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Investigation of the Extraction Complexes of Light Lanthanides(III) with Bis(2,4,4-trimethylpentyl)dithiophosphinic Acid by EXAFS, IR, and MS in Comparison with the Americium(III) Complex

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The structure of the extraction complexes of light lanthanides (La(III), Nd(III), Eu(III)) with bis(2,4,4-trimethylpentyl)-dithiophosphinic acid (HBTMPDTP) have been characterized with extended X-ray absorption fine structure spectroscopy (EXAFS), IR, and MS; the IR spectrum of the extraction complex of ^{241}Am with HBTMPDTP has been studied too. The molecular formula of the extraction complexes of lanthanides is deduced to be $HML_4 \cdot H_2O$ (M = La, Nd, Eu; L = anion of HBTMPDTP). The coordination number of Ln(III) in the complexes is 8; the coordinated donor atoms are 7 sulfur atoms from 4 HBTMDTP molecules and 1 O atom from a hydrated water molecule. With the increase of the atomic number of Ln, the coordination bond lengths of Ln–O and Ln–S decrease in the complexes. For La(III), Nd(III), and Eu(III), the coordination bond lengths of Ln–O are 2.70, 2.56, and 2.50, respectively, the coordination bond lengths of Ln–S are 3.01, 2.91, and 2.84, respectively, and the average distances between Ln and P atoms are 3.60, 3.53, and 3.46, respectively. The structure of the extraction complexes of Ln(III) with HBTMDTP is different from that of the Am(III) extraction complex. The results of IR show that there is no water coordinated with Am in the extraction complex. The molecular formula of the complex of Am(III) is deduced as being $HAmL_4$, and there are 8 S atoms from 4 HBTMPDTP molecules coordinated with Am. Composition and structure differences of the extraction complexes may be one of the most most important factors affecting the excellent selectivity of HBTMPDTP for Am(III) over Ln(III).

Introduction

The minor actinides (MA), Np, Am, and Cm, constitute the main long-term radioactive hazard of nuclear waste from nuclear power generation. One strategy for reducing the main long-term hazard of radioactive wastes is to separate MA from high-level liquid waste (HLLW) and transmute them into short-lived or stable nuclides by nuclear reactions in nuclear reactors or accelerator-driven transmutation systems.[1] In a transmutation fuel cycle, the separation of actinides from fission product lanthanides (Ln), which constitute nearly 30% of the mass of fission products, is necessary, because some lanthanides have a very high neutron absorption cross section, thus act as neutron poisons, absorbing neutrons and reducing the efficiency of the transmutation process. However, due to the almost identical chemical and physical properties of Am(III), Cm(III), and Ln(III), it is very difficult to separate Am(III) and Cm(III) from Ln(III). Many studies on their separation have been carried out and reviewed in detail.[2] It is well-known that the extractants containing so-called soft donor atoms (N and S) have a certain selectivity for An(III) over Ln(III).[3−6] This effect can be explained by a greater complex stability (metal−ligand covalent bonding) between the transplutonides(III) and the soft donor ligands. However, there are few structural studies on those extraction systems and little clear explanation on the selectivity for An(III) over Ln(III) published up to now. In 1995, Zhu[7,8] found that bis-

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Table 1. Structural Data for Eight Coordinate Tetrakis Complexes[10,a]

R	M	D_{M-S}/Å	D_{M-P}/Å	$D_{M-S} - D_{M-P}$/Å	$R_{M(III)}$/Å
Et	La(III)	2.981	3.578	0.60	1.16
EtO	La(III)	2.989	3.581	0.61	1.16
Me	Ce(III)	2.991	3.592	0.60	1.14
MeO	Ce(III)	2.969	3.560	0.59	1.14
Me	Pr(III)	2.976	3.589	0.61	1.13
PrO	Nd(III)	2.984	3.577	0.59	1.11
PrO	Ho(III)	2.865	3.478	0.61	1.02
Et	Er(III)	2.859	3.478	0.62	1.00
MeO	Er(III)	2.856	3.470	0.59	1.00
EtO	Er(III)	2.858	3.471	0.61	1.00
Me	Tm(III)	2.870	3.487	0.62	0.994

[a] R: substitutive group, alkyl or alkoxyl group. M: metal ion. D_{A-B}: distance from A to B. $R_{M(III)}$: the radii of the metal ion M(III).

(2,4,4-trimethylpentyl)dithiophosphinic acid (HBTMPDTP, purified Cyanex301) has excellent selectivity for Am(III) over Ln(III); the separation factor is over 5000. Further study shows that the structure of the alkyl group of dialkyldithiophosphinic acid has substantial effect on extraction power but has no strong effect on the selectivity for Am(III) over Ln(III).[9] To understand the origin of the differences in dialkyldithiophosphinic acid extraction process between An(III) and Ln(III), studying the structure of the extraction complexes is essential.

The complexes of Ln(III) with ligands where the donor atoms are sulfur are considered to be unstable, because the ions of f-block transition elements are hard acids and sulfur atoms are soft bases. Pinkerton[10] and co-workers have prepared and characterized a number of complexes in the crystalline state of the trivalent lanthanides with the sulfur donor chelating dithiophosphinate, $R_2PS_2^-$, and dithiophosphate, $(RO)_2PS_2^-$, ligands. These complexes of dithiophosphinate ligands (R = methyl, ethyl) and dithiophosphate (R = methyl, ethyl, propyl) ligands with Ln(III) are prepared under anhydrous conditions and are sensitive to humidity. Characterized by X-ray diffraction (XRD), these complexes are tetrakis anionic complexes $[Ln(S_2PR_2)_4]^-$, and the Ln(III) ions are surrounded by 8 sulfur atoms in an almost perfect D_{2d} dodecahedral configuration. Table 1 lists some bond lengths of these eight coordinated tetrakis complexes. The average coordination bond length of Ln−S in these eight coordinated tetrakis complexes decreases as the atomic number of Ln increases. A study on the preparation and characterization of the complexes of Ln(III) with $R_2PS_2^-$ from or in water solution has not been reported up to date. As a part of our ongoing studies on the separation of Am(III) from Ln(III) in water solution, we are making an effort to investigate the structure of the extraction complexes of Ln(III) and Am(III) with HBTMPDTP.

Besides X-ray diffraction (XRD),[10] techniques such as infrared spectroscopy (IR),[11] nuclear magnetic resonance (NMR),[12,13] and fluorescence spectroscopy[14,15] are the major tools for f-element compound structural investigation. In recent years, the application of synchrotron-based EXAFS is becoming the most important method to characterize lanthanide and actinide complexes, because extended X-ray absorption fine structure (EXAFS) can provide information on coordinating atoms, coordination numbers, and the distances of the chosen atoms to their nearest neighbors.[16] Recently a few papers have reported studies on the complexes of Np and transplutonium elements.[17−23] In earlier work, we have studied the structure of two extraction complexes of Am(III) with HBTMDTP and Am(III) with di-*n*-octyldithiophosphinic acid (HDODTP) using EXAFS. The EXAFS results indicate that the two extraction complexes have similar eight coordinate tetrakis structure which are analogous to the structure of the complexes of Ln(III) with sulfur bidentate ligands $R_2PS_2^-$ and $(RO)_2PS_2^-$ reported in refs 10 and 24. We report here an EXAFS, IR, and MS study on the structure of the extraction complexes of light Ln(III) with HBTMPDTP in comparison with the structure of the extraction complex of Am(III) to explain the excellent selectivity for Am(III) over Ln(III).

Experimental Section

(A) Solution and Sample Preparation. The sample preparations were operated at the Institute of Nuclear Energy Technology (INET), Tsinghua University, Beijing. Cyanex301 provided by Cytec Canada Inc., which mainly consists of ~80% bis(2,4,4-trimethylpentyl)dithiophosphinic acid, was purified as in ref 8. The

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organic solutions were prepared by dissolving weighed quantities of extractant in toluene. The nitrate solutions of La, Nd, and Eu were prepared by dissolving the oxides of La, Nd, and Eu into 2 M HNO_3, removing the excess HNO_3 under vacuum (about 20 mmHg) at 80 °C, and finally dissolving into 1 M $NaNO_3$. La_2O_3, Nd_2O_3, and Eu_2O_3 were provided by Yuelong Facility, Shanghai, China, with purity better than 99.99%. The radionuclide ^{241}Am as a nitrate solution was obtained from the Institute of Atomic Energy, Beijing.

The extraction complexes of Ln(III) were prepared by combining 5 mL of 0.3 M $Ln(NO_3)_3$ in 1 M $NaNO_3$ solution with 5 mL of 0.5 M HBTMPDTP in toluene saponified to about 25 mol % with 4 M NaOH or 25% ammonia before used. After centrifugation and phase separation, the organic phase was sampled to measure the mass spectrum on a PE MS 3000 mass spectrometer. For EXAFS measurement, after the solvent in the organic phase samples was removed under 10 mmHg below 60 °C, the very viscous residue was mixed with about 1 g of solid paraffin wax. In EXAFS collection, the mixture was put into a 20 mm × 10 mm × X mm ($X = 0.5-5$) polytetrafluorethylene cell with two Mylar film windows. For IR determination in transmission mode, the solvent in the organic phase (including the reference sample of free HBTMPDTP) was removed under vacuum about 10 mmHg at 60 °C. For IR determination in the ATR mode, four samples loading different amounts of Nd(III) were prepared with 0.5 M HBTMPDTP in toluene with different degrees of saponification, and the solvent was quickly vaporized on the ZnSe crystal before measurement. The concentrations of Ln(III) in the organic phase were determined with a Thermo Jerrell Ash Iris ICP-AES after Ln(III) was stripped and diluted with 0.5 M HNO_3.

To prepare the complex of Am(III), a portion of nitrate solution containing 15 mg of ^{241}Am was sampled into a test tube and was slowly evaporated to dryness to eliminate the excessive nitric acid at 80 °C; 1 mL of a 1 M $NaNO_3$ solution was added to dissolve the residue and combined with 1 mL of 0.5 M HBTMPDTP in toluene for 30 min at room temperature. The organic phase was saponified by about 40 mol % with 25% ammonia before used. After centrifugation and phase separation, 0.5 mL of organic phase was sampled and the solvent was removed under vacuum of about 20 mmHg at 60 °C to get the sample of Am(III) extraction complex for IR determination, and 0.05 mL of organic phase was sampled and diluted with toluene to determine the concentration of Am(III) as being 15 mg/mL (by α-counting using a Packard Tri-carb 2200CA liquid scintillation analyzer). The sample of Am(III) complex was spread about 2 mm × 2 mm on the center of a KBr crystal slice (i.d. 32 mm) with a glass stick and then was covered with another KBr crystal slice (i.d. 32 mm), and at last the two pieces of KBr crystals were sealed with Parafilm.

(B) IR Spectra. The FT-IR spectra of the extraction complexes were recorded on a Nicolet FT470 spectrometer. For all Ln(III) samples, the spectra were recorded in both modes of ZnSe-attenuated total reflection (ATR) and KBr transmission. The spectrum of the sample of Am(III) sealed in two pieces of KBr crystal was recorded in KBr transmission mode. IR spectra were obtained in the 4000−600 cm^{-1} (4000−400 cm^{-1}) region by collecting 32 scans at 2 cm^{-1} resolution. The empty ATR accessory was used as the reference in ZnSe-attenuated total reflection (ATR) mode, and one piece of KBr crystal was used as the reference in KBr transmission mode.

(C) MS Measurement. The mass spectra of all complexes of Ln(III) were recorded on a PE3000 MS. Before sample injection, the organic solutions of extraction complexes were diluted by $10^4\times$ with methanol. The MS measurement was recorded in both the negative and positive ion modes, and the selected region was from 200 to 5000 au.

(D) EXAFS Data Collection and Analysis. X-ray absorption spectra at the L_{III} edge were collected at the Beijing Synchrotron Radiation Laboratory on wiggler beam line 4W1B under dedicated ring conditions (2.2 GeV, 40−110 mA) using a Si(111) double-crystal monochromator. The higher order harmonic content of the beam was rejected with detuning the crystals in the monochromator by about 50% of its maximum at the scan ending energy. The vertical slit width was 0.5 mm, which reduces the effects of beam instabilities and monochromator glitches while providing photon flux. Spectra were collected in transmission mode using 75% N_2−25% Ar filled ionization chamber detectors. Energy calibration was carried out with using Cr foil (5994.6 eV) for the La and Nd edge and Fe foil (7131.3 eV) for the Eu edge. The path length of the cells was designed to be changeable so that the edge jump and the beam strength transmitted by the samples can achieve optimum values during data collection. Three EXAFS scans were collected on each sample at 295 K and averaged to improve the statistics.

EXAFS data reduction was performed by standard methods reviewed elsewhere using a suite of programs EXCURVE92.[25] A four-region spline function was used to fit the background over the EXAFS region which extended out to $k = 10.1$, 11.2, and 12.3 $Å^{-1}$ for La, Nd, and Eu, respectively. Fourier transforms of the k^3-weighted data were calculated over the different k ranges of the three Ln elements with a Gaussian window function of 0.2 $Å^{-1}$ half-width. Back-transforms were done from $R = 1.8$ to 3.8 Å using a Gaussian window function. Curve-fitting was done on this Fourier-filtered EXAFS data over the different k ranges of the three Ln elements. All fits included contributions from the first shell of directly coordinated O atoms from water ligands and sulfur atoms from the extractant and the second shell of phosphorus atoms from the extractant. For each fitting, the bond lengths (R), the coordinaton numbers (CN), and the Debye−Waller factor (σ) were allowed to vary (the coordination number of O was allowed to vary as an integer number).

Results and Discussion

In the initial extraction experiment using HTMPBTP to separate Am(III) from Ln(III), kerosene was used as solvent due to its good chemical and physical properties suitable for the nuclear industry.[7,8] However, our recent work indicated that the solubility of the complexes of Ln(III) with HTMPDTP in kerosene is not sufficient, and kerosene is not a good solvent in the structural investigation work. While the aqueous phase was 0.6 M $NaNO_3$ and the organic phase was 0.5 M HTMPDTP in kerosene, the maximum allowable degree of saponification with 4 M NaOH or 25% ammonia solution was about 14 mol % for organic phase without the third phase formation. Toluene is a good solvent, under the same conditions, and the degree of saponification can be up to 75 mol % without the third formation. The separation factors for Am(III) over Ln(III) and the extraction properties other than solubility of the extraction complexes are almost the same in kerosene as in toluene.[9] Therefore, in this work, toluene is used as solvent on the supposition that the structures of the extraction complexes of Ln(III) and Am(III) are the same in toluene as in kerosene. Another reason

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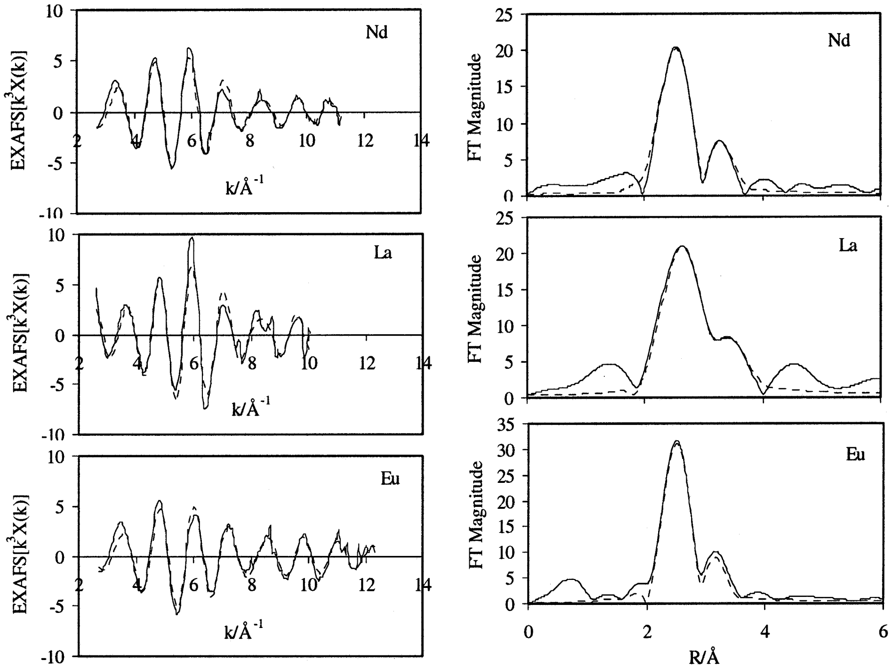

Figure 1. Background-subtracted k^3-weighted EXAFS spectra of the extraction complexes and comparison of the corresponding Fourier transforms of the experimental data (solid line) with those of the theoretical signal (dashed line).

Table 2. Summary of EXAFS Curve-Fitting Results[a]

	O shell			S shell			P shell		
compd	CN	R_O/Å	σ^2/Å^2	CN	R_S/Å	σ^2/Å^2	CN	R_P/Å	σ^2/Å^2
Am[20]				7.8	2.98	0.007	3.8	3.58	0.008
La	1.0	2.70	0.001	7.4	3.01	0.018	4.0	3.60	0.012
Nd	1.0	2.56	0.001	7.1	2.91	0.018	3.7	3.53	0.011
Eu	1.0	2.50	0.003	7.3	2.84	0.021	4.0	3.46	0.023

[a] σ^2: the Debye−Waller factor. Errors in distances (0.015 Å) and coordination numbers (±15%) are estimated from the deviation between fitting results from models of known strucure and their values.

for using toluene as solvent is that it is easy to remove toluene from the organic phase without decomposing the extractant and the extraction complexes.

(A) EXAFS. Figure 1 shows the L_{III}-edge EXAFS of La, Nd, and Eu in the complexes and corresponding Fourier transforms (FTs). The results of the curve-fittings are also shown in Figure 1. The three EXAFS plots indicate that the data quality is good, the noise is relatively low, and the oscillation signal is quite clear over the noise in all these spectra. The Fourier transforms reveal the relative positions and the numbers of the nearest neighbors around the central ion in the extraction complexes. The peaks are not corrected with the EXAFS phase shift, $\alpha = 0.2-0.5$ Å.

The EXAFS data for La only extend out to $k = 10.1$ Å^{-1} due to the onset of the L_{II} edge. This limits the attainable resolution for shells of identical near-neighbors ($\Delta R = \pi/2k_{max}$, where $\Delta R = R_2 - R_1$). The O−La bond length is about 2.5 Å, and the S−La bond length is about 2.7 Å. Therefore, in the FT the peak responding to O atoms in the first coordination shell is diminished and cannot been discerned, and the peak corresponding to P atoms in the second shell becomes a shoulder of the peak for S atoms in the first coordination shell. However, from refs 8 and 9 and the IR spectra (see below), it can be deduced that, in the extraction complexes of Ln, the coordination atoms should be O atoms from H_2O and S atoms from HBTMPDTP and no O atom from NO_3^-. In curve-fitting, O atoms were considered to be included in the model. In Table 2 the results of data fitting indicate that there is one O atom in the first coordination sphere of La(III).

For Eu(III) and Nd(III), the EXAFS data are enough to get a good resolution for shells of identical nearest neighbors. In the FTs, the peak corresponding to the O atom in the first coordination shell also is an indistinct shoulder of the peak for S atoms and cannot been discerned, but the peak corresponding to P atoms in the second shell can be clearly discerned. With the same reason as for the complex of La(III), in curve-fitting, O atoms had to be considered to be included in the model.

In Table 2, the results of data fitting indicate that there is one O atom in the first coordination sphere of Nd(III) or Eu(III) as well as La(III). For all the three extraction complexes, the coordination numbers of sulfur atoms and phosphorus atoms is close to 7 and 4, respectively. This means that there are three HBTMPDTP's as bidentate ligands and one as a monodentate ligand coordinated with Ln(III) in the extraction complexes. Because the error of coordination number from EXAFS is about 15%, so an S coordination

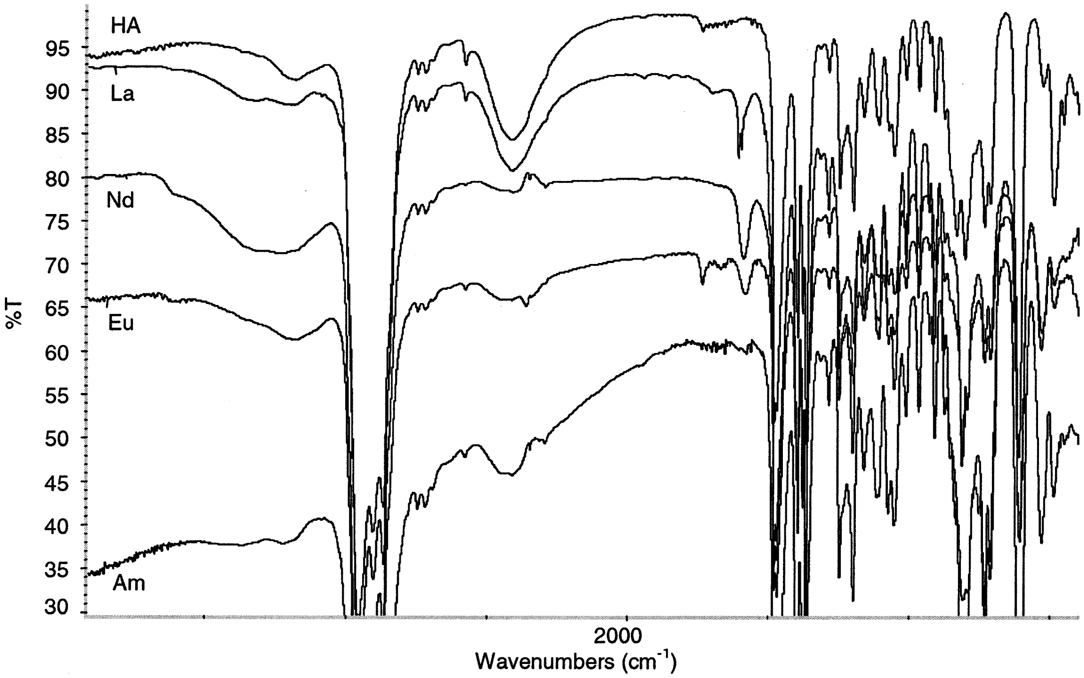

Figure 2. IR spectra of HBTMDTP and the extraction complexes.

number of 6 or 8 is also a reasonable result; i.e., there are three or four HBTMPDTP molecules as bidentate ligands around the metal ion. However, the results of an extraction experiment[8,9,24] and MS (see below) show that there are four HBTMPDTP molecules in the compexes, although the ligands being bidentate or monodentate cannot be determined. From the work of Pinkerton[10] and coordination chemistry intuition, four bidentate dithiophosphorus ligands (dtp) are too large to allow the formation of the Ln(III) complexes with nine coordinated atoms (eight S and one O). While one dtp in the complexes of $[Ln(S_2PR_2)_4]^-$ is a monodentate ligand, a more stable complex with seven coordinated S atoms (six from three dtps and one from the monodentate dtp) will form.[10] It can be concluded that there are one water molecule and four HBTMPDTP molecules coordinating to Ln(III) in the extraction complexes. The coordination number cannot be completely determined to be 8 and needs investigation with other techniques.

The distances between the Ln(III) and coordination shells decrease with the order of La, Nd, and Eu. These results are consistent with the order of the radii of Ln(III) $R_{La(III)} > R_{Nd(III)} > R_{Eu(III)}$. The difference between the distances of Ln−S and Ln−P is 0.59, 0.61, and 0.60 Å for La(III), Nd(III), and Eu(III), respectively, all of which are close to 0.60 Å.

From these results, some structural information of the extraction complexes could be deduced: the complexes are mononuclear complexes but not polynuclear complexes; the general molecular formula for the complexes is $HLnL_4 \cdot H_2O$, in which most probably three extractants are bidentate ligands and one is a monodentate ligand. This structure is different from the structure of the extraction complexes of Ln(III) with dialkylphosphoric acids such as bis(2-ethylhexyl)phosphoric acid (HDEHP). In the case of HDEHP, when the ratio of HDEHP/Ln(III) ≥ 6 and the extraction complex is a mononuclear complex, in the extraction complexes of Ln(III) with HDEHP there are 6 extractant molecules around Ln(III) and they are monodentate; when the ratio of HDEHP/Ln(III) < 6 and the extraction complex is a polynuclear complex, there are bridge coordination and the extractant molecules are bidentate. The EXAFS results of the extraction complexes of Ln(III) are also different from that of Am(III).[24] The CN's of S and P in the complex of Am(III) are 8 and 4, respectively. The Am−S and Am−P distances are 2.98 and 3.58 Å, respectively, comparing favorably to the Nd−S and Nd−P distances found in the solid structure of $[AsPh_4][Nd(S_2PR_2)_4]$, from which a dodecahedral geometry coordination of $[Nd(S_2PR_2)_4]^-$ and bidentate ligation of ligands were observed.[10,21]

(B) IR Spectra. In Figure 2 the IR spectra of the extraction complexes of three Ln(III) and Am(III) are compared to the spectrum of free HBTMPDTP. The spectra were collected in the mode of KBr transmission mode except for the La complex. The main region of interest is in the near- and middle-infrared field including the vibration band of H_2O. The difference is obvious between the spectra of the extraction complexes and free extractant. For the extraction complexes of three Ln(III) and Am(III), the relative strength of the stretching vibration absorption of of S−H at about 2500 cm^{-1} becomes small and new absorption peaks at about 3300 and 1604 cm^{-1} rise from the stretching vibration and scissors vibration of coordinated H_2O (the absorption of free H_2O is a band with several peaks at about 1730 cm^{-1}). Figure 3 shows the spectra in the range from 400 to 1700 cm^{-1}. For free HBTMPDTP, the interested peaks are the middle absorption at 488 cm^{-1} responding to ν_{P-SH}, the very strong absorption at 613 cm^{-1} responding to $\nu_{P=S}$, and the strong absorption at 795 and 813 cm^{-1} responding to $\delta_{S=P-SH}$. For

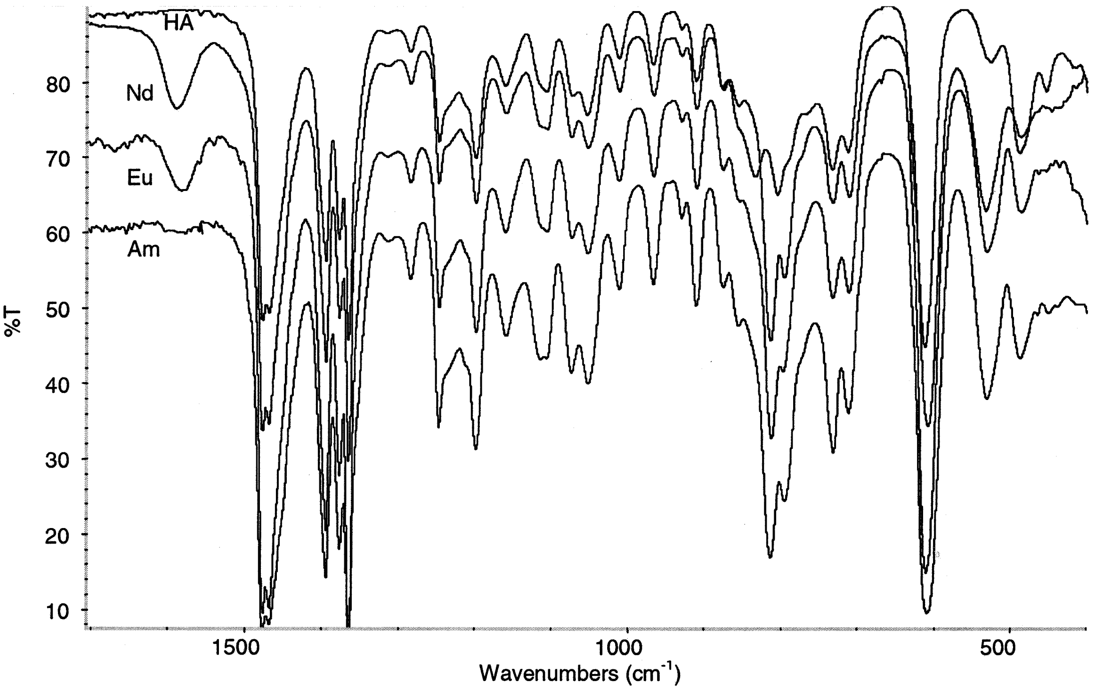

Figure 3. Extended IR spectra of HBTMDTP and the extraction complexes in range from 400 to 1700 cm^{-1}.

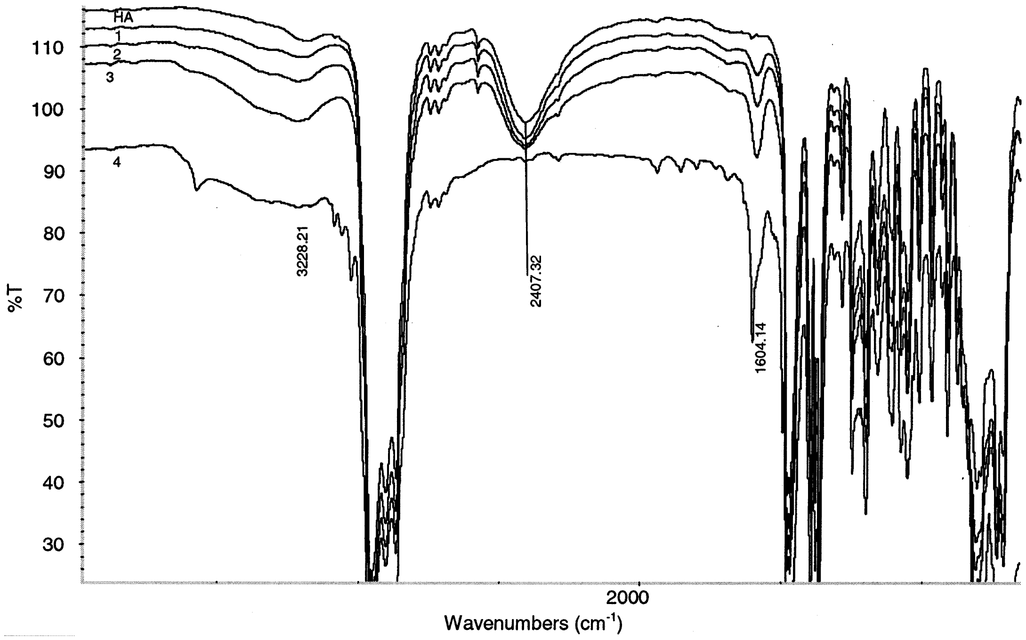

Figure 4. IR spectra of the organic phases loaded with different amounts of Nd(III). Curves 1−4 correspond to the concentrations of Nd(III) in the organic phase of 3.34, 5.70, 9.33, and 16.49 g/L, respectively.

the extraction complexes of Am(III) and Ln(III), due to the formation of the coordination bonds of M−S═P and M−S−P, the new absorption responding to $\nu_{\text{P-SM}}$ occurs at 533 cm^{-1} and the absorption at 488 cm^{-1} responding to $\nu_{\text{P-SH}}$ decreases; the absorption responding to $\nu_{\text{P=SM}}$ combined with the absorption at 613 cm^{-1} responding to $\nu_{\text{P=S}}$ occurs at 608 cm^{-1}. The difference between the spectra of HBTMPDTP and those of the complexes of Ln(III) and Am(III) is very clear, but the difference between the spectra of the Ln(III) complexes and that of the Am(III) complex is not clear. Figure 4 shows the spectra of the samples with different loading amounts of Nd(III) in the organic phase. The spectra were collected in the mode of ZnSe-attenuated total reflection. With same conditions except for the different amount of Nd(III), the relative absorption strength of the functional group of coordinated H_2O varies with the relative amount of the complex in the sample. The amount of Nd(III) loaded in the organic phase is 3.34, 5.70, 9.33, and 16.49 g/L, respectively, with a ratio of 1:1.70:2.79:4.93. The area of the peak at about 1590 cm^{-1} is 0.763, 1.320, 2.102, and 3.851, respectively, with a ratio of 1:1.72:2.75:5.04. It is clear that the absorption strength of H_2O at about 1590 cm^{-1} is proportional to the amount of Nd(III) loaded in the organic phase.

More recently, Pinkerton and co-workers[26] reported that $UO_2Cl_2 \cdot 3H_2O$ reacting with NaS_2PMe_2 gives a binuclear uranium(IV) species $[U\{S_2PMe_2\}_2\{O(S)PMe_2\}_2\{\mu\text{-}O_2PMe_2\}_2]_2$. In the reaction, U(VI) is reduced to U(IV) and $[S_2PMe_2]^-$ is oxidized to $[O(S)PMe_2]^-$ and $[O_2PMe_2]^-$.[26] To investigate the oxidation of HBTMDTP in the extraction process, the IR spectrum of the used extractant was measured. After extraction and standing over 1 week, Ln(III) loaded in the organic phase was stripped with 0.5 M HNO_3 and the organic phase was sampled to measure IR. The IR spectrum of the used extractant was the same as that of the fresh one, and no characteristic absorption of $\nu_{S=P-OH}$ at about 1700 cm^{-1}, a strong broad absorption as in $HO(S)PR_2$, was observed. This result indicates that HBTMDTP is not oxidized in the extraction process.

The results of IR conform to the conclusion from EXAFS that the structure of Ln(III) complexes is different from that of Am complex with HBTMDTP; there is coordinated water in the extraction complexes of Ln(III) but no coordinated water in the extraction complex of Am(III).

(C) MS Measurement. In both positive and negative modes the mass spectra of the extraction complexes of La(III), Nd(III), and Eu(III) were measured by a electrospray mass spectrometer. The MS results of the three Ln(III) extraction complexes are similar with each other, so the MS result of the Nd(III) complex is selected as a representative to be discussed. In negative mode, the MS chart is very simple and there are only four main peaks. The maximum peak at *m*/*e* 1429 is corresponding to $HNdL_4$, and the peaks at *m*/*e* 965, 643, and 321 are corresponding to HL, $[HL]_2$, and $[HL]_3$, respectively. In the positive mode, the MS chart is more complicated. Besides the reciprocal peaks as in the negative mode, there are more peaks; the peaks at *m*/*e* 1108 and 786 are for $HNdL_4$ which lost one and two A^-, respectively; the peaks at *m*/*e* 1305, 1186, 942, and 786 were not identified.

The results of MS show that in the extraction complexes of Ln(III) with HBTMDTP there are four extractant molecules around one Ln(III) and the extraction complexes are mononuclear complexes. These are consistent with the results of the EXAFS and the extraction experiment from which the molecular formula of the complexes of Am(III) and Nd(III) with HBTMPDTP are deduced as being HML_4 (M = Am and Nd, L = anion of HBTMPDTP).[8,20] However, the results of MS indicate that there is no water in the compound responding to the maximum molecular ion peak at *m*/*e* 1429 for Nd(III). This might be explained as that the coordination bond between Ln(III) and water in the extraction complexes is very weak and the coordination water is lost in the process of ionization during MS measurement. This needs further study in the future.

From above, one might postulate the molecular formulas of the anionic complexes of Ln(III) and Am(III) with HBTMPDTP (HL) are $[LnL_4 \cdot H_2O]^-$ and $[AmL_4]^-$, respectively. The counterpart cation is another interested thing for the system. No matter which kind of base, sodium hydroxide solution or ammonia solution, is used to saponify HBTMBTP, after the extraction of Ln(III) from the aqueous solution of 0.3 M Ln(III) nitrate in 1 M $NaNO_3$, neither sodium ion nor ammonium ion can be detected in the organic phase. This means the molecular formulas of the extraction complexes of Ln(III) and Am(III) are $HLnL_4 \cdot H_2O$ and $HAmL_4$, respectively.

Conclusion

The results of the EXAFS, IR, and MS measurements and extraction experiment illustrate that the structures of the extraction complexes of Am(III) and Ln(III) with HBTMDTP are different. The molecular formula of the complex of Am(III) is deduced as being $HAmL_4$, and the molecular formula of the complex of Ln(III), as being $HLnL_4 \cdot H_2O$. There are 8 S atoms from 4 extractant molecules coordinated to Am in the extraction complex of Am, and there are most probably 7 S atoms from 4 extractant molecules and 1 O atom from H_2O coordinated to Ln in the extraction complex of Ln(III). The excellent selectivity of HBTMDTP for Am(III) over Ln(III) in the extraction process may partly derive from the different compositions and coordination structures of the complexes of Am(III) and Ln(III). This case is a particular example of the theory that trivalent actinides are softer acids than trivalent lanthanides and are easier to form coordination bonds with soft bases such as N and S donors.

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Supporting Information Available: Figures showing IR spectra and EXAFS data and fits. This material is available free of charge via the Internet at http://pubs.acs.org.

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