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**ARTICLE**

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**Lanthanides complexation properties of O, N-hetero donor ligand PTA**

Toru Kobayashi\*, Shinichi Suzuki, Hideaki Shiwaku and Tsuyoshi Yaita

*Actinide Chemistry Group, Materials Sciences Research Center, Japan Atomic Energy Agency, 1-1-1 Koto, Sayo-cho, Sayo-gun, Hyogo 679-5148, Japan*

The complexation properties of *N*-alkyl-*N*-phenyl-1,10-phenanthroline-2-carboxamide (PTA) with trivalent lanthanides ( $\text{Ln}^{3+}$ ) were investigated based on structural analysis by using X-ray crystallography and extended X-ray absorption fine structure (EXAFS) methods. As a result, it is revealed that two PTA molecules coordinate with  $\text{Ln}^{3+}$  as tridentate ligand via two nitrogen in phenanthroline moiety and one oxygen in amide moiety in both crystal and solution states. The slight difference in coordination bond distances are observed between  $\text{Eu}^{3+}$  and  $\text{Nd}^{3+}$  complexes, this difference corresponds to the difference in ionic radius between  $\text{Nd}^{3+}$  and  $\text{Eu}^{3+}$ . This result indicates slight difference in ionic radii of  $\text{Ln}^{3+}$  hardly affects coordination properties of PTA.

**Keywords:** *lanthanide; extraction; separation; crystallography; EXAFS*

**1. Introduction**

The development of extractant, which can efficiently separate actinides, is of increasing importance because it concerns establishment and simplification of separation techniques in nuclear fuel cycle and/or decontamination of radioactive waste. Particularly, in nuclear fuel cycle, long-lived radionuclide such as Am and Cm would be key techniques to develop the simple separation system [1,2]. However, the separation of a specific actinide, especially the separation of trivalent actinides and lanthanides, is difficult due to their similarities in chemical properties.

On the molecular design of novel actinides separation reagent, the HSAB theory by Pearson is still useful to discuss the selective interaction between metal ions and donor atoms [3]. Actinides and lanthanides are categorized into hard ions, so they generally show high affinity for hard donor ligands. In fact, many oxygen donor ligands show high complexation ability for both trivalent actinides ( $\text{An}^{3+}$ ) and trivalent lanthanides ( $\text{Ln}^{3+}$ ) [4,5]. The interaction between hard ions and hard donors is based on electrostatic interaction, and so the affinity often depends on charge density of metal ions and/or donor atoms. Therefore, the hard donor ligand can hardly separate  $\text{An}^{3+}$  over  $\text{Ln}^{3+}$  which have same stable valence and similar ionic radii. On the other hand, the selective separations of  $\text{An}^{3+}$  over  $\text{Ln}^{3+}$  were observed in some aza-aromatic nitrogen ligands such as BTP and TPTZ [6,7]. The aza-aromatic nitrogen donor can be categorized into comparatively soft donor. The soft donor atoms generally show strong interaction with soft

metal ions based on covalency in chemical bond. The selectivity of BTP and/or TPTZ also can be attributed to covalent bond formation with trivalent  $\text{An}^{3+}$ , which shows slightly softer character than  $\text{Ln}^{3+}$  [8]. However, most of the aza-aromatic nitrogen ligands are not effective for extraction of  $\text{An}^{3+}$  under highly acidic condition due to protonation of nitrogen atoms, although the spent nuclear fuel and/or high level nuclear waste are under highly acidic conditions.

To develop the excellent actinide separation reagent, which allows both high selectivity and extractability for  $\text{An}^{3+}$  even in highly acidic condition, the combination of both oxygen and nitrogen donors into one molecule has been proposed [9]. That is, introduction of oxygen donor, which is not affected by protonation, into soft nitrogen donor ligand is expected to promote the binding with metal ion over the competing protonation reaction by the oxygen acts as coordinative donor together with nitrogen donor. Bearing this in mind, we developed PTA, (*N*-alkyl-*N*-phenyl-1,10-phenanthroline-2-carboxamide) composed by phenanthroline moiety and amide group as two nitrogen donors and an oxygen donor, respectively [9,10], and revealed that the OcTolPTA, which contains octyl and tolyl groups as substituent on amide nitrogen, shows high extractability for  $\text{Am}^{3+}$  over  $\text{Eu}^{3+}$  even in highly acidic condition [9]. Although the selective extraction of  $\text{Am}^{3+}$  by PTA may be derived from covalency in chemical bond between soft nitrogen donors and  $\text{An}^{3+}$ , the difference in ionic radii between  $\text{Am}^{3+}$  and  $\text{Eu}^{3+}$  may also affect the selectivity. Thus, in this study, we investigated structural properties of Ln-PTA complex, and discussed effect of ionic radii on coordination properties.

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\*Corresponding author. Email: tohru-k@spring8.or.jp

## 2. Experiment

### 2.1. X-ray crystallography

$\text{Ln}^{3+}$  complex of MePhPTA were obtained as follow: 2 equivalent ethanol solution of MePhPTA was added to ethanol solution of  $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ , and the mixture was stirred for few minutes at approximately  $75^\circ\text{C}$ . The solution was cooled to room temperature and then a precipitate appeared. It was filtered and washed several times with a small amount of ethanol. The solid product was recrystallized from hot ethanol.

X-Ray diffraction data were obtained using a Rigaku CCD detector (Saturn724) with graphite monochromated  $\text{Mo-K}\alpha$  radiation and a rotating anode generator. The crystal was mounted on a loop wire. This crystal was stable during measurement. Data were collected and processed using CrystalClear program (Rigaku). The structure was solved by the direct method and expanded using Fourier techniques. The data was refined using package program, CrystalStructure. All the non-hydrogen atoms were refined anisotropically. Although the positions of almost all the hydrogen atoms were determined from a difference Fourier maps, all the hydrogen atoms were refined using riding model at the final stage of refinement.

### 2.2. Extended X-ray absorption fine structure (EXAFS) measurement

The solution samples measured in this study were prepared by mixing 50mM of  $\text{Ln}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  and from 0 to 200mM of ligand in methanol. EXAFS spectra were measured at the BL11XU at the SPring-8. The incident radiation was monochromated with the liquid nitrogen-cooled  $\text{Si}(311)$  [11]. EXAFS measurement was performed on Eu-K edge and Nd-K edge. Each sample was measured five times, and the spectra were averaged. All measurements were performed at room temperature.

The obtained EXAFS spectra were analyzed according to a standard method using the program WinXAS (ver. 3.1) [12]. Theoretical phase shifts and back scattering amplitude functions were calculated by the program code FEFF8.00 [13] and the input files of this code were prepared by the coordinates of crystallographic data. Most of the significant single scattering paths were taken into account in the curve fittings. The amplitude of reduction factor,  $S_0^2$ , was fixed as 0.9.

### 2.3. Calculation of speciation diagram

Stability constants of Eu complexes of MePhPTA were determined by spectroscopic titration study in our previous study [9]. The speciation diagram was drawn with the HySS program under the condition the initial concentration of Eu is 50 mM and ligand concentration is varied from 0 to 200 mM.

## 3. Results and discussion

To discuss the coordination properties of PTA, the measurements of X-ray crystallography and EXAFS of Ln-PTA complexes were performed. On the crystallo-

graphic study, MePhPTA, which is PTA derivative containing methyl group and phenyl group as substituent on amide nitrogen and show good crystalline, was used instead of OcTolPTA due to poor crystallinity of OcTolPTA.  $\text{Eu}(\text{NO}_3)_3$  and MePhPTA were crystallized as  $[\text{Eu}(\text{MePhPTA})_2(\text{NO}_3)_2] \cdot \text{NO}_3(\text{EtOH})_2$  complex in the monoclinic system with  $\text{P2}_1/\text{n}$  space group. The ORTEP drawing is shown in **Figure 1**. Both of oxygen and nitrogen donors of MePhPTA coordinate directly to  $\text{Eu}^{3+}$  with tridentate fashion, and form mononuclear complex. That is, two MePhPTA molecules coordinate as tridentate ligand via two nitrogen atoms in phenanthroline moiety and one oxygen atom in amide moiety, and two nitrate ions coordinate as bidentate ligand via two oxygen atoms. One nitrate ion and two ethanol molecules are in outer sphere. In our previous study, we determined crystal structure of MePhPTA without metal ion, and revealed that the conformation of MePhPTA, in which an amide oxygen and two nitrogen in phenanthroline moiety are oriented to same side, seems to be suitable for coordination with metal ion as tridentate ligand [10]. Even when MePhPTA coordinates with  $\text{Eu}^{3+}$ , MePhPTA keeps similar conformation as expected. The average Ln-O distances derived from bonding of amide oxygen (2.406 Å) is shorter than the average Ln-N distances derived from phenanthroline nitrogen (2.603 Å) or average Ln-O distance derived from nitrate ion (2.523 Å). This result might indicate strong coordination of amide oxygen. In our previous study, we investigated the complexation properties based on speciation and extraction studies, and concluded that the presence of oxygen donor promotes coordination to lanthanides against the competing protonation reaction in acidic solution [9]. The strong coordination by amide oxygen supports this our previous discussion.

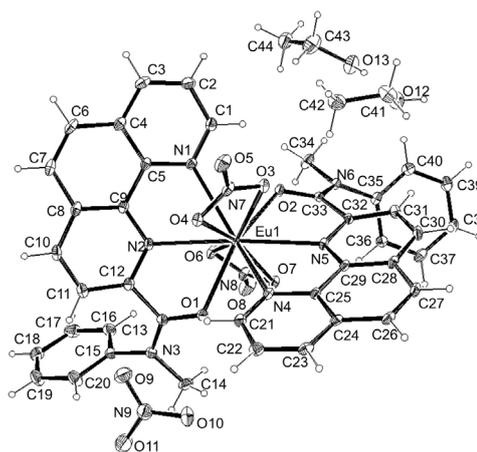


Figure 1. ORTEP view of  $[\text{Eu}(\text{MePhPTA})_2(\text{NO}_3)_2] \cdot \text{NO}_3(\text{EtOH})_2$ .

To investigate the structure of PTA complex in solution state, EXFAS of methanol solutions containing  $\text{Eu}(\text{NO}_3)_3$  and MePhPTA were measured. **Figure 2(a)** shows Radial structural functions (RSF) of mixed methanol solution of  $\text{Eu}(\text{NO}_3)_3$  and MePhPTA, when the

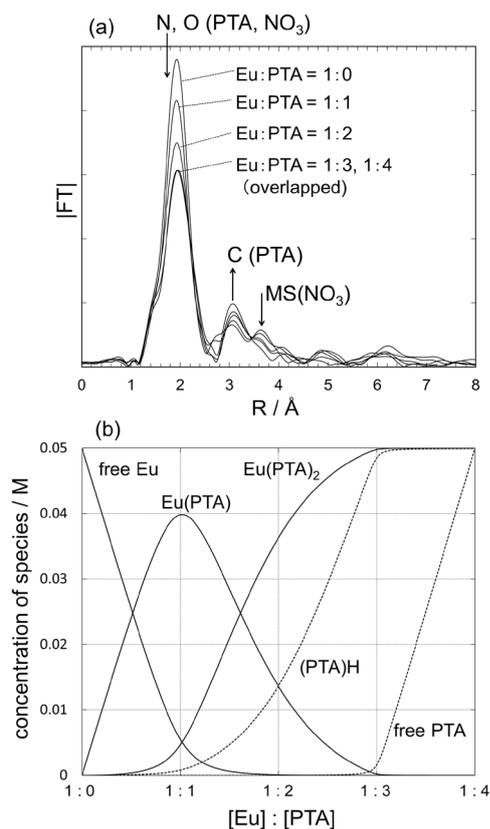


Figure 2. Radial structural functions of mixed methanol solution of  $\text{Eu}(\text{NO}_3)_3$  and MePhPTA (a) and speciation diagram of Eu-MePhPTA system as a function of ligand/metal ratio (b). For the EXAFS measurement, the metal : ligand ratios was changed from 1:0 to 1:4. The speciation diagram has already been reported in our previous literature<sup>[9]</sup>, and this diagram was calculated anew under the same condition as EXAFS measurement.

metal : ligand ratios was changed from 1:0 to 1:4. The RSFs of each samples display a peak at 1.9 Å and distinguishable peaks at 3.1 and 3.7 Å. Considering the crystal structure, the first peak can be attributed to N and O atoms of MePhPTA and nitrate ion in first coordination sphere, and the second peak corresponds to C atoms of MePhPTA. The third peak arises from multiple scattering of nitrate ion. The decreasing of first peak might result from disorder and resulting broadening caused by formation of several kind of chemical bond by coordinating a ligand in addition to nitrate ions and/or water molecules. The increasing of second peak indicates the coordination of MePhPTA with inner sphere of  $\text{Eu}^{3+}$ . The decreasing of third peak might indicates that nitrate ions coordinated with inner sphere of  $\text{Eu}^{3+}$  are partly replaced with water molecule in solution state. The changes in RSFs with an increase of ligand ratio were saturated at the ratio of 1:3 or 1:4. This result well corresponds to speciation diagrams shown in **Figure 2(b)**, in which the formation of Eu : MePhPTA = 1 : 2 complex was saturated around this ratio.

Thus, the curve-fitting to the experimental spectra of Eu-MePhPTA solution under the condition of metal : ligand = 1:4 was performed. Back scattering amplitude and phase shift based on structural model of

$[\text{Eu}(\text{MePhPTA})_2(\text{NO}_3)_2] \cdot \text{NO}_3$  crystal was calculated by Feff800 code and used for this fitting. The results and obtained structural parameters are shown in **Figure 3** and **Table 1**, respectively. The curve-fitting results presented good agreement with the experimental data. The fitted bond distances gives about 2.43 Å for 4 oxygen and/or nitrogen atoms, 2.63 Å for 6 oxygen or nitrogen atoms, and 3.58 Å for 9-10 carbon atoms, respectively. Although the precise assignment of first peak is difficult, considering the crystal structure, the bond at 2.43 Å is expected to be derived from amide oxygen and/or water molecules, and bond at 2.63 Å is probably derived from nitrogen in Phen moiety and oxygen in nitrate ions. The similar coordination numbers and the bond distances between crystal and solution system suggests direct coordination of two MePhPTA molecules as tridentate ligand also in solution state. The bond distances between  $\text{Eu}^{3+}$  and Phen moiety or nitrate ions in solution system become a little longer than those in crystal system. This result could be attributed to equilibrium and/or motional dynamics in solution state. It might also be affected by steric hindrance between  $\text{Eu}^{3+}$  and MePhPTA or two MePhPTA molecules.

The EXAFS measurements and curve-fittings for Eu-OcTolPTA and Nd-OcTolPTA solutions were also performed by same method. The mixed metal : ligand ratios of each sample are 1 : 4, in which dominant species were also estimated as  $\text{Ln}^{3+} : \text{OcTolPTA} = 1 : 2$  species by stability constants. The results are also shown in Figure 3 and Table 1. The EXAFS spectra and structural parameters of Eu-OcTolPTA system were very similar to those in Eu-MePhPTA system, indicating that two OcTolPTA molecules also could coordinate with

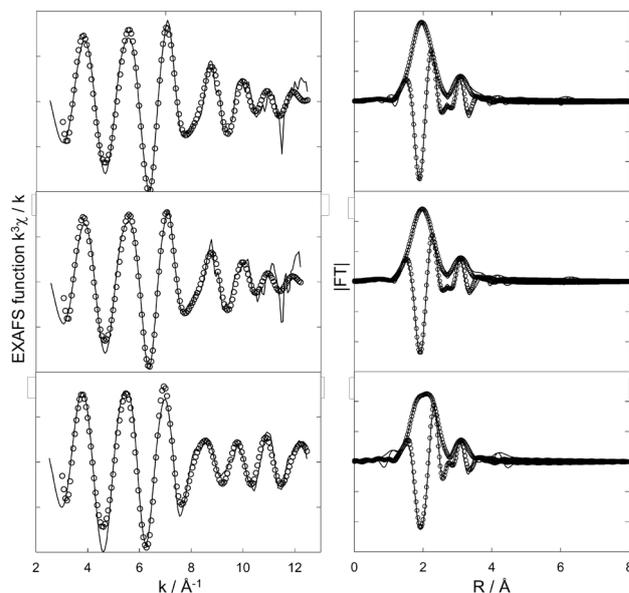


Figure 3. A results of curve-fitting to  $k^3$ -weighted Eu-K edge EXAFS oscillations (left) and corresponding fourier transformed EXAFS oscillations (right) of Eu-MePhPTA (upper), Eu-OcTolPTA (middle) and Nd-OcTolPTA (lower) in methanol solution. The solid lines are experimental data and symbols are fitting results.

Table 1. Structural parameters of Eu-MePhPTA crystal determined by crystallography, and Eu-MePhPTA, Eu-OcTolPTA and NdOcTolPTA solution calculated by curve fittings to EXAFS spectra.

Complex	Shell	C.N.	R / Å	$\sigma^2$	$\Delta E_0$
Eu-MePhPTA (Crystal structure)	Eu-O (PTA)	2	2.41		
	Eu-N, O (PTA, NO <sub>3</sub> )	8	2.56		
	Eu-C (PTA)	10	3.44		
Eu-MePhPTA Methanol solution	Eu-O (PTA, H <sub>2</sub> O)	3.9	2.43	0.006	2.8
	Eu-N, O (PTA, NO <sub>3</sub> )	6.0	2.63	0.006	18.1
	Eu-C (PTA)	9.4	3.58	0.006	18.1
Eu-OcTolPTA Methanol solution	Eu-O (PTA, H <sub>2</sub> O)	4.0	2.43	0.007	1.7
	Eu-N, O (PTA, NO <sub>3</sub> )	6.3	2.63	0.008	18.8
	Eu-C (PTA)	10.1	3.58	0.007	18.8
Nd-OcTolPTA Methanol solution	Nd-O (PTA, H <sub>2</sub> O)	4.0	2.46	0.006	3.5
	Nd-N, O (PTA, NO <sub>3</sub> )	6.3	2.67	0.005	19.3
	Nd-C (PTA)	9.2	3.61	0.008	19.3

C.N.: coordination number, R(Å): bond distance,  $\sigma^2(\text{Å}^2)$ : Debye-waller factor squared,  $\Delta E_0$  (eV): energy shift parameter

inner sphere of Eu<sup>3+</sup> as tridentate ligand. That is, the local structure of Eu-PTA complex could be not much different even the substituent were modified. Also in the case of Nd-OcTolPTA system, the coordination numbers were almost same, indicating the two OcTolPTA molecules works as tridentate ligand. Although the bond distances were 0.03-0.04 Å longer than those of Eu complex, this difference corresponds to the difference in ionic radius between Nd<sup>3+</sup> and Eu<sup>3+</sup>. Therefore, the local structure of Nd-OcTolPTA complex is considered essentially same as Eu-OcTolPTA complex, and it indicates that slight difference in ionic radii of Ln<sup>3+</sup> hardly affects coordination properties of PTA.

#### 4. Conclusion

The structure of Ln-PTA complexes were investigated by X-ray crystallography and EXAFS method, and revealed that two PTA molecules coordinates with Eu<sup>3+</sup> as tridentate ligand via two nitrogen atoms in phenanthroline moiety and one oxygen atom in amide moiety in both crystal and solution state. The slight difference in coordination bond distances are observed between Eu<sup>3+</sup> and Nd<sup>3+</sup> complexes, and this difference corresponds to the difference in ionic radius between Nd<sup>3+</sup> and Eu<sup>3+</sup>. This result indicates that PTA shows essentially same coordination properties toward both Eu<sup>3+</sup> and Nd<sup>3+</sup>, hardly affected by difference in ionic radii.

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#### References

- [1] C. Madic, M. Lecomte, P. Baron and B. Boullis, Separation of long-lived radionuclides from high active nuclear waste, *C.R. Physique*. 3 (2002), pp. 797-811.
- [2] Z. Kolarik, Complexation and separation of lanthanides(III) and actinides(III) by heterocyclic N-donors in solutions, *Chem. Rev.* 108 (2008), pp. 4208-4252.
- [3] R.G. Pearson, Hard and soft acids and bases, *J. Am. Chem. Soc.* 85 (1963), pp. 3533-3539.
- [4] E.P. Horwitz, A.C. Muscatello, D.G. Kalina and L. Kaplan, The extraction of selected transplutonium(III) and lanthanide(III) ions by dihexyl-*N*, *N*-diethyl carbamoylmethylphosphate from aqueous nitrate media, *Sep. Sci. Technol.* 16 (1981), pp. 417-437.
- [5] Y. Sasaki, Y. Sugo, S. Suzuki and S. Tachimori, The novel extractants, diglycol amides, for the extraction of lanthanides and actinides in HNO<sub>3</sub>-*n*-dodecane system. *Solvent Extr. Ion Exch.* 19 (2001), pp. 91-103.
- [6] N. Boubals, M.G.B. Drew, C. Hill, M.J. Hudson, P.B. Iveson, C. Madic, M.L. Russell and T.G.A. Youngs, Americium(III) and europium(III) solvent extraction studies of amide-substituted triazine ligands and complex formed with ytterbium(III), *J. Chem. Soc., Dalton Trans.* 1 (2002), pp. 55-62.
- [7] Z. Kolarik, U. Mullich and F. Gassner, Selective extraction of Am(III) over Eu(III) by 2,6-ditriazolyl- and 2,6-ditriazinyl pyridines, *Solvent Extr. Ion Exch.* 17 (1999), pp. 23-32.
- [8] G.R. Choppin, Covalency in f-element bonds, *J. Alloys Compd.* 344 (2002), pp. 55-59.
- [9] T. Kobayashi, T. Yaita, S. Suzuki, H. Shiwaku, Y. Okamoto, K. Akutsu, Y. Nakano and Y. Fujii, Effect of the introduction of amide oxygen into 1,10-phenanthroline on the extraction and complexation of trivalent lanthanide in acidic condition, *Sep. Sci. Technol.* 45 (2010), pp. 2431-2436.
- [10] T. Kobayashi, S. Suzuki, H. Shiwaku and T. Yaita, Crystal structure of *N*-methyl-*N*-phenyl-1,10-phenanthroline-2-carboxamide. X-ray Struct, *Anal. Online*, 28 (2012), pp. 77-78.
- [11] H. Shiwaku, T. Mitsui, K. Tozawa, K. Kiriyama, T. Harami and T. Mochizuki, Cryobenucally cooled monochromator with multi-crystal switching system on BL11XU at Spring-8, *AIP Conf. Proc.* 705 (2004), pp. 659-662.
- [12] T. Ressler, WinXAS: a program for X-ray absorption spectroscopy data analysis under MS-Windows, *J. Synchrotron. Radiat.* 5 (1998), pp. 118-122.
- [13] A.L. Ankudinov, B. Ravel, J.J. Rehr and S.D. Conrad, Real-space multiple-scattering calculation and interpretation of X-ray-absorption near-edge structure, *Phys. Rev. B* 58 (1998), pp. 7565-7576.