This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal’s standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.
Characterization of the Extracted Complexes of Trivalent Lanthanides with Purified Cyanex 301 in Comparison with Trivalent Actinide Complexes

Xihong He, a,c Guoxin Tian, *a,b,c Jing Chen a and Linfeng Rao b

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

The extracted complexes of trivalent lanthanides (LnIII) with purified Cyanex 301 (bis(2,4,4-trimethylpentyl)dithiophosphinic acid, denoted as HA) were investigated by extended X-ray absorption fine structure spectroscopy (EXAFS), UV-Vis and fluorescence spectroscopy. In the complexes prepared under the same conditions of solvent extraction, the light LnIII ions are mainly coordinated by the sulfur atoms of the ligands, and the middle LnIII ions are coordinated by mixed donors, the sulfur atoms of the ligands and the oxygen atoms of extracted water, while the heavy LnIII ions are completely hydrated in the organic phase without any sulfur atoms of the ligands in the coordination shell. As the atomic number increases, the extracted water molecules gradually replace the sulfur atoms of the ligands in the first coordination shell of LnIII, and simultaneously the ligand anions become counterions just for balancing the positive charge of the fully hydrated heavy LnIII ions. The effect of the change in the complex structures on the extraction of LnIII ions with HA was evaluated by the co-extraction of other thirteen individual LnIII together with NdIII. In contrast to most ligands bonding more strongly to heavier LnIII, HA preferentially extracts lighter LnIII, suggesting the unusual extraction capability of HA for LnIII might originate from the difference in the complex structures with LnIII ions.

Introduction

In lanthanides the 4f-orbitals are ordinarily considered to be deeply buried beneath the valence shell and they rarely play a substantial role in bonding, so that the physicochemical properties of trivalent lanthanide (LnIII) are similar in spite of the number of the 4f electrons increasing from 0 for LaIII to 14 for LuIII. Indeed, except for a few ligands bearing soft donors such as N and S,1,2 for most ligands there is often only an isostructural series of LnIII complexes observed,3,4 and the trend of the stability for LnIII complexes in solution is mainly governed by the charge density of the metal ions.11-13 For example, the stability constant for the formation of ethylenediaminetetracetic acid (EDTA) complexes increases from 10^{5.5} for [La(EDTA)] to 10^{19.8} for [Lu(EDTA)] with an average stepwise increasing factor of about 2.06 across the LnIII series. Using di-(2-ethylhexyl)phosphoric acid (HDEHP) as extractant, the extraction equilibrium constant for LuIII is about 10^7 times higher than that for LaIII.14 Besides the trivalent cations in the lanthanide series, the AnIII ions are also similar as LnIII in chemical properties because of the same charge, similar size and valence electron configuration. For instance, the formation constants of 10^{16.4} for [Am(EDTA)] is very close to the value of 10^{19.23} for [Eu(EDTA)] as the ionic radii of AmIII is comparable to that of EuIII.11,15-17

Due to the very similar chemical properties of LnIII and AnIII of similar ionic size, even the separation of light lanthanides from heavy lanthanides is relatively easy to be achieved, the separation of AnIII from LnIII of similar ion size is of great challenge as well as the separation of the adjacent lanthanide elements from each other. However, in naturally occurring ores, the Rare Earth minerals usually are dominated by one group or the other, depending on which size-range best fits the structural lattice; and in spent nuclear fuel, the light lanthanides representing 30% of fission products co-exist with Am and Cm, one portion of the major long-term radioactive hazards generated in the nuclear reactors. It has been a very challenging task for scientists to develop efficient processes for separating adjacent lanthanides from each other in their production and for separating Am and Cm from the light lanthanides in spent nuclear fuel reprocessing. In our previous work on the separation of AnIII from LnIII, we found that dialkyldithiophosphinic acids have excellent selectivity for AnIII and CmIII over light LnIII, and the selectivity originates from the difference in structure and composition between the AnIII and LnIII complexes.18 Solvent extraction separation processes based on the dialkyldithiophosphinic acid extractants might be used to solve the very challenging task of AnIII/LnIII separation for the advanced nuclear energy system.19 However, even though the overall selectivity of HA for AnIII over light LnIII is outstanding, the values of 3500, 1000, 1900, and 4500, respectively for the separation factors SFAm/La, SFAm/Ce,Pr, SFAm/Nd, and SFAm/Sm do...
not well fall in the trend of the ionic radii of these Ln\textsuperscript{III} ions.\textsuperscript{18b} To help understanding the separation mechanism, the complex structure of Ln\textsuperscript{III} with HA has been compared with that of An\textsuperscript{III}. Neutral bidentate complexes LnA\textsubscript{2} and AnA\textsubscript{2} were reported with no discernible water molecules in the first coordination shell of the Ln\textsuperscript{III} at very low loading conditions in a study using UV-Vis absorption spectroscopy and EXAFS.\textsuperscript{20} However, our previous studies with EXAFS, IR, MS, TRDFS on samples of varying metal loading suggested that the molecular formula of the Ln\textsuperscript{III} complexes that formed at high metal loading might be LnA\textsubscript{3}•2H\textsubscript{2}O or HLnA\textsubscript{2}•H\textsubscript{2}O and the water molecules should coordinate to the light Ln\textsuperscript{III}. These controversies over the structures and composition of Ln\textsuperscript{III} complexes remain to be verified. Further, only few Ln\textsuperscript{III} samples were prepared in those studies and the structure of the complexes for different Ln\textsuperscript{III} were considered to be isostructural or similar, even though it was found that the hydration number might vary with different Ln\textsuperscript{III} ions in the complexes.

In this work, we revisit the extracted Ln\textsuperscript{III} complexes with HA and focus on the change in structure of the extracted complexes across the lanthanide series. The results show that the extracted Ln\textsuperscript{III} complexes change along with the Ln\textsuperscript{III} series, which is quite different from the common observation of forming isostructural complexes. To evaluate the effect of the change in the complex structure and composition on the extraction, co-extraction experiments of other individual Ln\textsuperscript{III} together with Nd\textsuperscript{III} have also been performed and monitored by UV-Vis absorption.

Results and Discussion

EXAFS of the complexes of HA with representative Ln\textsuperscript{III} prepared by extraction method (Figure 1) shows that in the first coordination shell of Pr\textsuperscript{III}, Nd\textsuperscript{III}, and Sm\textsuperscript{III}, there are some oxygen donors existing besides the dominant sulfur donors. The distance between the Ln\textsuperscript{III} center and the sulfur donors and the relative amount of phosphorous atoms in the second coordination shell (P shell) indicate that the ligands directly bond to Pr\textsuperscript{III}, Nd\textsuperscript{III}, and Sm\textsuperscript{III} through two sulfur atoms as bidentate (Table 1). For Eu\textsuperscript{III} complex, however, the amount of oxygen atoms is much less in the first coordination shell of Eu\textsuperscript{III}, and it is comparable with the amount of the sulfur atoms. When the atomic number increases further, in the heavier lanthanides (Gd, Tb, Dy) complexes Ln\textsuperscript{III} ions are fully hydrated, and the fitting shows that there are only oxygen donors but no sulfur atom existing in the first coordination shell of these Ln\textsuperscript{III}.

The results from nonlinear least-squares fitting of the L\textsubscript{3}-edge EXAFS data are summarized in Table 1. Even though the uncertainty of the coordination numbers (O, S or P) for some complexes is a little high, the trend of the increasing coordination number of O (from water) and the decreasing coordination number of S (from HA) from light to heavy Ln\textsuperscript{III} is crystal clear.

To further confirm the change of the extracted complexes in structure and composition along with the series, the absorption/fluorescence spectra of some Ln\textsuperscript{III} extracted complexes were collected in comparison with the spectra of those Ln\textsuperscript{III} ions in aqueous solutions (Figure 2). The apparent changes of the absorption/fluorescence spectra of Pr\textsuperscript{III}, Nd\textsuperscript{III}, and Sm\textsuperscript{III} indicate the coordination environments of these ions in the extracted complexes are quite different from those in aqueous solutions. By contrast, the spectra of the Tb\textsuperscript{III}, Dy\textsuperscript{III}, Ho\textsuperscript{III}, Er\textsuperscript{III}, and Tm\textsuperscript{III} extracted complexes in the organic phase are almost identical to the corresponding spectra of the aqua Ln\textsuperscript{III} ions, suggesting for these ions the extraction by HA does not change the coordination environment of the aqua ions very much. These results are consistent with the observation in the EXAFS study.

As mentioned above, there are some controversies over the structure and composition of some light Ln\textsuperscript{III} complexes in previous studies.\textsuperscript{18c,d,20} The most obvious argument is about the existence of water molecules in the first coordination shell of Ln\textsuperscript{III} (i.e. hydration number) in the extracted complexes, which may be caused by two reasons. First, the samples were prepared under different conditions. For example, for the neutral bidentate complexes LnA\textsubscript{2} reported by Jensen et al.,\textsuperscript{20} the samples were prepared with low metal loading (the ratio of Ln\textsuperscript{III} to total HA in the organic phase, [Ln\textsubscript{o}]\textsubscript{o}/[HA\textsubscript{o}]\textsubscript{o} = 1/100), while in our previous studies the metal loading varies, some of the corresponding samples were prepared with very high metal loading ([Ln\textsubscript{o}]\textsubscript{o}/[HA\textsubscript{o}]\textsubscript{o} = 1/5), and the solvent in the samples was removed by nitrogen gas blowing before EXAFS data collection. It is possible that different species might be formed under different experiment conditions.\textsuperscript{18} Second, in our previous works, even though it was found that the hydration number does vary with Ln\textsuperscript{III} ions by the fluorescence lifetime measurement of the samples with very low metal loading, no other techniques were employed to confirm the complex speciation which might be dramatically changed by the very small amount impurity in the ligand as the metal loading is very low. In this work, the samples were prepared with high metal loading under same conditions and the samples were studied as prepared.
Figure 2. The absorption/fluorescence spectra of selected Ln$^{III}$ in the extracted complexes prepared by the extraction of 30% neutralized 0.5 M HA and 0.087 M Ln$^{III}$ with phase ratio of 1/1.15. For clarity, the fluorescence spectra were normalized to the highest intensity of the correlated spectra.
Based on the EXAFS measurement and the results of spectroscopy study, we may speculate that for those light LnIII ions the extracted complexes might exist as small neutral molecules dissolved in the non-polar solvent. Then here rises an interesting question about the form of the fully hydrated heavy LnIII extracted in the organic phase. If the A' anions are closely associated with the fully hydrated LnIII through hydrogen bonding between negative charged sulfur atoms of A' and those water molecules in the first coordination shell, those extracted heavy LnIII ions might exist in small molecules too. However, it might be in a completely different case. The organic phase loaded with those heavy LnIII ion might be similar as the organic phase neutralized by NaOH, there are organized assemblies formed like reverse micelles in which the hydrated LnIII ions and the extracted water molecules form the aqueous phase core surrounded by head-in ligand anions. These will be further investigated separately.

To evaluate the effect of the change in complex structure and composition on the extraction of LnIII ions with HA, the co-extraction of individual LnIII ions with NdIII were carried out to compare with that of NdIII by monitoring the absorption of NdIII in UV-Vis region. Each initial aqueous solution contains an individual LnIII and NdIII of same concentration (0.05 M LnIII and 0.05 M NdIII). After the extraction with the same volume of 0.5 M HA, for 30 min, the absorption spectra of the NdIII complexes co-extracted with other LnIII in the organic phase were shown in Figure 4. There is only one isobestic point for each absorption band at 590 nm, 750 nm, and 810 nm, indicating that two NdIII complex species are formed in the organic phase. The sharp peak at 590 nm decreases briefly with the increases of the atomic number of the co-extracted LnIII till EuIII. The intensity of the 590 nm band is particularly sensitive to the presence of softer, more covalent donor atoms, and it generally increases with the metal-ligand bond of more covalent character. The change in Figure 4 upper part indicates that the coordination number of O and S in the two NdIII species is different, and the percentage of the species with a higher O coordination number (less covalent character in the NdIII complex) increases with the atomic number of the co-extracted LnIII ions. It is consistent with the results of EXAFS. From Pr to Eu, the hydration number of the LnIII complexes increases, meaning more water was carried into the organic phase as the atomic number of LnIII increases (Ln = Ce-Eu) in the experiment of co-extraction. More water in the organic phase results in an increasing percentage of the NdIII species with a higher O coordination number. However, from Gd to Lu, all the extracted LnIII ions in the organic phase were fully hydrated, and the amount of the carried-on water was almost same for all the heavier LnIII ions (Ln = Gd-Lu), so the speciation of co-extracted NdIII does not change much. This is well illustrated by the

![Figure 3](315x392 to 548x556)

**Figure 3.** Distribution ratio of LnIII ions in comparison with NdIII and the separation factor for NdIII over other LnIII. The parameters for preparing the samples: organic phase: 0.50 M HA, 30% neutralized, aqueous phase: 0.087 M LnIII, Vorganic/Vaqueous = 1:1.15.

The absorption spectra of the NdIII complexes co-extracted with other LnIII in the organic phase are shown in Figure 4. There is only one isobestic point for each absorption band at 590 nm, 750 nm, and 810 nm, indicating that two NdIII complex species are formed in the organic phase. The sharp peak at 590 nm decreases briefly with the increases of the atomic number of the co-extracted LnIII till EuIII. The intensity of the 590 nm band is particularly sensitive to the presence of softer, more covalent donor atoms, and it generally increases with the metal-ligand bond of more covalent character. The change in Figure 4 upper part indicates that the coordination number of O and S in the two NdIII species is different, and the percentage of the species with a higher O coordination number (less covalent character in the NdIII complex) increases with the atomic number of the co-extracted LnIII ions. It is consistent with the results of EXAFS. From Pr to Eu, the hydration number of the LnIII complexes increases, meaning more water was carried into the organic phase as the atomic number of LnIII increases (Ln = Ce-Eu) in the experiment of co-extraction. More water in the organic phase results in an increasing percentage of the NdIII species with a higher O coordination number. However, from Gd to Lu, all the extracted LnIII ions in the organic phase were fully hydrated, and the amount of the carried-on water was almost same for all the heavier LnIII ions (Ln = Gd-Lu), so the speciation of co-extracted NdIII does not change much. This is well illustrated by the

<table>
<thead>
<tr>
<th>Ln</th>
<th>O Shell</th>
<th>S Shell</th>
<th>P Shell</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CN</td>
<td>R₀/Å</td>
<td>ΔE₀/eV</td>
</tr>
<tr>
<td>Pr</td>
<td>1.6(3)</td>
<td>2.56(6)</td>
<td>1.9f</td>
</tr>
<tr>
<td>Nd</td>
<td>1(1)</td>
<td>2.53(5)</td>
<td>1.9f</td>
</tr>
<tr>
<td>Sm</td>
<td>2.5(9)</td>
<td>2.47(4)</td>
<td>1.9f</td>
</tr>
<tr>
<td>Eu</td>
<td>4.6(5)</td>
<td>2.45(1)</td>
<td>1.9f</td>
</tr>
<tr>
<td>Gd</td>
<td>8.5(5)</td>
<td>2.41(1)</td>
<td>2.2(6)</td>
</tr>
<tr>
<td>Tb</td>
<td>8.1(9)</td>
<td>2.40(1)</td>
<td>1.7(9)</td>
</tr>
<tr>
<td>Dy</td>
<td>8.3(7)</td>
<td>2.38(1)</td>
<td>1.8(8)</td>
</tr>
</tbody>
</table>

*The amplitude reduction factor S₀f was held constant at 1; f - fixed.
ignorable variation in the spectra of Nd\textsuperscript{III} co-extracted with Gd\textsuperscript{III} through Lu\textsuperscript{III}. Besides, La\textsuperscript{III} is an exception. $D_{\text{ex}}$ is between $D_{\text{Nd}}$ and $D_{\text{La}}$, and the corresponding spectrum is also plotted between the spectra from the co-extraction organic phase solutions of Nd\textsuperscript{III}-Nd\textsuperscript{III} and Sm\textsuperscript{III}-Nd\textsuperscript{III}.

The Ln\textsuperscript{III} with less hydration number in the extracted complexes with HA is extracted preferentially, indicating that the extraction behavior of Ln\textsuperscript{III} by HA is obviously associated with the structure of the complexes, especially the hydration number. In previous study it has been reported that water is not present in the An\textsuperscript{III} complexes with HA (both high and low metal loading), therefore, the difference in the complex structure would be one of the reason for the selectivity of An\textsuperscript{III} over Ln\textsuperscript{III} by HA.\textsuperscript{18}

It also should be pointed out the ‘Gadolinium Break’ is clearly present in the Ln\textsuperscript{III} complexes structure and the extraction of Ln\textsuperscript{III} with HA, which also observed in the complexation/extraction of Ln\textsuperscript{III} with other ligands/extractants.\textsuperscript{2,4}

The aqueous phase of 0.10 M Ln\textsuperscript{III} solution was prepared by dissolving Ln(NO\textsubscript{3})\textsubscript{3}·nH\textsubscript{2}O in H\textsubscript{2}O and the concentration of Ln\textsuperscript{III} was determined by titrations with EDTA standard solutions. For all the Ln\textsuperscript{III} solution, the pH was adjusted to about 3.5 using NaOH and HNO\textsubscript{3} solutions.

Sample preparation

For EXAFS, 3.0 mL of 0.50 M HA in toluene was neutralized by 30% with 1.0 M NaOH solution, and then contacted with 3.0 mL of 0.10 M Ln\textsuperscript{III} solution for 8 hrs at 25°C. For co-extraction experiments, the samples were prepared by following the same procedure except for using a mixture of 1.50 mL of 0.10 M Nd\textsuperscript{III} and 1.50 mL of 0.10 M other Ln\textsuperscript{III} solution instead. After extraction, phase separation was enforced by centrifugation.

Concentration measurement

The concentrations of Nd\textsuperscript{III} and Ln\textsuperscript{III} + Nd\textsuperscript{III} in aqueous solutions were determined with spectrophotometric method and EDTA standard titrations, respectively, and the concentration of Ln\textsuperscript{III} was deduced from subtracting the concentration of Nd\textsuperscript{III} from the concentration of Nd\textsuperscript{III} + Ln\textsuperscript{III}. The concentration of Nd\textsuperscript{III} and Ln\textsuperscript{III} in organic phase was determined after the metal ions were stripped off from the organic phase into aqueous solution with 1.0 M HNO\textsubscript{3}.

Spectroscopy

The absorption spectra were collected on Lambda 800 spectrophotometer, and the fluorescence spectra were acquired on a FluoroMax-4P fluorometer at 25°C at Tsinghua University.

Because some absorption bands of other Ln\textsuperscript{III} ions overlap with those of Nd\textsuperscript{III}, the standard spectra of these Ln\textsuperscript{III} ions in the extracted complexes were collected at first so that corrections could be made to account for the absorption of other co-extracted Ln\textsuperscript{III} ions. A separate set of samples of Ln\textsuperscript{III} ion complexes with HA in the organic phase were prepared under similar conditions of the co-extraction experiment, and the spectra were collected accordingly.

EXAFS measurement

Organic phases containing Ln\textsuperscript{III} complex were loaded in 0.5-1.0 mm thick aluminum holders with a rectangular opening of 20 mm × 2 mm sealed with two Kapton film windows. The $L_3$-edge EXAFS spectra of Nd, Sm, and Tb were collected on beam line 4-3 at the Stanford Synchrotron Radiation Laboratory (SSRL), and the spectra of Pr, Eu, Gd and Dy were collected on beam line 1W1B at Beijing Synchrotron Radiation Facility (BSRF). All data were collected in fluorescence mode with a Lytle detector at room temperature. Three or four scans were performed and averaged for each sample. The EXAFS data were analyzed with the program WinXAS,\textsuperscript{21} using parameterized phase and amplitude functions generated by FEFF8.\textsuperscript{22}

Conclusions

In summary, different from most of other extractants/ligands, the complex structure of Ln\textsuperscript{III} with HA varies across the series from light to heavy, and the light Ln\textsuperscript{III} is extracted preferentially by HA. The unusual complexation/extraction of Ln\textsuperscript{III} with HA furnishes a striking piece of experimental evidence for the participation to
bonding of the 4f orbitals in the light Ln^{III} ions. Moreover, the Ln^{III}/An^{III} complexes provide a perfect subject for the computational study on Ln^{III}/An^{III} complexation. The system of Ln^{III}/An^{III} complexes with HA has been computationally investigated with efforts.\(^\text{23-27}\) However, without solid guidelines from illustrative experimental studies, water molecules as one of the most important roles in the system have been ignored, and the results therein cannot well help imaging the complexes and understanding the origin of the excellent selectivity for An^{III} over An^{III} with purified commercial product Cyanex301. We anticipate our observation to be a starting point for precise investigation of the 4f5f orbital participating to bond by both experimental and computational methods.

**ACKNOWLEDGMENT**

This work was supported mainly by the project XDA 3010402 under “Strategy Priority Research Program” of the Chinese Academy of Science. Preparation of the samples of Nd, Sm, and Tb for EXAFS studies was performed at Lawrence Berkeley National Laboratory (LBNL) and supported by the Director, Office of Science, Office of Basic Energy Science of the U.S. Department of Energy (DOE), under Contract No. DOE-AC02-05CH11231 at LBNL. EXAFS data of Nd, Sm, and Tb were collected at Stanford Synchrotron Radiation Laboratory (SSRL), operated for the Office of Science, U.S. DOE by Stanford University, while the EXAFS data of Pr, Eu, Gd and Dy were collected at Beijing Synchrotron Radiation Facility (BSRF). X. H. acknowledges the partial financial support from LBNL for his one-year visit to LBNL.

**Notes and references**

Dialkyldithiophosphinate forms different extracted Ln(III) complexes across the lanthanide series not following the trend of lanthanide contraction.