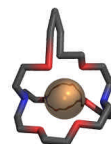# Selective Extraction of Lanthanide Cations by tetra-phosphineoxide substituted Calix[4]arenes: a Molecular Dynamics Study at a Water / Chloroform Interface

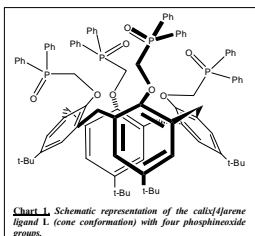## M. Baaden [a], M. Burgard [a], D. Matt [a] and G. Wipff [*,b]

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Chart 1. Schematic representation of the calix[4]arene ligand L (cone conformation) with four phosphineoxide groups.

Abstract

Recent studies of the competitive extraction of 11 rare-earth metal ions (La, Pr, Nd, Sm, Eu, Gd, Dy, Ho, Er, Yb and Y) for the substituted calixarene L (see Chart 1) have revealed a higher extraction efficiency and a better separation factor than for tri-n-octylphosphine oxide (TOPO), as well as an increased selectivity for cations of the middle of the series (see Figure 1 on the right). [1] We have simulated LMX_3 complexes with M=La3+, Eu3+, Yb3+ and X=NO3- using molecular dynamics in "bulk" chloroform solution and at a water/ chloroform interface represented explicitly. The position and orientation of the complexes at the interface and the coordination of M3+ by L are investigated.

☞ L is facially coordinated to M3+

☞ The cation is *not* shielded from solvent molecules
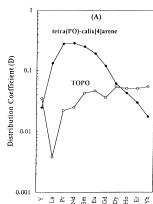
Figure 1. Distribution coefficient for the competitive extraction of 11 rare-earth metal ions by ligand L, compared to tri-n-octylphosphine oxide.
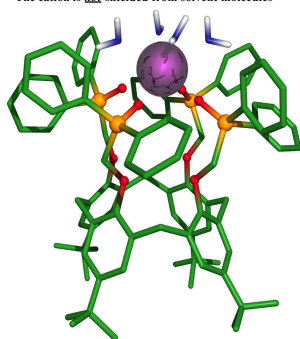
Figure 2. A typical view of LEu3+ with selected solvent molecules at the interface.

Introduction

The search for efficient receptor molecules for the extraction and separation of trivalent rare earth metal ions is of increasing importance. A new class of neutral receptor molecules bearing a calix[4]arene platform and four phosphine oxide arms (see Chart 1) are promising candidates for the selective extraction of M3+ lanthanide cations. [1] Although the extraction properties of these species are well characterized, little is known about the structure of the extracted species LMX3 and the binding mode of L and X.

We present a theoretical investigation (MD calculations) of the structural features related to cation complexation and extraction, in terms of the intrinsic binding mode of the ligand L and of counterion effects as a function of the cation size and of the solvent environment. For this purpose we modelbuilt different starting structures for LMX3 complexes and simulated them in "bulk" solution (chloroform) and at a liquid-liquid interface (water/ chloroform) with explicit solvent. The importance of the interface has already been pointed out for analogous extractant molecules, which are highly surface active. [2-3] Furthermore the interface bears some analogy with a water saturated extraction phase as it provides at the same time a hydrophilic and hydrophobic microenvironment for the complex that is going to be extracted.

Methods

All initial structures were model built, starting from X-Ray data for the uncomplexed ligand L [4] and introducing a cation into the lower rim cavity, in order to make all four "P=O"-arms converge towards the cavity center. We assumed a 1:1 stoichiometry, as indicated by experiment. After minimization by MM, we performed MD simulations at 300 K and constant volume with 3D periodic boundary conditions using the SHAKE algorithm.

The simulations were carried out with a modified version of AMBER 4.1. The force field parameters were taken from former work and from literature data. Charges were derived from electrostatic potentials that were calculated ab initio at the HF 6-31G* level. We chose a non-covalent representation of the interactions between the 3+ charged cation and the ligand L, using a pairwise additive 1-6-12 potential.
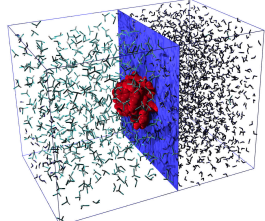

Figure 3. Simulation box for the water/chloroform interface.

The liquid-liquid interface was built from 2 adjacent water and chloroform solvent boxes with about 1500 TIP3P water molecules and 500 OPLS chloroform molecules.
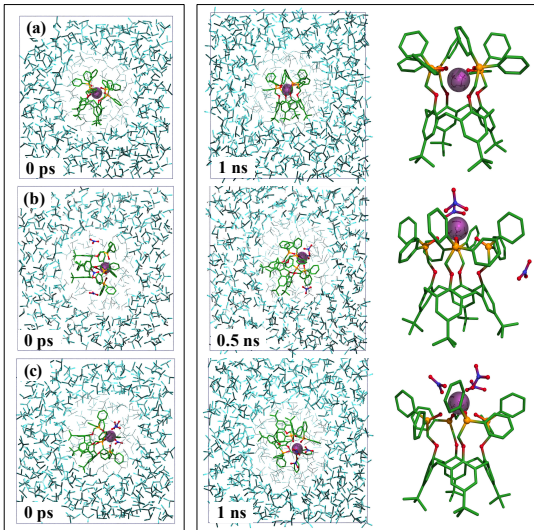

Figure 4 LEu3+ (a) and LEu(NO3)3 (b),(c) in "bulk" chloroform. Snapshots of initial (0 ps; left) and final (right) structures. The chloroform molecules around the solute are displayed differently from those of the "bulk" for clarity.

☞ When no counterions or water molecules are present, the complex is of inclusive type (a).

☞ Up to three NO3- counterions can coordinate directly to Eu3+, which is facially coordinated (c).
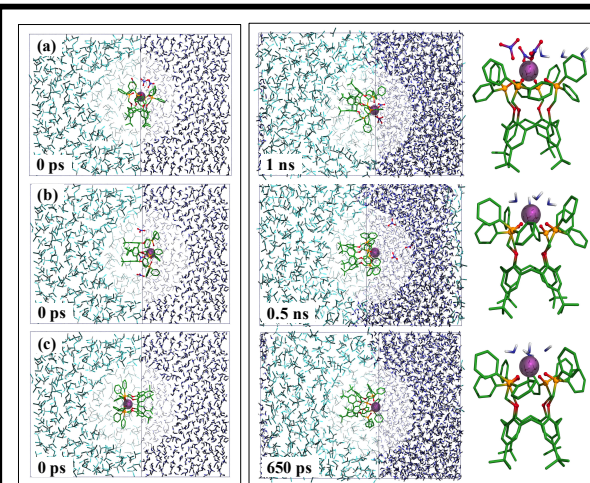
Figure 5. LEu(NO3)3 (a),(b) and LEu3+ (c) at the water/chloroform interface. Snapshots of initial (left) and final (right) structures. The solvent molecules around the solute are displayed differently from those of the "bulk" for clarity.

☞ In all cases the complex adopts an amphiphilic orientation : (a) to (c).

☞ One to four water molecules and up to three counterions complete the coordination sphere of Eu3+. The total coordination number is eight in all cases.

☞ When the counterions are initially in an equatorial position, they dissociate.

(a) LLa3+ at 0.7 ns   (b) LYb3+ at 1 ns   (c) LYb3+ at 380 ps
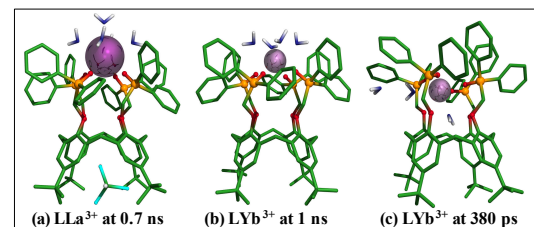
Figure 6. LLa3+ (a) and LYb3+ (b),(c) after MD at a water/chloroform interface. Snapshots of the final structures with selected solvent molecules.

☞ The coordination number for trivalent rare earth metal ions changes from 9 for La3+ (a) to 8 for the heavier lanthanides Eu3+ (Figure 4) and Yb3+ (b).

☞ Solvent molecules can enter the cone of L (a),(c). In case (c) a water molecule from the cone coordinates directly to the cation.

Results

☞ The cation coordination strongly depends on the solvent environment and the binding mode of the counterions.

☞ In all cases we started our simulations (0 ps) from 1:1 complexes with four coordinating phosphoryl arms, which remained firmly bound to the cation.

☞ The coordination sphere of M3+ can easily be completed by ONO2- or OH2, if these species are present.

☞ The four ether oxygens of the calixarene cavity are weakly involved in the cation coordination. L thus exhibits a more facial coordination to M3+ (Figure 2).

I. LEu3+ and LEu(NO3)3 in "bulk" chloroform

We simulated the LEu3+ complex in dry chloroform and investigated counterion effects. In a first simulation (a) we omitted counterions in order to check wether complete inclusion of the cation would occur or not (Figure 4). Two other simulations were carried out, one with the counterions initially in an equatorial position (b) and one with 3 NO3- directly coordinated to the cation (c). Figure 3a shows that the absence of counterions favors inclusion of M3+, but the contribution of the four ether oxygens, which are at 2.6 to 3.0 Å from M3+, is less than that of the phosphoryl ones at about 2.3 Å. In case (b), two of the nitrates move to the lower rim and directly coordinate to M3+, the third one stays in an equatorial position. In this case the complex is not inclusive. The same is true for (c), where all 3 NO3- remain coordinated to Eu3+.

As electroneutrality has to be fulfilled in order to enable the extraction of M3+, counterions should be present in the extracted species. Furthermore a good shielding of the hydrophilic parts of the complex is desirable in order to facilitate the "solvation" by the organic phase.

II. LM3+ and LM(NO3)3 at the water/chloroform interface

In all simulations the complexes adopted an amphiphilic orientation at the interface: cation immerged in water and tBu in the organic phase. This orientation was obtained regardless of the presence or absence of counterions and starting from any of 3 different initial positions (a) to (c) (see Figure 5). This amphiphilic orientation cannot spontaneously lead to the extraction of the complex, as the cation remains highly hydrated and attracted by the water phase.

Simulations with La3+ and Yb3+ cations at the interface reveal a coordination number change along the lanthanide series (see Figure 6 for details). The distance between M3+ and $O_{P=O}/ O_{OH2}$ decreases from La (2.6 and 2.7 Å respectively) via Eu (2.4 / 2.5 Å) to Yb (2.2 / 2.3 Å). In all cases but (c) of Figure 6, a facial coordination of L to M3+ is observed.

Conclusions

Our simulations confirm that the LMX3-type complexes are highly surface active. They should stimulate further experimental work on the nature of the species that are adsorbed at the interface and on the involved extraction mechanism (synergism, ion pairing, pH and salting out effects, ...).

Our results show that the ligand can coordinate to the cation with its four phosphoryl groups simultaneously, but in the presence of water, the cation is not completely shielded from solvent molecules.

The quantitative assessment of the binding selectivity is undertaken in our laboratory and will be presented subsequently

References

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