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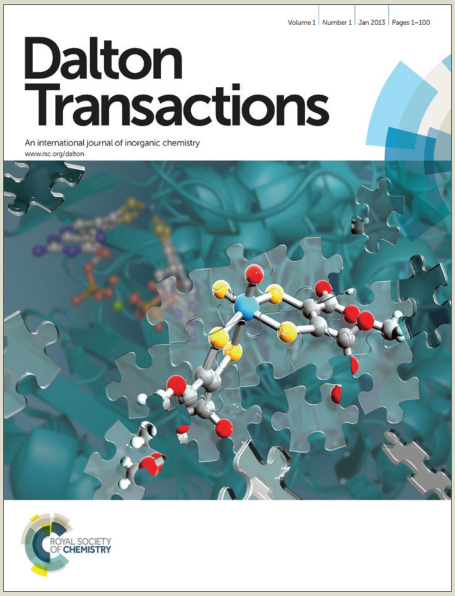

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ARTICLE TYPE

Characterization of the Extracted Complexes of Trivalent Lanthanides with Purified Cyanex 301 in Comparison with Trivalent Actinide Complexes

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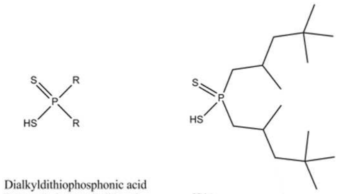
The extracted complexes of trivalent lanthanides (Ln^{III}) with purified Cyanex 301 (bis(2,4,4-trimethylpentyl)dithiophosphinic acid, denoted as H**A**) were investigated by extended X-ray absorption fine structure spectroscopy (EXAFS), UV-Vis and fluorescence spectroscopy. In the complexes prepared under the same conditions of solvent extraction, the light Ln^{III} ions are mainly coordinated by the sulfur atoms of the ligands, and the middle Ln^{III} ions are coordinated by mixed donors, the sulfur atoms of the ligands and the oxygen atoms of extracted water, while the heavy Ln^{III} 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 Ln^{III}, and simultaneously the ligand anions become counterions just for balancing the positive charge of the fully hydrated heavy Ln^{III} ions. The effect of the change in the complex structures on the extraction of Ln^{III} ions with H**A** was evaluated by the co-extraction of other thirteen individual Ln^{III} together with Nd^{III}. In contrast to most ligands bonding more strongly to heavier Ln^{III}, H**A** preferentially extracts lighter Ln^{III}, suggesting the unusual extraction capability of H**A** for Ln^{III} might originate from the difference in the complex structures with Ln^{III} 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 (Ln^{III}) are similar in spite of the number of the 4f electrons increasing from 0 for La^{III} to 14 for Lu^{III}. Indeed, except for a few ligands bearing soft donors such as N and S,[1-4] for most ligands there is often only an isostructural series of Ln^{III} complexes observed,[5-10] and the trend of the stability for Ln^{III} complexes in solution is mainly governed by the charge density of the metal ions.[11-17] For example, the stability constant for the formation of ethylenediaminetetraacetic acid (EDTA) complexes increases from $10^{15.5}$ for $[\text{La(EDTA)}]^-$ to $10^{19.8}$ for $[\text{Lu(EDTA)}]^-$ with an average stepwise increasing factor of about 2.06 across the Ln^{III} series. Using di-(2-ethylhexyl)phosphoric acid (HDEHP) as extractant, the extraction equilibrium constant for Lu^{III} is about 10^5 times higher than that for La^{III}.[14] Besides the trivalent cations in the lanthanide series, the An^{III} ions are also similar as Ln^{III} in chemical properties because of the same charge, similar size and valence electron configuration. For instance, the formation constants of $10^{16.4}$ for $[\text{Am(EDTA)}]^-$ is very close to the value of $10^{16.23}$ for $[\text{Eu(EDTA)}]^-$ as the ionic radii of Am^{III} is comparable to that of Eu^{III}.[11,15-17]

Due to the very similar chemical properties of Ln^{III} and An^{III} of similar ionic size, even the separation of light lanthanides from heavy lanthanides is relatively easy to be achieved, the separation of An^{III} from Ln^{III} 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.



Dialkyldithiophosphonic acid
R = n-octyl, 1-methylheptyl,
2-ethylhexyl

HA:
Bis(2,4,4-trimethyl)dithiophosphonic acid

In our previous work on the separation of An^{III} from Ln^{III}, we found that dialkyldithiophosphinic acids have excellent selectivity for Am^{III} and Cm^{III} over light Ln^{III}, and the selectivity originates from the difference in structure and composition between the An^{III} and Ln^{III} complexes.[18] Solvent extraction separation processes based on the dialkyldithiophosphinic acid extractants might be used to solve the very challenging task of An^{III}/Ln^{III} separation for the advanced nuclear energy system.[19] However, even though the overall selectivity of H**A** for An^{III} over light Ln^{III} is outstanding, the values of 3500, 1000, 1900, and 4500, respectively for the separation factors $SF_{Am/La}$, $SF_{Am/Ce,Pr}$, $SF_{Am/Nd}$, and $SF_{Am/Sm}$, do not well fall in the trend of the ionic radii of these Ln^{III} ions.[18b]

To help understanding the separation mechanism, the complex structure of Ln^{III} with H**A** has been compared with that of An^{III}. Neutral bidentate complexes Ln**A**$_3$ and An**A**$_3$ were reported with no discernible water molecules in the first coordination shell of the Ln^{III} at very low loading conditions in a study using UV-Vis absorption spectroscopy and EXAFS.[20] However, our previous studies with EXAFS, IR, MS, TRLFS on samples of varying metal loading suggested that the molecular formula of the Ln^{III} complexes that formed at high metal loading might be Ln**A**$_3$•2H$_2$O or HLn**A**$_4$•H$_2$O and the water molecules should coordinate to the light Ln^{III}. These controversies over the structures and composition of Ln^{III} complexes remain to be verified. Further, only few Ln^{III} samples were prepared in those studies and the structure of the complexes for different Ln^{III} were considered to be isostructural or similar, even though it was found that the hydration number might vary with different Ln^{III} ions in the complexes.

In this work, we revisit the extracted Ln^{III} complexes with H**A** and focus on the change in structure of the extracted complexes across the lanthanide series. The results show that the extracted Ln^{III} complexes change along with the Ln^{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^{III} together with Nd^{III} have also been performed and monitored by UV-Vis absorption.

Results and Discussion

EXAFS of the complexes of H**A** with representative Ln^{III} prepared by extraction method (**Figure 1**) shows that in the first coordination shell of Pr^{III}, Nd^{III}, and Sm^{III}, there are some oxygen donors existing besides the dominant sulfur donors. The distance between the Ln^{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^{III}, Nd^{III}, and Sm^{III} through two sulfur atoms as bidentate (**Table 1**). For Eu^{III} complex, however, the amount of oxygen atoms is much less in the first coordination shell of Eu^{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^{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^{III}.

The results from nonlinear least-squares fitting of the L_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 H**A**) from light to heavy Ln^{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^{III} extracted complexes were collected in comparison with the spectra of those Ln^{III} ions in aqueous solutions (**Figure 2**). The apparent changes of the absorption/fluorescence spectra of Pr^{III}, Nd^{III}, and Sm^{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^{III}, Dy^{III}, Ho^{III}, Er^{III}, and Tm^{III} extracted complexes in the organic phase are almost identical to the corresponding spectra of the aqua Ln^{III} ions, suggesting for these ions the extraction by H**A** does not change the coordination environment of the aqua ions very much. These results are consistent with the observation in the EXAFS study.

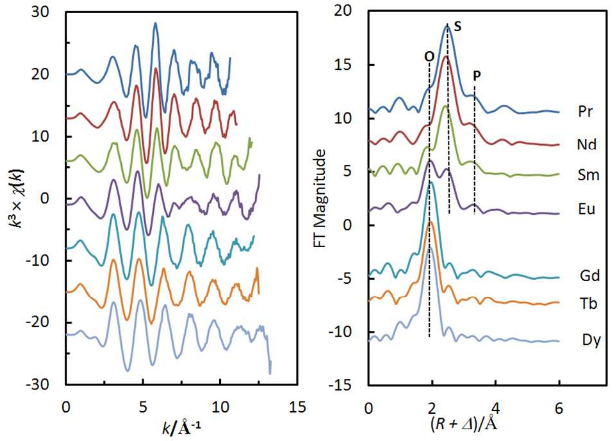


Figure 1. The L_3-edge EXAFS of the extracted Ln^{III} complexes with **HA** and the magnitude of the Fourier Transformations.

As mentioned above, there are some controversies over the structure and composition of some light Ln^{III} complexes in previous studies.[18c,d,20] The most obvious argument is about the existence of water molecules in the first coordination shell of Ln^{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 Ln**A**$_3$ reported by Jensen et al,[20] the samples were prepared with low metal loading (the ratio of Ln^{III} to total HA in the organic phase, $[\text{Ln}]_o/[\text{HA}]_o = 1/100$), while in our previous studies the metal loading varies, some of the corresponding samples were prepared with very high metal loading ($[\text{Ln}]_o/[\text{HA}]_o = 1/5$), 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.[18] Second, in our previous works, even though it was found that the hydration number does vary with Ln^{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.

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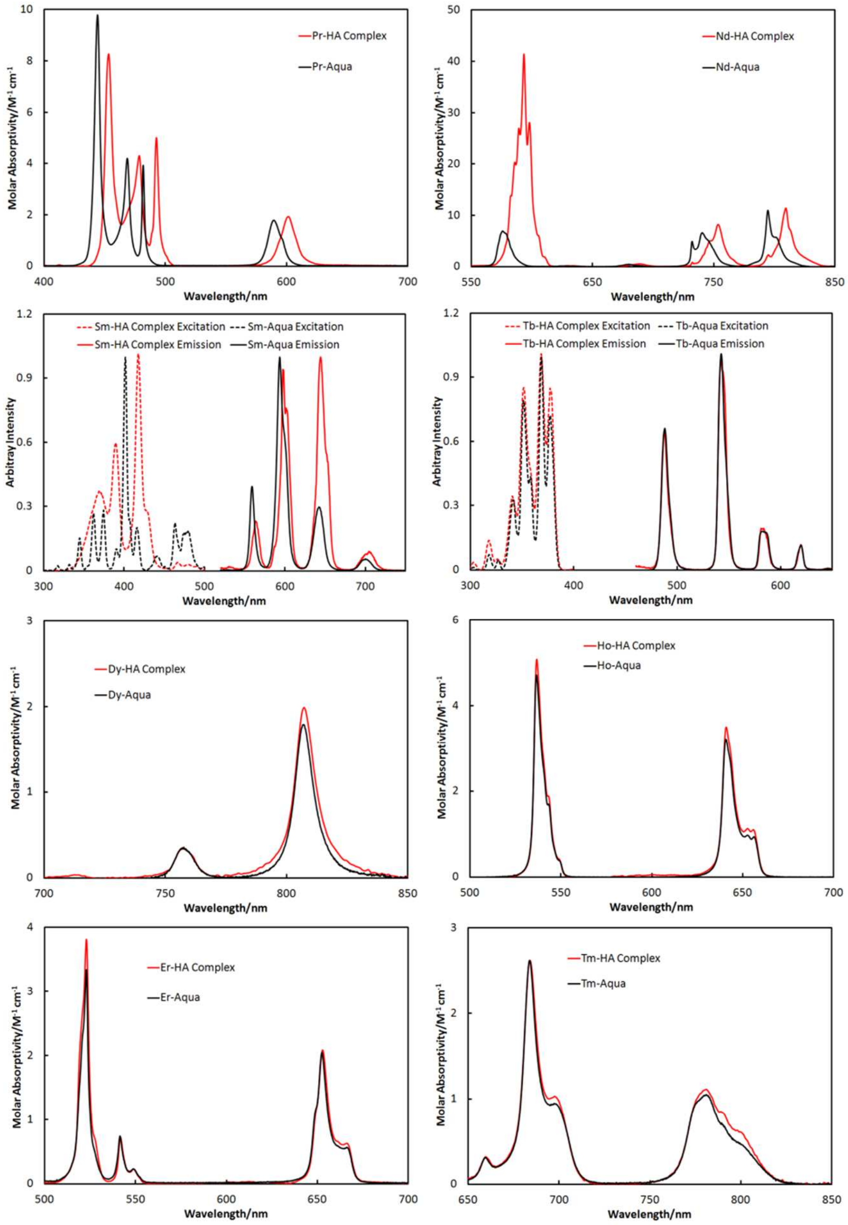

Figure 2. The absorption/fluorescence spectra of selected Ln^{III} in the extracted complexes prepared by the extraction of 30% neutralized 0.5 M H**A** and 0.087 M Ln^{III} with phase ratio of 1/1.15. For clarity, the fluorescence spectra were normalized to the highest intensity of the correlated spectra.

Table 1 EXAFS fitting parameters for the extracted lanthanide species*

Ln	O Shell				S Shell				P Shell			
	CN	R_O/Å	ΔE_0/eV	σ^2/Å^2	CN	R_S/Å	ΔE_0/eV	σ^2/Å^2	CN	R_P/Å	ΔE_0/eV	σ^2/Å^2
Pr	1.6(8)	2.56(6)	1.9^f	0.008^f	7.3(6)	2.93(3)	4(3)	0.009^f	4(2)	3.56(5)	7(4)	0.013(6)
Nd	1(1)	2.53(5)	1.9^f	0.008^f	7.(1)	2.90(1)	2(1)	0.009(2)	4(2)	3.54(3)	6(2)	0.010(3)
Sm	2.5(9)	2.47(4)	1.9^f	0.008^f	7(2)	2.88(3)	2(2)	0.007(5)	3(2)	3.51(6)	4(6)	0.004(8)
Eu	4.6(5)	2.45(1)	1.9^f	0.008^f	4(1)	2.87(2)	2(2)	0.011(3)	2(1)	3.61(5)	7(5)	0.009(7)
Gd	8.5(5)	2.41(1)	2.2(6)	0.008(1)								
Tb	8.1(9)	2.40(1)	1.7(9)	0.009(1)								
Dy	8.3(7)	2.38(1)	1.8(8)	0.008(1)								

*The amplitude reduction factor S_0^2 was held constant at 1; f - fixed.

Based on the EXAFS measurement and the results of spectroscopy study, we may speculate that for those light Ln^{III} 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 Ln^{III} extracted in the organic phase. If the **A**$^-$ anions are closely associated with the fully hydrated Ln^{III} through hydrogen bonding between negative charged sulfur atoms of **A**$^-$ and those water molecules in the first coordination shell, those extracted heave Ln^{III} ions might exist in small molecules too. However, it might be in a completely different case. The organic phase loaded with those heavy Ln^{III} ion might be similar as the organic phase neutralized by NaOH, there are organized assemblies formed like reverse micelles in which the hydrated Ln^{III} 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 Ln^{III} ions with H**A**, the co-extraction of individual Ln^{III} ions with Nd^{III} were carried out to compare with that of Nd^{III} by monitoring the absorption of Nd^{III} in UV-Vis region. Each initial aqueous solution contains an individual Ln^{III} and Nd^{III} of same concentration (0.05 M Ln^{III} and 0.05 M Nd^{III}). After the extraction with the same volume of 0.5 M H**A** in toluene neutralized by 30% with 1.0 M NaOH during the extraction, the absorption spectra of the organic phase were collected, and the distribution ratios of Ln^{III}, Nd^{III} and Ln^{III} + Nd^{III} (D_{Ln}, D_{Nd}, and D_{Ln+Nd}) were determined (**Figure 3**). The definition of the distribution ratio D for a ion is the ratio between the concentrations of the ion in the equilibrated organic and aqueous phases, D_{Ln} = $[Ln]_o/[Ln]_a$. In general, D_{Ln+Nd} slightly decreases while the corresponding D_{Ln} decreases noticeably at first and reaches the bottom at Gd, then increases unambiguously through the rest of the heavy lanthanide series. This result presents an unusual trend of extraction of Ln^{III}, which contrasts with the effect of lanthanide contraction on the formation of complexes with most ligands (**Figure 3**). Another interesting point is that across the complete Ln^{III} series the separation factor ($SF_{La/Ln}$ = D_{La}/D_{Ln}) changes less than three times. Usually the separation factor for a pair of adjacent Ln^{III} ions might just be less than 10, but across the whole Ln^{III} series, it ($SF_{La/Lu}$) might change several orders of magnitude due to the lanthanide contration.[14]

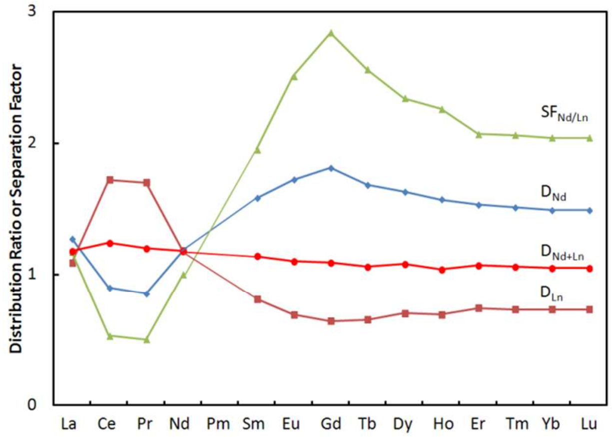

Figure 3. Distribution ratio of Ln^{III} ions in comparison with Nd^{III} and the separation factor for Nd^{III} over other Ln^{III}. The parameters for preparing the samples: organic phase: 0.50 M HA, 30% neutralized, aqueous phase: 0.0.087M Ln^{III}, V_o/V_a=1:1.15.

The absorption spectra of the Nd^{III} complexes co-extracted with other Ln^{III} 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 Nd^{III} 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 Ln^{III} till Eu^{III}. 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 Nd^{III} species is different, and the percentage of the species with a higher O coordination number (less covalent character in the Nd^{III} complex) increases with the atomic number of the co-extracted Ln^{III} ions. It is consistent with the results of EXAFS. From Pr to Eu, the hydration number of the Ln^{III} complexes increases, meaning more water was carried into the organic phase as the atomic number of Ln^{III} increases (Ln = Ce-Eu) in the experiment of co-extraction. More water in the organic phase results in an increasing percentage of the Nd^{III} species with a higher O coordination number. However, from Gd to Lu, all the extracted Ln^{III} ions in the organic phase were fully hydrated, and the amount of the carried-on water was almost same for all the heavier Ln^{III} ions (Ln = Gd-Lu), so the speciation of co-extracted Nd^{III} does not change much. This is well illustrated by the ignorable variation in the spectra of Nd^{III} co-extracted with Gd^{III} through Lu^{III}. Besides, La^{III} is an exception. D_{La} is between D_{Nd} and D_{Sm} and the corresponding spectrum is also plotted between the spectra from the co-extraction organic phase solutions of Nd^{III}-Nd^{III} and Sm^{III}-Nd^{III}.

The Ln^{III} with less hydration number in the extracted complexes with **HA** is extracted preferentially, indicating that the extraction behavior of Ln^{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^{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^{III} over Ln^{III} by **HA**.[18]

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

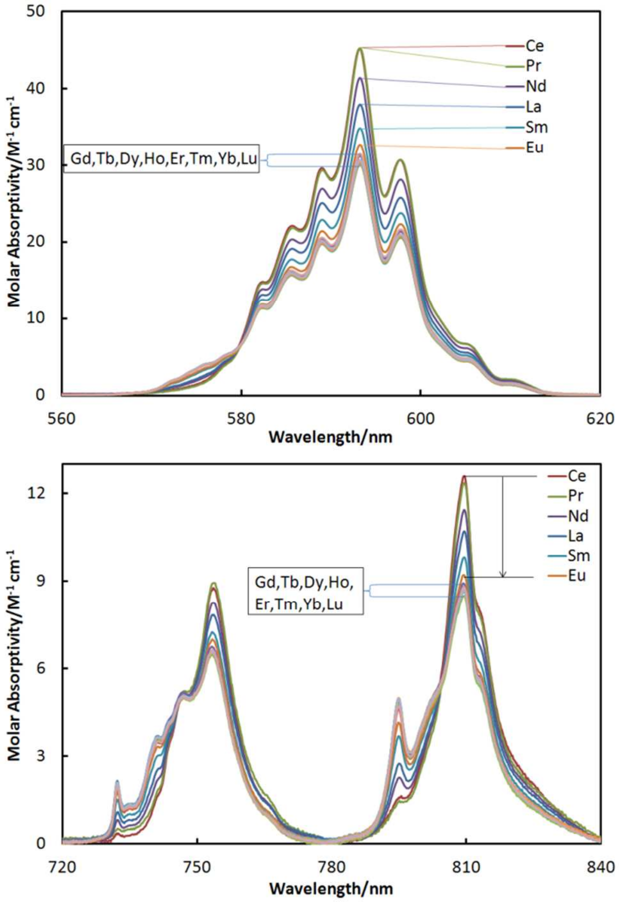

Figure 4. Normalized spectra of Nd^{III}-HA complexes co-extracted with other Ln^{III} ions in the organic phase. The parameters for preparing the samples: organic phase: 0.50 M HA, 30% neutralized, aqueous phase: 0.087 M Ln^{III}, V_o/V_a=1:1.15.

Experimental Section

Materials

Cyanex301 was kindly provided by Cytec Industries, which mainly consists of 80% bis(2,4,4-trimethylpentyl) - dithiophosphinic acid (H**A**), was purified as in ref 18a, other chemicals were AC-grade or higher. The organic phase of 0.50 M H**A** solution was prepared by dissolving purified H**A** in toluene. The aqueous phase of 0.10 M Ln^{III} solution was prepared by dissolving $Ln(NO_3)_3$•nH_2O in H_2O and the concentration of Ln^{III} was determined by titrations with EDTA standard solutions. For all the Ln^{III} solution, the pH was adjusted to about 3.5 using NaOH and HNO_3 solutions.

Sample preparation

For EXAFS, 3.0 mL of 0.50 M H**A** in toluene was neutralized by 30% with 1.0 M NaOH solution, and then contacted with 3.0 mL of 0.10 M Ln^{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^{III} and 1.50 mL of 0.10 M other Ln^{III} solution instead. After extraction, phase separation was enforced by centrifugation.

Concentration measurement

The concentrations of Nd^{III} and Ln^{III} + Nd^{III} in aqueous solutions were determined with spectrophotometric method and EDTA standard titrations, respectively, and the concentration of Ln^{III} was deduced from subtracting the concentration of Nd^{III} from the concentration of Nd^{III} + Ln^{III}. The concentration of Nd^{III} and Ln^{III} + Nd^{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_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^{III} ions overlap with those of Nd^{III}, the standard spectra of these Ln^{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^{III} ions. A separate set of samples of Ln^{III} ion complexes with H**A** 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^{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,[21] using parameterized phase and amplitude functions generated by FEFF8.[22]

Conclusions

In summary, different from most of other extractants/ligands, the complex structure of Ln^{III} with H**A** varies across the series from light to heavy, and the light Ln^{III} is extracted preferentially by H**A**. The unusual complexation/extraction of Ln^{III} with H**A** 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 H**A** has been computationally investigated with efforts.[23-27] However, without solid guideline 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 4f/5f orbital participating to bond by both experimental and computational methods.

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