for $OPPh_3$, 0.40 to 0.47 e for Amid-Me_2, and 0.33 (for Pyr-NO_2) to 0.61 e (for Pyr-NMe_2; see Tables 3−5). As expected, in the pyridine derivatives, the transfer increases in the series X = NO_2 (0.33 to 0.38 e) < Me (0.41 to 0.50 e) <NMe_2 (from 0.53 to 0.61 e). In the Na^+ and Sr^{2+} complexes, the charge transfer is less than in the lanthanide complexes (about 0.1 and 0.2 e, respectively; Tables 3−5). We also notice a dramatic electron reorganization on the ligand. In particular, the ligand's atom bound to M^{n+} becomes much more negatively charged. For the La^{3+} complexes, Δq amounts to −0.37 e (for O_{OPPh_3}), −0.48 e (for $O_{Amid-Me_2}$), and −0.73 e (for $N_{Pyr-NMe_2}$)! Thus, *the electron transfer to the cation does not originate from the bound atom of the ligand but from the adjacent ones*. From a methodological point of view, as far as force field models of such complexes are concerned, it is thus stressed that atomic charges derived on the uncomplexed ligands may poorly describe the complexed state.

The geometries of the ligands are also perturbed upon complexation. The trends can be understood by the polar resonance forms presented in Figure 2, whose weights increase with the interaction energy ΔE, i.e. from La^{3+} to Yb^{3+}. For example, upon complexation of $OPPh_3$, the O=P bond lengthens (from 1.51 Å in the free ligand to 1.69 and 1.70 Å in the La^{3+} and Yb^{3+} complexes, respectively) while the polarity of the phosphoryl bond increases (from $O^{-0.65}{-}P^{+0.60}$ in the free ligand to $O^{-1.00}{-}P^{+0.64}$ in the Yb^{3+} complex). Similarly, upon cation coordination to the Amid-Me_2 ligand, the C=O bond lengthens (from 1.24 to 1.36 Å with La^{3+} and to 1.37 Å with Yb^{3+}), while the C−N bond shrinks (from 1.37 to 1.29 Å with both La^{3+} and Yb^{3+} ions). We notice the nonequivalence of the two N-Me groups, as Me-*trans* is more positively charged than Me-*cis* (Δ = 0.08 e) in all M^{3+} complexes, in agreement with the scheme of Figure 2 and expectations from polarization effects. We also notice, following the same trends (Table 4), that, upon complexation, the polarity of the $O^{\delta-}{-}C^{\delta+}{-}N$ fragment increases and becomes largest for the Yb^{3+} complex where the oxygen charge becomes most negative (by 0.47 e). Polarization effects and charge−dipole interactions are enhanced when the cation deviates from a collinear arrangement with the C=O bond and moves "trans" to the C−N bond. The optimized structures reveal such a trend in all complexes where the $M^{3+}\cdots O{=}C$ angle is about 172° (Table 4). If one now compares the different amides interacting with a given cation (Table 4), similar trends are observed, which follow the order of interaction energies ΔE, the order of polarizabilities on Amid-XY (H < Me < Ph), and the stereochemical requirements for electron transfer (trans > cis). The weakening of C=O or P=O bonds upon complexation is fully consistent with the infrared shifts reported in CMPO ligands upon complexation of M^{3+} cations.[63,64]

When the Pyr-X ligands interact with the cations, the pyridine skeleton also reorganizes as suggested by the "polar" mesomeric form (Figure 2): the two d_1 bonds acquire "double bond"

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(59) The interaction of pyridine with Eu^{3+} is, however, much higher than the one with 1,3,5-triazine (123 kcal/mol; Muzet, N.; Wipff, G. Unpublished results.) central fragment of TPTZ.

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Table 4. Optimized Parameters and Mulliken Charges in the (Amid-XY)M^{n+} and (Amid-Me$_2$)$_2$MCl$_3$ Complexes (HF/DZ//HF/DZ Calculations)[a]

			optimized dists and angles[b]			Mulliken charges			
X	Y	M^{n+}	d(O···M^{n+})	d(C═0)	α	q(M)	q(O)	q(C)	q(N)
				(Amid-XY)M^{n+} 1:1 Complexes					
H	H	none[c]		1.231			−0.440	0.500	−0.808
		La^{3+}	2.109	1.344	174	2.658	−0.933	0.718	−0.651
		Eu^{3+}	2.015	1.350	174	2.622	−0.947	0.734	−0.639
		Yb^{3+}	1.931	1.353	174	2.592	−0.940	0.737	−0.633
		Sr^{2+}	2.224	1.289	175	1.850	−0.840	0.682	−0.723
Me	H	none[c]		1.235			−0.461	0.489	−0.593
		Eu^{3+}	2.001	1.364	173	2.590	−0.957	0.712	−0.437
		Sr^{2+}	2.209	1.300	174	1.838	−0.873	0.672	−0.508
H	Me	none[c]		1.234			−0.457	0.534	−0.608
		Eu^{3+}	2.004	1.352	173	2.595	−0.950	0.723	−0.421
		Sr^{2+}	2.213	1.292	174	1.839	−0.874	0.706	−0.509
Ph	H	none[c]		1.234			−0.452	0.458	−0.724
		La^{3+}	2.077	1.373	171	2.565	−0.974	0.618	−0.528
		Eu^{3+}	1.987	1.378	171	2.528	−0.971	0.620	−0.522
		Yb^{3+}	1.906	1.383	171	2.501	−0.964	0.622	−0.517
		Sr^{2+}	2.203	1.309	172	1.828	−0.906	0.628	−0.611
		Na^{+}	2.063	1.267	172	0.902	−0.695	0.566	−0.674
Me	Me	none[c]		1.238			−0.479	0.531	−0.390
		La^{3+}	2.079	1.365	172	2.596	−0.960	0.706	−0.237
		Eu^{3+}	1.988	1.370	172	2.561	−0.958	0.707	−0.228
		Yb^{3+}	1.909	1.374	172	2.532	−0.950	0.711	−0.224
		Sr^{2+}	2.200	1.303	172	1.829	−0.895	0.700	−0.307
		Na^{+}	2.057	1.267	170	0.900	−0.700	0.633	−0.348
				(Amid-Me$_2$)$_2$MCl$_3$ 2:1 Complexes					
Me	Me	La^{3+}	2.387	1.266	180[d]	1.501[e]	−0.770	0.689	−0.307
		Eu^{3+}	2.277	1.265	180[d]	1.399[e]	−0.776	0.698	−0.305
		Yb^{3+}	2.179	1.263	180[d]	1.338[e]	−0.773	0.710	−0.310

[a] See Chart 2 for definitions. A more extended table is given as Supporting Information (Table S4). [b] d_i distances in Å and α angle in deg. [c] Uncomplexed ligand. [d] Unoptimized parameter. [e] The total charge of MCl$_3$ is −0.215 for M = La, −0.216 for M = Eu, and −0.227 for M = Yb.

Chart 2. Definition of Atoms and Parameters in the M^{n+}···Amid-XY Complexes

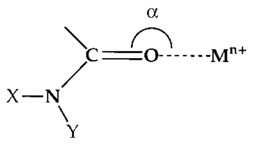

Chart 3. Definition of Atoms and Parameters in the M^{n+}···Pyr-X Complexes

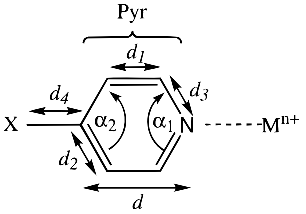

Table 5. Optimized Parameters and Mulliken Charges in the (Pyr-X)M^{n+} and (Pyr-X)$_2$MCl$_3$ Complexes (HF/DZ//HF/DZ Calculations)[a]

		dists (Å);	Mulliken charges			
X	M^{n+}	d(N···M^{n+})	q(M)	q(N)	q(Pyr)[b]	q(X)
		(Pyr-X)M^{n+} 1:1 Complexes				
NO$_2$	none[c]			−0.165	0.434	−0.434
	La^{3+}	2.33	2.674	−0.862	0.554	−0.228
	Eu^{3+}	2.22	2.624	−0.876	0.595	−0.219
H	none[c]			−0.195	0.000	0.221
	La^{3+}	2.290	2.630	−0.874	0.370	0.340
	Eu^{3+}	2.185	2.582	−0.884	0.418	0.344
	Yb^{3+}	2.101	2.538	−0.868	0.462	0.347
Me	none[c]			−0.198	0.068	−0.068
	La^{3+}	2.266	2.593	−0.899	0.258	0.149
	Eu^{3+}	2.175	2.545	−0.909	0.298	0.157
	Yb^{3+}	2.082	2.502	−0.895	0.335	0.163
NMe$_2$	none[c]			−0.225	0.198	−0.198
	La^{3+}	2.206	2.469	−0.956	0.265	0.266
	Eu^{3+}	2.123	2.423	−0.958	0.294	0.282
	Yb^{3+}	2.034	2.390	−0.944	0.319	0.291
	Sr^{2+}	2.391	1.832	−0.803	0.138	0.030
	Na^{+}	2.251	0.928	−0.557	0.169	−0.097
		(Pyr-H)$_2$MCl$_3$ 2:1 Complexes				
H	La^{3+}	2.653	1.547[d]	−0.648	0.039	0.235
	Eu^{3+}	2.540	1.405[e]	−0.653	0.051	0.234
	Yb^{3+}	2.440	1.381[f]	−0.641	0.056	0.234

[a] See Chart 3 for definitions. A more extended table is given as Supporting Information (Table S5). [b] Pyr is the C$_5$H$_4$N fragment of the ligand. [c] Uncomplexed ligand. [d] The total charge of LaCl$_3$ is −0.078. [e] The total charge of EuCl$_3$ is −0.100. [f] The total charge of YbCl$_3$ is −0.135.

character and shorten, while the d_2 and d_3 bonds acquire single bond character and lengthen (Table 5 and Chart 3). These changes depend on the binding strength of the cation, i.e. increase in the order Na$^+$ < Sr^{2+} < M^{3+} in the cation series and Pyr-NO$_2$ to Pyr-NMe$_2$ in the ligand series (Table S5). Upon binding of Yb^{3+} to Pyr-NMe$_2$, the changes are $\Delta d_1 = -0.04$, $\Delta d_2 = +0.05$, $\Delta d_3 = +0.10$ Å, and $\Delta d_4 = -0.08$ Å, while upon binding of Na$^+$, all changes are about ±0.02 Å or less (Table S5).

The comparison of the 2:1 **L**$_2$MCl$_3$ complexes with the corresponding 1:1 **L**M^{3+} ones reveals a marked lengthening of the cation−ligand distance (for instance, for Eu^{3+} complexes, $\Delta = 0.36$ Å for Pyr-H, 0.29 Å for Amid-Me$_2$, and 0.31 and 0.28 Å for Me$_3$PO; see Figure 3 and Table 4), related to the

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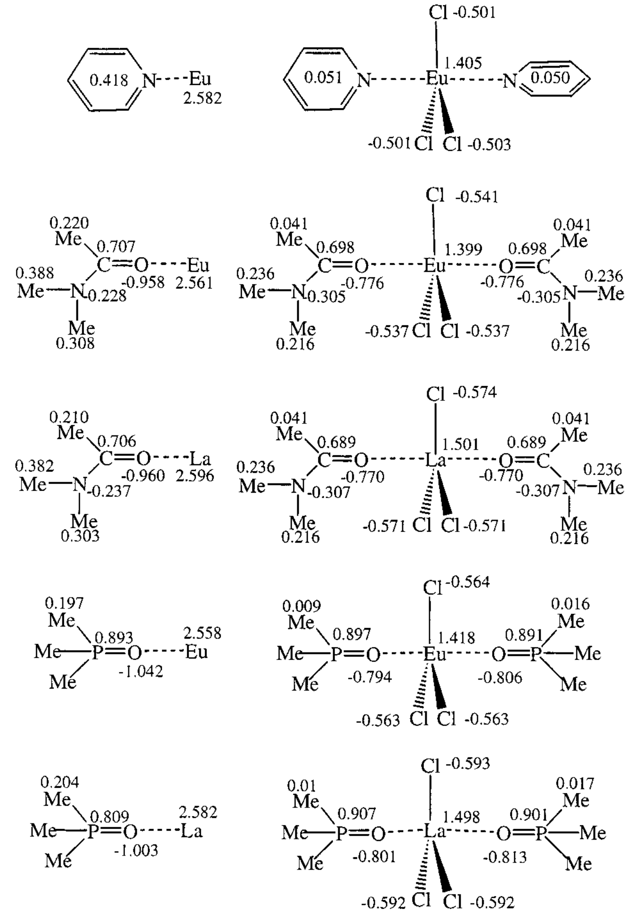

Figure 4. Mulliken charges (e) in $\mathbf{L}M^{3+}$ and $\mathbf{L}_2MCl_3$ complexes.

weaker interaction of **L** in $\mathbf{L}_2MCl_3$. The geometry of the ligand is also less perturbed in $\mathbf{L}_2MCl_3$ than in $\mathbf{L}M^{3+}$. For instance, the C=O bond in $(\text{Amid-Me}_2)_2MCl_3$ is 0.03 Å longer than in the free ligand but 0.10 Å shorter than in the Amid-Me_2···M^{3+} complex. Similarly, the P=O bond in $(Me_3PO)_2EuCl_3$ is 0.03 Å longer than in the free ligand but 0.13 Å shorter than in the Me_3PO···Eu^{3+} complex.

The electron loss Δq on **L** upon complexation is also much weaker in $\mathbf{L}_2MCl_3$ than in $\mathbf{L}M^{3+}$ (for Eu^{3+} and Yb^{3+} complexes, Δq is 0.05 vs 0.42 e for Pyr-H, 0.11 vs 0.44 e for Amid-Me_2, and 0.13 vs 0.46 e for Me_3PO; see Figure 4 and Table 4) but still follows the order R_3PO > Amid-Me_2 > Pyr-H of binding strengths. It is also less in the La^{3+} than in the Eu^{3+} and Yb^{3+} complexes. The C=O and P=O bonds are less polar in the $\mathbf{L}_2MCl_3$ than in **L**···M^{3+} complexes (Figure 4). Concerning the MCl_3 moitey of the 2:1 complex, we notice that the cation charge ranges from +1.39 to +1.50 e, due to the electron transfer from the chloride anions (from 0.50 to 0.41 e per anion). Compared to the $\mathbf{L}M^{3+}$ complexes, the cationic charge is thus reduced by about 1.1 e. This analysis thus suggest that modeling the cation in force field methods with a +3 charge may lead to an overestimation of its interactions with anions and ligands and that the charges on the different fragments of the complexes are far from being constant and transferable from one complex to the other.

3. Angular Flexibility of Cation Coordination. All results reported above concern the "linear" mode of cation coordination to a given ligand. In this section, we address the question of angular flexibility of cation coordination to the three types of ligands, i.e., the energy cost ΔE_α to deviate from a linear coordination ($\alpha = 180°$ in $OPPh_3$, Amid-XY, and Pyr-X complexes), keeping the cation in the plane of the molecule ($\beta = 0°$; see Table S6). In the amide and pyridine systems, the out-of-plane deformation energy ΔE_β was also calculated. The ΔE_α and ΔE_β energies were obtained from single point HF/DZ calculations on 1:1 $\mathbf{L}M^{n+}$ complexes, starting from the structures optimized with $\alpha = 180°$, and changing α to 180 ± 20 and $180 \pm 40°$ (keeping $\beta = 0°$) and $\beta = \pm 20°$ (keeping $\alpha = 0°$). In all cases examined the cation coordination is quite flexible. In the Eu^{3+}···Pyr-X complexes, $\Delta E_{20°}$ ranges from 2.4 to 4.1 kcal/mol depending on the X-substituent. In the M^{3+}···Amid-Me_2 complexes, the $\Delta E_{20°}$ energies confirm that bending trans to the C−N bond is easier than cis (about 1 and about 7 kcal/mol, respectively), as observed in the optimized complexes (see Table 4). With the $OPPh_3$ ligand, we calculated the Eu^{3+} complex only and also found that bending the Eu···O=P bonds is a very easy process, somewhat more facile trans than cis, with respect to a PPh group ($\Delta E_{20°} = 1.1$ and 1.5 kcal/mol, respectively). When $\Delta\alpha$ is further increased from 0° to ±40°, the interaction energies drop markedly in the M^{3+} amide and pyridine complexes (where $\Delta E_{40°}$ is about 10 and 30 kcal/mol, respectively) but less in the $OPPh_3$ complex ($\Delta E_{40°} = 6$ and 9 kcal/mol for trans and cis bending). This led us to optimize the Eu^{3+}···$OPPh_3$ complex, without imposing a linear cation coordination, and found $\alpha_{opt} = 180°$, which confirms that the linear binding corresponds to a flat energy minimum. We also notice that the Na^+ and Sr^{2+} complexes of Amid-Me_2 and Pyr-NMe_2 display the same trends as the M^{3+} complexes, as far as the angular flexibility of ion binding is concerned (Table S6).

Discussion and Conclusion

We report a quantum mechanical study of the binding of "large"/"average"/"small" trivalent lanthanide cations to three important classes of ligands used to complex actinides or lanthanides: phosphoryl-containing $OPPh_3$ and $OPMe_3$ and several amide and pyridine derivatives. The calculations on 1:1 complexes provide insights into their intrinsic energy and structural features "in the gas phase", i.e., in the absence of other competing species. It is found that among all ligands studied (i) the $OPPh_3$ and $OPMe_3$ ligands have the highest binding energy, (ii) the binding energies of the best amide and pyridine ligands are not very different from each other, and (iii) substituents effects may be quite large and inverse the amide/pyridine binding to lanthanide ions. In addition, we describe the complexation-induced electronic reorganization (mostly in terms of polarization and charge-transfer effects). All results follow trends expected from the changes of basicity in a ligand series, but the changes in interaction energies as a function of the ligand are much larger than those as a function of the cation. The comparison of the $\mathbf{L}M^{3+}$ 1:1 complexes with selected $\mathbf{L}_2MCl_3$ ones demonstrates *the importance of multiple ligand and anion coordination to the cation on structural, energy, and electronic features.* In the following, we discuss structural features of lanthanide cations coordination to these ligands. We also address the important question of the validation of these results based on alternative computational approaches.

Structural Aspects of Cation Coordination. Generally speaking, the structures in the gas phase cannot be strictly compared with those condensed phases. For instance for the free ligands, according to experiment, the P=O length of phosphine oxides[65] or the C=O length of amides[66,67] are about

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0.02 Å shorter in the gas phase than in the solid state. In the condensed phases, the first coordination sphere of M^{3+} is saturated by several ligands, anions, and solvent molecules, which increase the electron density on the metal and thereby decrease the metal−ligand attractions. Furthermore, the ligands repulse each other and therefore may not adopt an optimal coordination mode for a given binding site. These effects lengthen the cation···ligand distances and perturb the geometry of the ligand, as confirmed by our comparison of **L**M^{3+} vs **L**$_2$MCl$_3$ complexes. We discussed this question previously for the phosphoryl-containing OPR$_3$ ligands interacting with UO$_2$$^{2+}$, Sr^{2+}, and lanthanide cations.[28,29] For instance, at the same computational level as the one used here (HF/DZ calculations), the PO···UO$_2$$^{2+}$ distance increased from 2.16 Å in Me$_3$PO···UO$_2$$^{2+}$ to 2.29 Å in Me$_3$PO···UO$_2$(NO$_3$)$_2$ and 2.33 Å in (Me$_3$PO)$_2$UO$_2$(NO$_3$)$_2$, while the O═P bond shortened from 1.61 to 1.54 and to 1.53 Å, respectively. Another shortening of 0.02 Å was observed in calculations on Me$_3$PO using a larger basis set (polarization functions added on all atoms), leading to a good agreement with the average experimental value of 1.51 Å. Similarly, in the Ph$_3$PO···M^{3+} complexes, the O···M^{3+} distance was found to increase by about 0.2 Å while the P═O shortens by about 0.13 Å when three Cl$^-$ counterions were added to the system.[28,29] The results obtained for the (Me$_3$PO)$_2$EuCl$_3$ and (Me$_3$PO)$_2$LaCl$_3$ complexes follow the same trends.

In the solid-state structures of lanthanide complexes with pyridine-, amide-, or phosphoryl-containing ligands, the cation is also directly coordinated to anions. For instance, in the EuCl$_3$(pyridine)$_4$ complex[60] the four pyridines bind formally to a neutral EuCl$_3$ species. As a result, the corresponding Eu^{3+}···N$_{\text{pyridine}}$ distances (from 2.59 to 2.62 Å) are larger than in our optimized Eu^{3+}···Pyr-Me 1:1 complex (2.17 Å) but close to those optimized in (Pyr-H)$_2$EuCl$_3$ (2.54 Å). Our optimized bond lengths of the complexed Pyr-H ligand follow the same trends and are close to the experimental ones[60] (see Table S5). In the X-ray structures of amide complexes of lanthanides, the metal is also coordinated and neutralized by anions.[66] This is the case in the La(PS$_2$(O^{i}Pr)$_2$)$_3$(Amid-Me$_2$)$_2$ complex,[62] where the La^{3+}···O$_{\text{Amid}}$ distances (2.41−2.43 Å) are about 0.35 Å larger than those optimized in the La^{3+}···Amid-Me$_2$ complex (2.08 Å) but close to those calculated in the (Amid-Me$_2$)$_2$LaCl$_3$ complex (2.39 Å). Increasing the coordination from five (in the calculated **L**$_2$MCl$_3$ complex) to about nine (in the solid-state structures) would further improve the agreement between calculated vs experimental coordination distances. The geometry of the amide ligand, found to be moderately pertubed by the metal in solid-state structures,[66] is also quite different in the calculated **L**M^{3+} vs **L**$_2$MCl$_3$ complexes. These comparisons point out the *nontransferability of the structural and electronic parameters, which markedly depend on the presence and nature of counterions and of other coordinants in the first coordination sphere of the cation.* Conversely, care should be taken in the interpretation of solid-state structures in terms of stereochemical features of cation−ligand interactions. As far as the fitting of force field parameters is concerned, it is thus clear that fittings based on ab initio optimizations on cation···ligand 1:1 species underestimate the metal ligand distances and exaggerate the related electronic effects (charge transfer and polarization per ligand), compared to those in saturated complexes.

Another concern is the linear vs bent coordination mode of the cation to monodentate/bidentate ligands. For instance, malonamides,[35,68] CMPO's,[30−33] or TPTZ[39] molecules which incorporate amide, O═PPh$_2$R, or pyridine groups (Figure 1) involve several binding sites and form complexes of stoichiometries larger than 1:1. In such complexes, a compromise has to be found between optimal binding of a given coordination site and distortions required for simultaneous binding to several sites. In the solid-state structures of simple amide complexes, the cation sits trans to the amide nitrogen,[66] as in the bidentate CMPO's. According to our calculations, this is energetically favorable, compared to a linear or cis coordination. In the complexes of Er(NO$_3$)$_3$,[61] Sm(NO$_3$)$_3$,[61] and La(PS$_2$(O^{i}Pr)$_2$)$_3$[62] with Amid-Me$_2$ as ligand, α ranges from 140 to 166°. With malonamides R$_2$NCOCH$_2$CONR$_2$ as bidentate ligands, the M^{3+} cation sits trans to the NR$_2$ groups, leading to smaller values of α (130−146° in the La^{3+}, Sm^{3+}, and Er^{3+} complexes[69−71]). For the O═P group, we calculate that the linear binding corresponds to a flat energy minimum. This is consistent with experimental observations on solid-state structures of lanthanide complexes of OPPh$_3$ (where α ranges from 152 to 178°; see Table 9 of ref 29) or of CMPO's (where α ranges from 165 to 180°; see discussion in ref 72). In pyridine complexes of La^{3+},[73] Eu^{3+},[60] or Yb^{3+} [74] the binding is more linear (α ranges from 180 to 174°). Thus, again, *the linear/bent coordination in the complexes cannot be interpreted solely on the basis of intrinsic coordination features*, as it also results from competitive interactions with the other binding sites in the first coordination sphere, as well as from possible packing effects in the crystal. Upon anion coordination to the metal, the ligand−metal bond becomes "softer" and less "ionic" than in **L**M^{3+} where electrostatic and polarization effects are dominant.

Relevance of the Calculated Data for Ion Complexation. Strictly speaking, the calculated interaction energies should be compared to binding data in the gas phase. In the case of alkali and alkaline earth cation 1:1 complexes, computations where the ligand is represented at a computational level comparable to the one used here[14] reproduce nicely experimental binding in the gas phase.[9] Such data are lacking for lanthanide and actinide ions, as they are lacking for the Na$^+$ and Sr^{2+} complexes we investigated. Our results however point out why ligands (of acyclic or macrocyclic type) incorporating such binding sites are used to extract trivalent lanthanide and actinide ions. For instance, Pyr-Me interacts much more with La^{3+}, Eu^{3+}, and Yb^{3+} than does a water molecule (by 70, 77, and 84 kcal/mol, respectively, from HF/DZ//HF/DZ calculations). Cation binding in solution is a more complex process, however, which depends on the ion:ligand stoichiometry and on the dynamic competition with counterions and solvent molecules. Its thermodynamics depends on enthalpic and entropic components and results partly from a compensation of large effects.

Our study points out the *importance of substituent effects on the ligands*, in relation with the induced change in "basicity". As shown in OPR$_3$ ligands, replacement of the phenyl by alkyl groups reduces the interactions with lanthanide ions.[28,29] This may explain why phenyl to alkyl substitution in calix[4]arene-CMPO's leads to a loss of cation extraction.[33] Liquid−liquid extraction of ions is based on the lipophilic character of the extractant molecules. It is generally believed that solubilizing

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alkyl or aryl substituents has little effect on the interactions between the cation and its first-shell ligands. Our comparison of amide (primary/secondary/tertiary) as well as in the pyridine (Pyr-H/Pyr-Me) 1:1 complexes shows that the related perturbations may be quite large. Looking at the large difference in interaction energies of a given lanthanide as a function of the ligand's substituent (up to 90 kcal/mol in 1:1 complexes), it is interesting to notice that this number is close to the difference in (de)hydration energies of the La^{3+}/Yb^{3+} cations (101 kcal/mol).[75] Therefore, the liquid−liquid extraction selectivity stems from a balance and partial compensation of quite large effects. Another feature concerns the role of counterions. Our comparison of **L**M^{3+} vs **L**$_2$MCl$_3$ complexes highlights the amplification of cation ligand interations and of substituent effects on **L** when no counterions are coordinated to the cation. This may be an important feature of extractant molecules whose binding sites, anchored to a molecular platform (like calixarenes[32,33,76] or resorcinarenes[77]), may wrap sufficiently around the cation to prevent direct contacts with the anions.

Computational Aspects. The results reported above are based on SCF calculations using a consistent basis set representation of the partners and a consistent level of geometry optimization. Concerning the representation of cations, we used a large core representation of the inner electrons of the lanthanides, which had therefore 11 valence electrons. We tested on the H$_3$PO$\cdots$Eu^{3+} complex another quasi relativistic pseudopotential (from ref 78), with a smaller core and 35 explicit valence electrons described by a (12s,11p,10d,9f)/[6s,5p,4d,4f] basis set taken from ref 79. The interaction energies turned out to be, as expected, larger with the small core but not very different (−199.2 instead of −195.0 kcal/mol for the optimized structures after BSSE correction). The energy difference related to the level of core representation of the cation is thus small, compared to the changes from a ligand to the other. The P=O bond lengths were nearly identical in both cases (1.646 versus 1.643 Å) while the H$_3$PO$\cdots$Eu^{3+} distances were as expected a little bit shorter (2.016 versus 2.025 Å).

Another methodological issue concerns the possible effect of electron correlation. This question was addressed in a previous paper, where HF results were compared to those obtained at the MP2 and DFT levels.[29] Tests performed on the M$^{3+}\cdots$OPH$_3$ complexes showed that the energy difference betwen La^{3+} and Yb^{3+} was practically constant. Similar conclusions were obtained by us on UO$_2$$^{2+}$ complexes of OPR$_3$ ligands[28] and by others in a study of the Gd(H$_2$O)$_9$$^{3+}$ hydrate.[18] We felt however that it would be important to perform similar tests on the systems studied here, in relation with the competition between two types of ligands for a given ion, as well as different ions competing for a given ligand. Thus, interaction energies ΔE were recalculated at the DFT/DZ//HF/DZ and MP2/DZ//HF/DZ levels for all Eu^{3+} complexes, as well as for all cation complexes of "the best ligands" (OPPh$_3$, Amid-Me$_2$, and Pyr-NMe$_2$). The adequacy of HF-optimized geometries was assessed on all M$^{n+}\cdots$Amid-Me$_2$ complexes, where the interaction energies ΔE obtained at the DFT/DZ//DFT/DZ and DFT/DZ//HF/DZ levels were, within less than 1 kcal/mol, identical. Table 1 shows that, for the lanthanide and Sr^{2+} complexes, the ΔE's calculated at the DFT-B3LYP or MP2 level are more attractive than those obtained at the HF level ($\Delta E_{\mathrm{DFT}} < \Delta E_{\mathrm{MP2}} < \Delta E_{\mathrm{HF}}$). Similar features have been recently observed for bond dissociation energies and exchange reactions in lanthanide trihalide systems.[25,26] For a given ligand, the energy lowering depends somewhat on the cation (e.g. for the La^{3+}/Eu^{3+}/Yb^{3+} complexes of Amid-Me$_2$, $\Delta E_{\mathrm{MP2}} - \Delta E_{\mathrm{HF}} = 16/18/19$ kcal/mol; $\Delta E_{\mathrm{DFT}} - \Delta E_{\mathrm{HF}} = 23/26/27$ kcal/mol). For a given cation, the shift in ΔE also depends on the ligand. For instance, for the Eu^{3+} complexes, $\Delta E_{\mathrm{MP2}} - \Delta E_{\mathrm{HF}} = 20$ for OPPh$_3$, 18 for Amid-Me$_2$, and 30 kcal/mol for Pyr-NMe$_2$. In Sr^{2+} complexes, the corrections are smaller (less than 2 kcal/mol) than the ones in the lanthanide complexes but follow the similar trends. The shifts are more erratic in the Na$^+$ complexes, but in this case the corrections are almost negligeable, likely due to the smaller polarization effects. Thus correlation effects in lanthanide complexes should not be overlooked for a *quantitative* assessment of the *absolute* interaction energies. However, at a *qualitative* level, all conclusions reported above when *comparing* cations or ligands are validated. For a given ligand, in the cation series, the sequence remains the same (Na$^+$ $\ll$Sr^{2+} $\ll$ La^{3+} < Eu^{3+} < Yb^{3+}). Lanthanide cations interact about four to five times stronger than Na$^+$ with a given ligand, mostly due to enhanced polarization and charge-transfer effects. Similarly, for a given M^{3+} cation, the ligand series is retained within a given class (Pyr-NO$_2$ < Pyr-H < Pyr-Me < Pyr-NMe$_2$) and when "the best" members of each class are compared (OPPh$_3$ > Pyr-NMe$_2$ $\geq$ Amid-Me$_2$). Furthermore, for lanthanide complexes, the range of interaction energies as a function of the ligand is about twice the one as a function of the cation.

To conclude, we emphasize the importance of computational approaches to compare the intrinsic binding features of various classes of ligands used in the complexation and liquid−liquid extraction of lanthanide and actinide cations. Our study provides a rationale for the use of aryl-substituted phosphoryl-containing ligands, which display the highest interaction energies among those we investigated. The comparison of amide to pyridine ligands also demonstrates the importance of substituent effects on the relative binding strengths. Substituents should also strongly modulate the spectroscopic features of related photoactive complexes.[80,81] Such computations should contribute to a better understanding of the structural and energy features of the complexes and the basis of efficient complexation and separation of lanthanides and actinides by known or putative ligands.

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Supporting Information Available: Tables of data for the quantum mechanical calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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