Quantum Chemistry Study on the Extraction of Trivalent Lanthanide Series by Cyanex301: Insights from Formation of Inner- and Outer-Sphere Complexes

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Supporting Information

ABSTRACT: The extraction of lanthanide series by Cyanex301, i.e., bis(2,4,4-trimethylpentyl)dithiophosphinic acid (HC301), has been modeled by density functional theory calculation, taking into account the formation of both inner- and outer-sphere complexes. The inner-sphere complex Ln(C301)3 and the outer-sphere complex Ln(H2O)9(C301)3 are optimized, followed by the analysis of interaction energy, bond length, Laplacian bond orders, and Mulliken populations. The covalency degree increases in Ln−S and Ln−O bonds in the inner- and outer-sphere complexes, respectively, as the lanthanide series is traversed. Mulliken population analysis indicates the important role of the 5d-orbital participation in bonding in the formation of inner- and outer-sphere complexes. Two thermodynamic cycles regarding the formation of inner- and outer-sphere complexes are established to calculate the extraction Gibbs free energies (ΔGextr), and relaxed potential energy surface scan is utilized to model the kinetic complexation of C301 anion with hydrated metal ions. Light lanthanides can form both inner- and outer-sphere complexes, whereas heavy lanthanides only form outer-sphere complexes in biphasic extraction. After adopting the data of forming inner-sphere complex for light Ln(III) and that of forming outer-sphere complexes for heavy Ln(III), the trend of the calculated −ΔGextr agrees very well with that of the experimental distribution ratios on crossing the Ln(III) series. Results from this work help to theoretically understand the extraction behavior of Cyanex301 with respect to different Ln(III).

INTRODUCTION

Lanthanides are a group of important strategic resources essential for varied areas, such as electronics, luminescence, catalysis, and magnetism, utilized almost everywhere in our modern life.1−12 The trivalent Ln(III) ions are dominant in both solution and solid state in most systems. However, the ionic radius of Ln(III) reduces only 0.15 Å on crossing the series due to the lanthanide contraction. Thus, the physicochemical properties of Ln(III) are very similar, which brings about difficulties in separation of Ln(III). Similar situation is also encountered in the separation of Ln(III) from trivalent minor actinides (An = Am and Cm). The separation of Ln(III) from one another as well as from An(III) has received worldwide attention.13−14 For now, considerable interests are still remained to develop new separation techniques, mainly focusing on seeking for organic or inorganic ligands with high efficiency and selectivity and evaluating the nature of lanthanide/actinide ligand bonding and the corresponding electronic structure.15−18

In 1995, Zhu et al. found that purified Cyanex301, i.e., bis(2,4,4-trimethylpentyl)dithiophosphinic acid (denoted as HC301, Figure 1), which is a S-donor ligand, could selectively extract Am(III) from Ln(III) with an extremely high separation factor over 1000.19−21 Since then, a number of experiments have been carried out to investigate the extraction behaviors and, especially, to identify of the extracted complexes of both An(III) and Ln(III) in organic phase.10−18 It was demonstrated by Jensen et al. that the structure and metal—donor atom bond distances are indistinguishable within experimental error for similarly sized trivalent lanthanide and actinide cations, despite the extraordinary selectivity of HC301 for trivalent actinide cations over trivalent lanthanide cations.10 In the extraction of the lanthanides series by HC301, however, our group...
RESULTS AND DISCUSSION

Figure 2. Calculated structures of Ln(C301)3 and Ln(H2O)9(C301)3.

previously observed different extracted complexes for different lanthanides under the same extraction condition.14 The light Ln(III) are mainly coordinated by the sulfur atoms of the ligands (inner-sphere complexes), and the middle Ln(III) are coordinated by mixed donors, the sulfur atoms of the ligands and the oxygen atoms of the extracted water, whereas the heavy Ln(III) are completely hydrated in the organic phase without any sulfur atoms of the ligands in the coordination shell (outersphere complexes). Furthermore, even for light Ln(III), such as Nd(III), water molecules are able to replace C301 anions in the first coordination shell to coordinate with the metal ions at high neutralization degree, forming outer-sphere complexes and even more complicated supramolecular aggregations in organic phase, i.e., water-in-oil (W/O) microemulsions.15 W/O microemulsions were also evidenced in the extraction of heavy Ln(III). The coordination environments of the heavy Ln(III) are identical along with the increase of neutralization degree.15 These studies indicate the complexity of the extraction of Ln(III) by Cyanex301, but to date, there has been no study to explain the different coordination behavior of Cyanex301 with respect to different Ln(III). Such dramatic differences must be related to the intrinsic properties of different lanthanide ions when they interact with C301 anions, which is imperative to be illuminated.

Density functional theory (DFT) calculation is a very powerful tool to predict and understand the coordination and extraction behavior of ligands in organic solvent toward metal ions in aqueous solution, especially in simulating the extraction separation process containing lanthanides and actinides,19–24 although there are still some challenges due to the difficulties especially in treating relativistic effect and the f-electron correlation effects. Theoretical investigation on the extraction of Ln(III) or An(III) with Cyanex301 has been carried out by DFT calculations to clarify the structure of the extracted complexes25–51 and to correlate the extraction properties with the electronic structure variations of the ligands.32–34 For example, Cao and co-workers carried out an excellent work of DFT calculation on the separation of An(III) (An = Am and Cm) from Eu(III) with Cyanex301.27 The results showed that the neutral complexes M(C301)3, where the C301 anion acts as a bidentate ligand and the metal ion is coordinated by six sulfur atoms, were likely the most stable extraction complexes, consistent with the experimental results reported by Jensen and co-workers.10 Furthermore, they obtained much more negative changes of Gibbs free energies for An(III) in the extraction reaction M3+ + 3HC301 → M(C301)3 + 3H+, in line with the thermodynamical priority for An(III).

In contrast to a relatively large number of investigations on the comparison of the extraction between An(III) and Ln(III) with Cyanex301, less attention has been paid to the theoretical calculation on the extraction of different Ln(III),25,26,28 not to mention the whole series of Ln(III). However, identical complexes for different Ln(III) were reported in the theoretical calculation, which was in contrast to the experimental results. Considering the pronounced differences in the extraction behavior of Cyanex301 across the Ln series in experimental study, it is urgent to find the relationship between extraction behavior and molecular/electronic structure of the extracted Ln(III) complexes by theoretical computations. This is also meaningful from the application aspect because there are several kinds of lanthanides in spent nuclear fuel. Understanding the mechanism of the extraction of different Ln(III) by Cyanex301 will be helpful for optimizing the process in lanthanide and actinide separation.

In this work, we present a DFT calculation on the extraction of Ln(III) series by purified Cyanex301. We first optimize the geometry of inner- and outer-sphere complexes of Ln(III) with Cyanex301, followed by the analysis of the molecular and electronic structure, such as interaction energy, bond length, Laplacian bond orders (LBOs), and Mulliken populations. Then, we calculate the changes of Gibbs free energy in the extraction of Ln(III) by Cyanex301 based on two established thermodynamic cycles, which take into account the formation of inner- and outer-sphere complexes. Finally, the variation of the calculated extraction Gibbs free energy on crossing the lanthanide series is compared to that of the corresponding distribution ratio in extraction experiment. We believe that results in this work will theoretically deepen the understanding of the coordination and extraction behavior of Cyanex301 with regard to different Ln(III).

Structures of Ln(C301)3 and Ln(H2O)9(C301)3. The complexation of Ln(III) with C301 was considered in two ways, i.e., inner- and outer-sphere complexes. The inner-sphere complexes of Eu(III) with C301 have been reported in the
The results indicate that the structures of HM(C301)$_4$ are slightly higher in energy than the separated M(C301)$_3$ and HC301 systems. Given that the ionic radii of Ln(III) are very close to each other, the most stable complex Eu(C301)$_3$ was extrapolated to all other Ln(III) complexes in the present work. As to the outer-sphere complexes, Ln(III) first coordinates with water molecules in the first coordination shell and the hydrated Ln(III) then interacts with C301 by hydrogen bonding. The hydration of Ln(III) has been investigated widely by experimental characterizations and also by theoretical calculations$^{35-38}$ but there are still some controversies on the hydration number of Ln(III). Nevertheless, the hydrated complexes Ln(H$_2$O)$_3$C301$^3+$ were studied in all cases in this work. In outer-sphere complexes, only three C301 anions were included to examine their interactions with Ln(H$_2$O)$_9$C301. We note that adding one or more neutral HC301 molecules might make the outer-sphere complexes more stabilized, but this would be too expensive to be calculated by our limited computing resource, as there have been already nearly 200 atoms in Ln-(H$_2$O)$_9$(C301)$_3$. Another reason that we did not include HC301 in the outer-sphere complexes is, under an extraction condition with 100% neutralization degree, all HC301 are neutralized to C301 anions and the hydrated Ln(III) interact with only three C301 anions without HC301 molecules.$^{16}$ This interaction was also observed in a homogeneous medium.$^{18}$ In combination, no neutral HC301 molecules were included in the outer-sphere complexes.

Typical structures for the complexes Ln(C301)$_3$ and Ln(H$_2$O)$_9$(C301)$_3$ are shown in Figure 2. For the structure of Ln(C301)$_3$ with sixfold metal coordination, the lanthanide ions are located nearly in the plane defined by the three phosphor atoms from the three C301 anions. However, we found no C$_3$ symmetry for Ln(C301)$_3$ as geometry optimizations were carried out without symmetry constraints. This is somewhat different from the results reported by Cao and co-workers, in which the application of two basis sets both led to C$_3$ symmetry as determined from the results of geometry optimization within C$_1$ and C$_3$ symmetries.$^{25}$ Such difference should be attributed to the different software or the different basis sets. Nevertheless, Eu−S bond length as averaged in Eu(C301)$_3$ is 2.842 ± 0.008 Å in our calculations, nearly identical to the value of 2.841 Å calculated with the basis set def2-TZVP for C, H, S, and P atoms by Cao and co-workers. These results also suggest that using relatively small basis sets for C and H atoms in the alkyl chain of C301 insignificantly influences the Ln−S bond length in Ln(C301)$_3$ complexes. The calculated bond lengths of Nd−S and Sm−S are 2.890 and 2.857 Å, respectively, a little longer than the available experimental values (2.852 and 2.803 Å) obtained by Jensen and co-workers.$^{10}$ For the structure of Ln(H$_2$O)$_9$(C301)$_3$, C301 anions no longer coordinate with the Ln(III) ions but form hydrogen bonding with the water molecules in the first coordination shell, resulting in a slight distortion of the three-capped trigonal prism structure of Ln(H$_2$O)$_9$C301$^3+$ in the core. The structures of the inner- and outer-sphere complexes across the lanthanide series were further analyzed by interaction energy ($E_{int}$), bond length, Laplacian bond orders, and Mulliken populations.

The interaction energies for the formation of inner- and outer-sphere complexes are defined by eqs 1 and 2, respectively.

\[
E_{int}(1) = E_{min}(\text{Ln(C301)}_3) - E_{min}(\text{Ln}^{3+}) - 3E_{min}(\text{C301})
\]

(1)

\[
E_{int}(2) = E_{min}(\text{Ln(H}_2\text{O)}_9\text{(C301)}_3) - E_{min}(\text{Ln(H}_2\text{O)}_9\text{)}^{3+} - 3E_{min}(\text{C301})
\]

(2)

where $E_{min}$ is the electronic energy in the minimum-energy geometry. The obtained results for $E_{int}$ are shown in Figure 3.

![Figure 3. Interaction energies for the formation of inner-sphere complex Ln(C301)$_3$ and outer-sphere complex Ln(H$_2$O)$_9$(C301)$_3$ across the lanthanide series.](image)

The interaction energy in the inner-sphere complex decreases from −3875 to −4278 kJ/mol, whereas that in the outer-sphere complex decreases from −2310 to −2376 kJ/mol, as the metal ion crossed from La to Lu. This result suggests the stronger interaction of C301 anion with heavy Ln(III) compared to light Ln(III) in both the formation of inner- and outer-sphere complexes. This is readily understood, as the charge density increases along the lanthanide series in both Ln(III) ion and hydrated Ln(III) ion would induce stronger electrostatic attraction to the negative C301 anion.

The variations of the average bond lengths for Ln−S in the inner-sphere complex Ln(C301)$_3$ and for Ln−O in the outer-sphere complex Ln(H$_2$O)$_9$(C301)$_3$ are presented in Table 1. Not surprisingly, the values for these bond lengths decrease with the increase in atomic number due to the decrease of the ionic radius of Ln(III) across the lanthanide series. After subtracting the value of the ionic radius of Ln(III), the data of R$_{Ln−S} − R_{Ln}$ in Ln(C301)$_3$ and R$_{Ln−O} − R_{Ln}$ in Ln(H$_2$O)$_9$(C301)$_3$ are also shown in Table 1. In general, a very slight decrease trend along the lanthanide series can be found in both cases. The bond length analysis can provide some information to some extent about the bonding nature between metal ions and ligands, such as the covalency. Usually, shorter bond length means higher covalency degree. The descendant trends in the values of R$_{Ln−S} − R_{Ln}$ in Ln(C301)$_3$ and R$_{Ln−O} − R_{Ln}$ in Ln(H$_2$O)$_9$(C301)$_3$, suggest the increase of covalency degree in the bonding of lanthanide with both sulfur in C301 anion and oxygen in water molecules as the lanthanide series crossed. This can be further verified by electron density at bond critical points (CPs), Laplacian bond orders (LBOs), and Mulliken orbital populations.
Table 1. Averaged Bond Lengths (Å) of Ln–S and Ln–O and Their Values after Reduction of Ln(III) Ion Radii in Ln(C301)3 and Ln(H2O)9(C301)3, Respectively

|        | Ln(C301)3 | Ln(H2O)9(C301)3 |
|--------|-----------|-----------------|
|        | R_{Ln-S} | R_{Ln-S} - R_{Ln}| R_{Ln-O} | R_{Ln-O} - R_{Ln} |
| La     | 2.949     | 1.917           | 2.613    | 1.581            |
| Ce     | 2.928     | 1.918           | 2.594    | 1.584            |
| Pr     | 2.908     | 1.918           | 2.576    | 1.586            |
| Nd     | 2.890     | 1.907           | 2.559    | 1.576            |
| Pm     | 2.873     | 1.903           | 2.543    | 1.573            |
| Sm     | 2.857     | 1.899           | 2.528    | 1.570            |
| Eu     | 2.842     | 1.895           | 2.514    | 1.567            |
| Gd     | 2.828     | 1.890           | 2.501    | 1.563            |
| Tb     | 2.814     | 1.891           | 2.488    | 1.565            |
| Dy     | 2.800     | 1.888           | 2.475    | 1.563            |
| Ho     | 2.787     | 1.886           | 2.463    | 1.562            |
| Er     | 2.775     | 1.885           | 2.452    | 1.562            |
| Tm     | 2.763     | 1.883           | 2.442    | 1.562            |
| Yb     | 2.751     | 1.883           | 2.432    | 1.562            |
| Lu     | 2.741     | 1.880           | 2.422    | 1.561            |

As shown in Figure 4A, the electron densities at the CPs of both the Ln–S bond in Ln(C301)3, and the Ln–O bond in Ln(H2O)9(C301)3 increase along the lanthanide series, signaling increasing bond strengths and increased covalency degree. This can be further demonstrated by Laplacian bond order. The Laplacian bond order (LBO) is defined as

\[
LBO_{A,B} = -10 \times \int \rho(r) \nabla^2 \rho(r) \, dr
\]

where A and B stand for atoms, \(\rho\) is the electron density, and \(w\) is a function determining the region of the atom by Becke’s scheme.\(^{39}\) The prefactor \(-10\) is introduced to make the magnitude of LBO consistent with one’s chemical intuition for typical covalent bonds. LBO only reflects the covalent component of a bond because \(\nabla^2 \rho < 0\) means that the electron density is locally concentrated, suggesting the covalent interaction. Figure 4B shows the variation of LBOs of Ln–S bonds in Ln(C301)3 and Ln–O bonds in Ln(H2O)9(C301)3. It can be seen that both of them linearly increase along the lanthanide series, indicating the increase of covalency degree. The values of LBOs of Ln–O bonds in Ln(H2O)9(C301)3 are comparable to those in Ln(III) aqua complexes,\(^{38}\) whereas those of Ln–S bonds in Ln(C301)3, are much higher, indicating higher covalency degree in Ln–S bonds.

Mulliken orbital populations can reflect some physical features for similar species under identical calculation procedures, although it is known to be basis set-dependent. Particularly, this method has been applied in the estimation of the covalency of metal–ligand bonding within f-elements complexes.\(^{7,41}\) The results of Mulliken orbital populations (6s, 6p, and 5d) and atomic charges on Ln in both the inner-sphere complex Ln(C301)3 and the outer-sphere complex Ln(H2O)9(C301)3 are shown in Figure 5. In general, considerable 6s, 6p, and 5d occupations are observed for both the inner- and outer-sphere complexes on crossing the lanthanide series, which indicate the metal–ligand bonding contributions from these shells. In detail, the 6s occupations are very similar in the complexes of Ln(C301)3 and Ln(H2O)9(C301)3, both increasing with the increase in atomic number. An increase tendency in 6p occupations is also observed for both the complexes, and 6p occupations for Ln in Ln(H2O)9(C301)3 are a little higher than those in Ln(C301)3. The most striking difference occurs in the 5d occupation. The 5d occupation for Ln in Ln(H2O)9(C301)3 increases with the atomic number, similarly to 6s and 6p occupations. Differently, it shows a generally decrease tendency in the case of Ln(C301)3. A similar trend was also observed by Lößle et al. when they studied the covalency degree in Ln–Cl bond by examining the complexes of lanthanide hexachloride.\(^{41}\) In combination, the atomic charges on Ln in both Ln(C301)3 and Ln(H2O)9(C301)3 decrease as atomic number increased, with a more slightly decreasing tendency in the variation for Ln(C301)3. Lower Mulliken charges on metal center imply more charge transfer from ligand to metal, thus indicating higher covalency degree in metal–ligand bonding. This is consistent with the trends in electron densities at CPs and LBOs in Figure 4. Besides, it can be seen that the 5d occupation is much larger than 6s and 6p occupations in both Ln(C301)3 and Ln(H2O)9(C301)3 complexes, indicating the more significant role of the 5d shells in bonding in the complexation of Ln(III) with C301 and water molecules.

We are aware that some studies have reported that the 5d electrons contribute largely in covalency bonding of Ln ligands.\(^{41–43}\) In our case, the significant contribution of 5d electrons in the metal–ligand bond is largely responsible for the formation of inner- and outer-sphere complexes. Contrary to

Figure 4. (A) Electron density at CPs and (B) LBOs of Ln–S bonds in Ln(C301)3 (black squares) and Ln–O bonds in Ln(H2O)9(C301)3 (red circles).

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the previous speculation of decrease in covalency degree on the formation of inner- and outer-sphere complexes between lanthanides series and C301 anion in a homogeneous solution,\(^{18}\) the heavy lanthanides are capable of forming stronger covalent bonds with C301 anions compared to the light lanthanides. The competition of water molecules with C301 anion induces different complexes for light and heavy lanthanides. In addition, contributions of 6s and 6p orbitals in the metal–ligand bonding should not be neglected, and we believe that, in the future, more efforts will be made to examine the role of 5d, 6s, and 6p orbitals of Ln in coordinating with diversified ligands containing O, S, and N donors, which are normally used in the extraction separation of trivalent actinides and lanthanides.\(^{5}\)

**Extraction Gibbs Free Energy.** For the extraction of Ln(III) by HC301 forming inner-sphere complexes, the extraction equation is

\[
\text{Ln}^{3+} + 3\text{HC301}_{\text{aq}} \rightarrow \text{Ln(C301)}_{3\text{org}} + 3\text{H}^+_{\text{aq}} \tag{4}
\]

whereas for the extraction forming outer-sphere complexes, the extraction equation is

\[
\begin{align*}
\text{Ln}^{3+} + 9\text{H}_2\text{O}_{\text{aq}} + 3\text{HC301}_{\text{org}} \\
\rightarrow \text{Ln(H}_2\text{O)}_{9\text{aq}}(\text{C301)}_{3\text{org}} + 3\text{H}^+_{\text{aq}}
\end{align*}
\tag{5}
\]

If the hydration of Ln(III) is treated explicitly, eqs 4 and 5 can be rewritten as eqs 6 and 7, respectively.

\[
\begin{align*}
\text{Ln(H}_2\text{O)}_{9\text{aq}}^{3+} + 3\text{HC301}_{\text{org}} \\
\rightarrow \text{Ln(3C01)}_{3\text{org}} + 9\text{H}_2\text{O}_{\text{aq}} + 3\text{H}^+_{\text{aq}}
\end{align*}
\tag{6}
\]

\[
\begin{align*}
\text{Ln(H}_2\text{O)}_{9\text{aq}}^{3+} + 3\text{HC301}_{\text{org}} \\
\rightarrow \text{Ln(H}_2\text{O)}_{9\text{org}}(\text{C301)}_{3\text{org}} + 3\text{H}^+_{\text{aq}}
\end{align*}
\tag{7}
\]

The change of extraction Gibbs free energy for eqs 6 and 7 can be obtained from the thermodynamic cycles, as shown in Schemes 1 and 2, respectively. The water cluster (H\(_2\)O)\(_9\) is used in the thermodynamic cycle, which shows more accurate solvation free energies than those using monomer cycle with nine distinct water molecules as reagents according to the literature.\(^{44}\) HC301, Ln(H\(_2\)O)\(_9\)\(^{3+}\), and the water cluster (H\(_2\)O)\(_9\) were all optimized. Their final structures are shown in Figure S1. The structure of Ln(H\(_2\)O)\(_9\)\(^{3+}\) is of three-capped trigonal prism, consistent with the result obtained by Ciupka and co-workers.\(^{36}\) For (H\(_2\)O)\(_9\) only the structure with global minima in energy, i.e., the nonamer with one water molecule hydrogen bonded to the cubic octamer,\(^{45-47}\) is used in calculating the extraction Gibbs free energy. The hydration energy of H\(^+\) was not calculated but used the experimental value of \(-1104.5\) kJ/mol.\(^{49}\) \(\Delta G^{\text{extr,s}}\) is the energy change of 1 mol of an ideal gas from 1 atm (24.46 L/mol) to 1 mol/L at 298.15 K, and its value is 7.92 kJ/mol according to the literature.\(^{50,51}\) The concentration of (H\(_2\)O)\(_9\) in liquid water is 6.15 mol/L; thus, a correction term of \(\Delta G^\text{l\rightarrow\text{aq}}\) is added. Its value for (H\(_2\)O)\(_9\) was calculated to be −4.5 kJ/mol. The components for the calculation of extraction Gibbs free energy are all tabulated in Supporting Information (Tables S1–S6).

As shown in Table 2, both the extraction Gibbs free energies obtained from Schemes 1 and 2 descend monotonously as the atomic number of Ln(III) increased. In general, the values of extraction Gibbs free energy for the formation of inner-sphere complex are lower than those for the formation of outer-sphere complex. The energy gap between the extraction Gibbs free energies for the formation of inner- and outer-sphere complexes is about 20 kJ/mol for all Ln(III).

As can be seen from Schemes 1 and 2, the difference in the change of extraction Gibbs free energies for different Ln originates from the Gibbs free energy of the reaction in gas phase (\(\Delta G^\text{extr,gas}\)) and the solvation energy (\(\Delta G^\text{solv}\)) of the extracted complexes (Ln(C301)\(_3\)) or Ln(H\(_2\)O)\(_9\)(C301)\(_3\) in organic phase and of Ln(H\(_2\)O)\(_9\)\(^{3+}\) in aqueous phase. Using La

Figure 5. Mulliken orbital populations (6s, 6p, and 5d) and atomic charge on the metal center Ln in the complexes of Ln(C301)\(_3\) (black squares) and Ln(H\(_2\)O)\(_9\)(C301)\(_3\) (red circles).
extraction system as a reference, the difference of these three components is illustrated in Figure 6. For the formation of both inner- and outer-sphere complexes, the fraction of ΔΔG extr,gas shows the most significant difference, followed by the solvation energy of Ln(H2O)93+ in aqueous phase. The contribution of the solvation energy of the extracted complexes is much smaller than that of the above two fractions. This is a little inconsistent with the findings for the separation of Am(III) and Eu(III) reported by Cao and co-workers, where the difference between the hydration energies for Am(III) and Eu(III) appears to be the decisive contribution for the observed preference of Cyanex301 for complex formation with the actinides rather than with the lanthanides.27 We also noted that the theoretical calculations in the work by Keith and co-workers indicated that the binding free energy of the ligands to metals is the primary contribution to the separation effect in the selective extraction of Am(III) and Eu(III) by two dithiophosphinic acids with different substituent groups.29 These findings, in combination,
suggest the complicated performance of dithiophosphinic acids in the extraction separation of trivalent lanthanides and actinides, which depends on varied factors such as metal-ion species and substituent groups.

It should be noted that the results in Table 2 show a monotonous decrease in the extraction Gibbs free energies for the formation of both inner- and outer-sphere complexes. However, as can be seen from Schemes 1 and 2, only the situations before and after the extraction of metal ions are modeled. That is, the kinetic process for the penetration of metal ions from aqueous phase into organic phase accompanied by the complexation of C301 anions with metal ions is not considered in the calculation of extraction Gibbs free energy. It must be admitted that the actual reaction mechanism of extraction process is too complex to be modeled by quantum chemical methods, and such a process might be successfully revealed by other theoretical methods, such as molecular dynamics with reactive force field. However, this has gone beyond the subject of this work. Nevertheless, we, in this work, used a relaxed potential energy surface (PES) scan method to preliminarily study the interaction of C301 anions with hydrated lanthanide ions, to see the process of replacement of water molecules by C301 anions. This cannot exactly simulate the actual extraction process, but it can indeed provide some useful information about the dynamic extraction process from thermodynamic aspect. The relaxed PES scan was carried out along the distance between the phosphor atom in C301 anion and the lanthanide atom in Ln(H_2O)_9 in 24 steps from 5.3 to 3.0 Å. Two lanthanide ions were selected in the relaxed PES scan, the representative of light lanthanides, Nd(III), and that of heavy lanthanides, Ho(III). The potential curves in the PES scan and the corresponding structures for selected Ln–P distances are summarized in Figure 7. It should be noted that, as C301 anion is progressively close to the Ln(III) ions, sulfur atoms of C301 anion replace water molecules to directly coordinate with Ln(III). In this context, the water molecules released will form hydrogen bonding with the water molecules remained in the first coordination shell, which makes the structure hard to be optimized successfully. Therefore, once a water molecule was released from the first coordination shell of Ln(III), it would be omitted from the relaxed PES scan. This treatment is actually very close to the actual process of the extraction occurred at the interface area between aqueous phase and organic phase, in which the water molecules replaced by C301 anions in coordination with Ln(III) remain in aqueous phase along with the partitioning of Ln(III).

For the interaction of C301 anion with Nd(H_2O)_9 in the PES scan as depicted in Figure 7, C301 anion interacts with Nd(H_2O)_9, forming a outer-sphere complex (Nd-1) at a Nd–P distance of 5.0 Å. The C301 anion replaces one water molecule by coordinating Nd(III) with one sulfur atom, forming a low-energy complex (Nd-2) at a Nd–P distance of 4.5 Å. Further closing C301 anion to Nd(III) induces another low-energy complex (Nd-3) at a Nd–P distance of 3.6 Å. In this structure, two water molecules are replaced by two sulfur atoms from the C301 anion in the first coordination shell of Nd(III). The energy gap between Nd-1 and Nd-3 is about 79.0 kJ/mol, indicating that the substitution of H_2O by C301 anion in interaction with hydrated Nd(III) is endothermic. This is in good agreement with the endothermic process of the extraction of trivalent lanthanides by Cyanex301.52 The PES scan also interprets the phenomena in the formation of W/O microemulsions reported by our group previously, in which both C301 anions and water molecules can coordinate with Nd(III), depending on the extraction conditions.16 As to the PES scan of Ho–P distance between Ho(H_2O)_9 and C301 anion, the energy curve is very different from that for Nd(III). Similarly, hydrated Ho(III) can also form outer-sphere complex with C301 anion with a Ho–P distance of 5.0 Å. Differently, as the phosphor atom of C301 anion further closing to Ho atom in Ho(H_2O)_9, no low-energy structure was achieved. Especially, the energy monotonously increases as Ho–P distance decreases from 4.2 to 3.0 Å. This is also consistent with our observation in the study of W/O microemulsions phenomena in extraction of Ho(III) by HC301, that is, the sulfur atoms from the C301 anions cannot replace the oxygen atoms from water molecules in the first coordination shell of Ho(III).53 In short, the relaxed PES scan demonstrates that light lanthanides can form both inner- and outer-sphere complexes, whereas heavy lanthanides can only form outer-sphere complexes with C301 free in the presence of water molecules. Therefore, the Gibbs free energies...
in the extraction of the Ln(III) series by Cyanex301 should adopt different data corresponding to different metal-ion species, as calculated in Schemes 1 and 2. Moreover, the extraction equilibrium constant for the formation of inner- and outer-sphere complexes can be written as eqs 8 and 9, respectively.

\[
K_{\text{extr},1} = \frac{[\text{Ln(C301)}_3 \text{org}] [\text{H}^+]^3}{[\text{ Ln}^3]^{aq} [\text{HC301}]^{aq}} = D_{\text{Ln}} \frac{[\text{H}^+]^3}{[\text{HC301}]^{aq}}
\]

(8)

\[
K_{\text{extr},2} = \frac{[\text{Ln(H}_2\text{O})_6 \text{C301)}_3 \text{org}] [\text{H}^+]^3}{[\text{Ln(H}_2\text{O})_6]^{aq} [\text{HC301}]^{aq}} = D_{\text{Ln}} \frac{[\text{H}^+]^3}{[\text{HC301}]^{aq}}
\]

(9)

Therefore,

\[
\Delta G_{\text{extr}} = -RT \ln K_{\text{extr}} = -RT \ln D_{\text{Ln}} + C
\]

(10)

where C is a constant depending on various factors, such as pH in aqueous phase, concentration of metal ion in aqueous phase, concentration of HC301 in organic phase, and neutralization degree. According to eq 10, the negative value of extraction Gibbs free energy (\(-\Delta G_{\text{extr}}\)) is proportional to the value of \(\ln D_{\text{Ln}}\). We compare the trend in the calculated \(-\Delta G_{\text{extr}}\) to that in the experimental \(\ln D_{\text{Ln}}\) across the Ln(III) series, and the results are presented in Figure 8. After adopting the data of formation

![Figure 8](image_url)

Figure 8. Comparison of the tendency in the calculated \(-\Delta G_{\text{extr}}\) (filled squares) and in the experimental \(\ln D_{\text{Ln}}\) on crossing the lanthanide series without Pm. For lanthanides of 57–60, data of forming inner-sphere complexes are adopted, whereas those of forming outer-sphere complexes are adopted for 64–71. The adapted data are presented in filled square form. The data of distribution ratio of Ln(III) are adopted from ref 13, in which toluene is used as the diluent. In the left Y scale, the value of \(-\Delta G_{\text{extr}}\) is from 70 to 130 kJ/mol with a \(\Delta \Delta G_{\text{extr}}\) of 60 kJ/mol. According to eq 9, \(\Delta \ln D_{\text{Ln}}\) should be about 24, thus the right Y scale is set in the range of −12 to 12.

of inner- and outer-sphere complexes for lighter and heavier lanthanides, respectively, the comparison shows an excellent agreement between calculation and experiment. This also further supports the validity of DFT calculation study on the extraction of Ln(III) by Cyanex301. The difference in the calculated \(-\Delta G_{\text{extr}}\) between different Ln(III) ions is very small (for most Ln, the difference is less than 3 kJ/mol). There is a little discrepancy for the middle lanthanides, mainly due to the transition from inner- to outer-sphere complexes in the extracted species. The middle lanthanides may coordinate with both water molecules and C301 anions simultaneously in the extraction system, which is a transition-mode complex. This was not investigated in our calculation, but one can infer from Figure 8 a formation of transition-mode complex for Eu(III). This is in line with our previous observations in both extraction system and homogeneous solution with high metal loading, but contrary to the results by using extended X-ray absorption fine structure with very low metal loading. Once again, this reflects the complexity of the extraction system using Cyanex301 as the extractant. In Figure 8, the calculated values of \(\Delta G_{\text{extr}}\) are all quite negative, whereas the distribution ratios are all very small (from 0.64 to 1.72). This is because the distribution ratios were determined at a very high metal-ion concentration and a low neutralization degree. As aforementioned, the constant C in eq 10 is affected by these two factors. Actually, if we use a low metal-ion concentration in aqueous phase relative to that of HC301 in organic phase, the distribution ratios will be very high at a very high neutralization degree.

**CONCLUSIONS**

The extraction of the Ln(III) series by Cyanex301 is successfully modeled by DFT calculation after considering the formation of both inner- and outer-sphere complexes. The interactions between lanthanide and C301 anion become stronger on crossing the lanthanide series in both the inner- and outer-sphere complexes, due to the stronger electrostatic attraction for C301 anion resulting from the greater charge density on metal center and the higher covalency in Ln–S and Ln–O bonds. All of the valence orbitals of 6s, 6p, and 5d contribute in covalency, among which 5d orbitals play a critical role in forming either inner- or outer-sphere complexes. As suggested by a relaxed PES scan, the competition between water molecules and C301 anion induces that light lanthanides can form both inner- and outer-sphere complexes, whereas the heavy lanthanide can only form outer-sphere complexes with C301 in the presence of water molecules. In the extraction Gibbs free energies, data of the formation of inner- and outer-sphere complexes are adopted for light and heavy lanthanides, respectively, and this treatment agrees perfectly with the trends in experimental distribution ratios across the lanthanide series. Results in this work also have ramifications for the extraction separation of trivalent actinide and lanthanide by using Cyanex301 and perhaps other ligands containing O and N donors. Questions in the extraction separation of trivalent actinide and lanthanide such as the formation of inner- and outer-sphere extracted complexes and the role of valence orbitals (5d/6d, 6s/7s, and 6p/7p, along with 4f/5f) in corresponding coordination behavior are valuable to be answered in the future.

**COMPUTATIONAL DETAILS**

All theoretical calculations were carried out using the Gaussian 09 software package (revision C.01). The generalized gradient approximation-type density functional BP86 was used, in which the Hartree–Fock exchange energy was approximated using the gradient-corrected exchange-energy function proposed by Becke in 1988 and the electron correlation energy was approximated using the density function proposed by Perdew in 1986. The BP86 functional has been demonstrated to be successful in calculation of Ln(III)
complexation with HC301. Standard def2-SVP basis sets as implemented in the Gaussian program were used for C and H, whereas standard def2-TZVP basis sets were used for S, P, and O atoms. As to Ln(III), we noted that both small-core (4f-in-valence) and large-core (4f-in-core) pseudopotentials (PPs) were utilized in the calculation of the interaction between Ln(III) and HC301. The electron configuration of Ln(III) is [Xe]4f0.27,29,31 However, the 4f orbital of Ln(III) is historically considered to be buried beneath the valence shell and is treated explicitly.30 Therefore, energy-consistent scalar-relativistic WB-adjusted 4f-in-core PPs in combination with the corresponding (7s6p5d)/[5s4p3d] standard basis sets were used for Ln(III) in this work.57

Associated Content

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b00359.

Optimized structures for HC301, Ln(H2O)3+, and (H2O)6 (Figure S1); calculated parameters for the complexes in Scheme 1 (Tables S1–S3); and calculated parameters for the complexes in Scheme 2 (Tables S4–S6) (PDF)

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Notes

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