Complexation Studies of Eu(III) by a Novel Soft N and Hard O Donor Combined Ligand Including N,N,N',N'-Tetrakis(2-pyridylmethyl)-1,3-diaminopropane-2-amide Structure: UV-vis Titration, X-ray Crystallography, EXAFS Spectroscopy Analysis

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A novel soft N and hard O donor combined ligand including N,N,N',N'-tetrakis(2-pyridylmethyl)-1,3-diaminopropane-2-amide structure (TPTNA) was successfully synthesized. Its structure and complexation of Eu\textsuperscript{3+} in solid state and methanol solution respectively were investigated by X-ray crystallography, UV-vis titration and EXAFS spectroscopy. As a result, the chemical stoichiometry of Eu\textsuperscript{3+} complex with TPTNA was determined to be 1 : 1 by X-ray crystallography. It was found that one amide unit, two pyridine groups from TPTNA coordinated with one Eu\textsuperscript{3+}. However, the Eu-O and Eu-N bond lengths obtained from theoretical fitting of the EXAFS data were consistent with the results from X-ray crystallography studies, reflecting retention of the structure in methanol solution.

1. Introduction

Lanthanide (Ln) elements play an important role in the field of advance materials, such as batteries, catalytic converters, and permanent magnets. Trivalent lanthanide ions (Ln\textsuperscript{3+}) are the most common oxidation states [1]. Owing to their similar coordination numbers, chemical properties and ionic radii, the mutual separation of Ln\textsuperscript{3+} from aqueous phase has been identified as one of the biggest technology challenges [2]. Ligands with only soft N donor atoms such as N,N,N',N'-tetrakis(2-pyridylmethyl)ethylenediamine (TPEN) have been directly utilized for the extraction of Ln\textsuperscript{3+} in nitric acid solution though protonation and water phase dissolution has been frustrating [3]. However, hard O donors such as amide oxygen donor can provide a stronger metal ion binding ability and at the same time lower the basicity of N-heterocycle, allowing practical application in a wider pH range [4]. Recently, ligands that contain not only hard O donor but also soft N donor have been under intense research concerning extraction and group recognition of actinides and lanthanides in nuclear fuel reprocessing process, and also offer considerable potential as extractants for mutual separation of Ln\textsuperscript{3+} from aqueous phase [5].
A fundamental issue for the design of such multidentate ligands lies in how to organize the N and O donor atoms in a ligand in a complementary arrangement to achieve more favourable interactions with the metal ion [6]. From previous studies, our research group has firstly synthesized a novel task-specific ionic liquid with \( N,N',N'',N'^\prime\)-tetrakis(2-pyridylmethyl)-1,3-propanediamine-2-amide structure ((IL-TPTNA)\(^{+}\)NTf\(_2^-\)), which mixed a hybrid O, N donor ligand, showed mutual recognition towards Ln\(^{3+}\) in nitric acid solution [7]. However, the possible complexation behaviour of (IL-TPTNA)\(^{+}\)NTf\(_2^-\) with Ln\(^{3+}\) was still unclear. Although many efforts have been made to prepare a single crystal of (IL-TPTNA)\(^{+}\)NTf\(_2^-\) with Ln\(^{3+}\), solids were not obtained for X-ray crystallography measurement. From previous reports, the donors required in the complex structure of a task specific ionic liquid with metal ions were considered to be similar to its ligand without ionic liquid moiety [8]. Therefore, in order to clarify whether both soft N and hard O donor are indispensable in the complexation process of (IL-TPTNA)\(^{+}\)NTf\(_2^-\) with Ln\(^{3+}\) and further clarify the possible coordination environment, in this study, a soft N and hard O donor combined ligand including \( N,N',N'',N'^\prime\)-tetrakis(2-pyridylmethyl)-1,3-diaminopropane-2-amide structure (TPTNA) without ionic liquid moiety was synthesized. Furthermore, UV-vis titration, X-ray crystallography and EXAFS spectroscopy analysis were combined to elucidate the structure and complexation behaviour of Eu\(^{3+}\) with TPTNA.

2. Experimental

2.1 Reagents and synthesis producers

All reagents were purchased from commercial suppliers at the highest grade that could be obtained and used without any further purification. All aqueous solutions were made with deionized water. TPTNA was synthesized by the routes summarized in Scheme 1. Briefly, 1a – 1g were prepared by methods described in previous studies [7]. Target material 1h was obtained by diluting hexanoyl chloride in dehydrated acetonitrile solution and was added dropwise into the dehydrated acetonitrile solution of 1g under the conditions of ice bath and protection of N\(_2\) gas [9]. Further purification of 1h was conducted by alumina chromatography (\( R_f = 0.3\), Ethyl acetate : Hexane = 3 : 1) to give 1h (0.38 g, 7.5%) as a yellow viscous wax.

2.2 UV-vis titration

The binding properties of obtained TPTNA with Eu\(^{3+}\) were first studied by UV-vis titration experiments in MeOH solution at 25°C. 50 \( \mu \)M, 3 mL stock solution of TPTNA was prepared in a specific glass tube which was suitable for UV-vis measurement. However, by dissolving Eu(NO\(_3\))\(_3\cdot\)6H\(_2\)O salt in MeOH solution to prepare 1 mM Eu\(^{3+}\) solution, both of these kinds of stock solutions were unbuffered. Then Eu\(^{3+}\) MeOH solution 30 \( \mu \)L was added into TPTNA MeOH solution and stirred to mix. The solution was mixed vigorously for 1 min, which was long enough to attain the complexation equilibrium. UV-vis spectra were obtained on a Jasco V-650 spectrophotometer over the wavelength range of 190 – 600 nm.
2.3 Single crystal preparation

The crystallographic experiment was performed by mixing an appropriate amount of Eu(NO₃)₃·6H₂O with TPTNA in MeOH in a 2 mL vial. The mixture was shaken vigorously for 1 h at room temperature and then put into a small 6 mL vial to which 1 mL anti-solvent ether had been preliminarily added and then sealed. The vial was put into refrigerator for more than 1 week. The well-formed single crystal was placed on top of a glass capillary and mounted on a goniometer [10]. Intensity data were collected by using an imaging plate area detector in Rigaku RAXIS RAPID with graphite monochromated Mo Kα radiation (λ = 0.71075 Å). Furthermore, the diffraction spots obtained were solved by direct method of SIR97 and expanded using Fourier techniques. In the reduction of data, an empirical absorption correction was applied. All non-hydrogen atoms were refined with anisotropical displacement parameters. All of the hydrogen atoms were introduced at ideal positions and refined isotropically based on the corresponding C-atoms. Full matrix least-squares refinement on $F^2$ was based on observed reflections and parameters, and converged with unweighted and weighted agreement factors, $R_1$ and $wR_2$, respectively [11]. All calculations were performed by using Crystal Structure 4.3 software package. The structural data was visualized using Ortep3 with thermal ellipsoids at a 50% probability level.

2.4 EXAFS measurement

EXAFS titration of methanol solutions dissolving Eu(NO₃)₃·6H₂O with TPTNA was measured. All of the EXAFS experiments were conducted at Super Photon Ring–8 GeV (SPring-8), beamline BL11XU. First, two kinds of concentrated stock solution were prepared: (i) 100 mM, 200 µL Eu(NO₃)₃·6H₂O methanol solution (as background); (ii) 400 mM, 1 mL TPTNA MeOH solution. Then, a sample series used in the titration experiments was prepared by adding solution (ii) into solution (i) to obtain the following stoichiometric ratio of ligand : Eu³⁺: 0 : 1, 1 : 1, 2 : 1, 4 : 1. For Eu³⁺, the K absorption edge was used in the experiments with a silicon (311) surface and an undulator light source. Three to five scans were conducted.
on each sample and the spectra were averaged. All measurements were conducted at room temperature. The EXAFS oscillations were extracted from raw data under the standard procedures for pre-edge subtraction, spline removal, data normalization, and Fourier transformation etc. by using the WinXAS (ver.3.2) program [12]. For example: A linear function for the pre-edge region and a second-order polynomial in the post-edge region were used for normalization; The $\chi(k)$ functions were extracted using a cubic spline and were Fourier transformed with $k^2$-weighting over the approximate $k$-range 2.5 – 11 Å$^{-1}$. Figure 4 showed the radial structural functions (RSFs) of the mixed MeOH solution of TPTNA with Eu$^{3+}$.

3. Results and Discussion

3.1 UV-vis titration analysis

The titration results are shown in Figure 1. Black line was 50 μM TPTNA MeOH solution in the absence of metal ions. A significant peak was observed with absorption maximum at 260 nm, which clarifying as the UV-vis absorption from TPTNA. Upon addition of Eu$^{3+}$, the absorption maximum at 260 nm gradually decreased in intensity, and a new band above 278 nm slightly increased. At the same time, two isosbestic points were observed at around 238 and 278 nm respectively during the titration, which implied the existence of a single equilibrium between metal ion complexing and non-complexing ligands. Benesi–Hildebrand equation [13] (as shown in equation 1) was adopted to evaluate the binding stoichiometry of Eu$^{3+}$ with TPTNA in MeOH. Stability constant of Eu$^{3+}$ with TPTNA was temporarily defined by the following equilibrium reaction as shown in equation 2. As can be seen in Figure 2, the plot of $1/(A-A_0)$ vs $1/[\text{Eu}^{3+}]$ didn’t fit well with a straight line, its correlation coefficient was calculated as only 0.96, indicating that even though 1 : 1 stoichiometry of Eu$^{3+}$ complex formed in MeOH solution could be considered as the dominant species, other species with different ratio may co-exist.

$$\frac{1}{A-A_0} = \frac{a}{a-b} \left( \frac{1}{K[M]} + 1 \right)$$

(1)

$$K_{\text{ML}} = \frac{[\text{Eu}(\text{TPTNA})^{3+}]}{[\text{Eu}^{3+}]\text{[TPTNA]}}$$

(2)

where, [M] is the concentration of cation; $A_0$ is the observed absorbance in the absence of M; A is the obtained absorbance with M added; $K$ is the stability constant. In addition, $a$ and $b$ are constants.

![Figure 1. UV-vis titration spectra of Eu$^{3+}$. [Eu$^{3+}$] / [TPTNA]= 0 – 6 equiv.](image)
3.2 X-ray crystallography analysis

In this study, Eu(NO$_3$)$_3$(TPTNA) was investigated, as depicted in Figure 3 and compiled in Table 1 (Cambridge Crystallographic Data Centre (CCDC): 1995927). It was found that each Eu$^{3+}$ was 10-coordinated by one O atom, three N atoms of TPTNA, and six O atoms of three bidentate nitrate ions to form a 1 : 1 complex. Both hard O donor and soft N donors of TPTNA were indispensable to the complexation process. However, not all N donors of TPTNA were involved. Only three N donors in the same side of TPTNA were coordinated with Eu$^{3+}$, another two pyridine groups still remained uncoordinated. Although pyridine N donor was a comparatively soft donor, N donors in TPTNA molecule coordinated with hard f-element metal ion even in the presence of other hard O donors such as nitrate ions. This tendency was exhibited due to the presence of amide oxygen in TPTNA which enhanced the binding ability with Eu$^{3+}$. Moreover, obtained Eu-O (amide unit) bond distance tended to be slightly shorter than Eu-N as shown in Table 2. However, the steric hinderance of pyridine groups and the coordination ability of nitrate ions were postulated as the probable reason for 1 : 1 coordination of TPTNA with Eu$^{3+}$ [14].

Figure 3. (a) Chemical structure and (b) Ortep3 plot of a single crystal of the Eu-TPTNA-nitrate complex for non-hydrogen atoms (ellipsoids are at the 50% probability level).
Table 1. Crystal data for the Eu-TPTNA-nitrate complex.

| Crystallographic Data of Eu(NO₃)₃(TPTNA) complex |
|-----------------------------------------------|
| Formula | C₃₃H₄₁EuN₁₀O₁₀ |
| Formula weight | 889.72 |
| Crystal size (mm) | 0.3*0.3*0.15 |
| Crystal system | monoclinic |
| Space group | Pc (#7) |
| a (Å) | 14.2603(4) |
| b (Å) | 8.5116(3) |
| c (Å) | 16.3797(6) |
| Alpha (deg) | 90.000 |
| Beta (deg) | 98.887(7) |
| Gamma (deg) | 90.000 |
| V (Å³) | 1964.27(12) |
| Z value | 2.00 |
| Calculated density (g/cm) | 1.416 |

Table 2. Selected atomic distances in the single crystal.

| Bond distance / Å |
|------------------|
| Eu-O(10)amide unit | 2.344(5) |
| Eu-N(6)amine | 2.675(3) |
| Eu-N(8)pyridine | 2.671(3) |
| Eu-N(10)pyridine | 2.659(2) |
| Eu-O(2)nitrate | 2.467(4) |
| Eu-O(3)nitrate | 2.491(6) |
| Eu-O(5)nitrate | 2.514(2) |
| Eu-O(6)nitrate | 2.530(2) |
| Eu-O(8)nitrate | 2.560(5) |
| Eu-O(9)nitrate | 2.617(2) |

3.3 EXAFS analysis

From the results of EXAFS titration experiments shown in Figure 4, as can be seen, before adding TPTNA solution, a main sharp peak shown as black line at 1.9 Å was found and it was assigned as the overall effect of N and O from H₂O, MeOH, and NO₃⁻ [15]. With increasing concentration of TPTNA into the solution, the intensity of the first peak was gradually decreased and the shape of the first peak became broadening. And this phenomenon can be speculated as the MeOH, H₂O molecules in the coordination sphere of Eu³⁺ were partly replaced by TPTNA and resulting the formation of several kinds of chemical bond by coordinating a ligand in addition to NO₃⁻. Taking into consideration the single crystal structure, the first peak was assigned as the effect of N and O atoms in TPTNA, NO₃⁻, or even MeOH and H₂O molecular formed in the first coordination shell [16]. Furthermore, the shape of the first peak became unsymmetrical and shifted slightly to a higher position, indicating the different distances of Eu–N(TPTNA) and Eu–O(TPTNA) [17]. When the ratio of Eu : TPTNA reached a relatively higher 1 : 4, the intensity of the first peak further decreased,
indicating the coordination environment surrounding Eu$^{3+}$ changed compared with other ratios, and this phenomenon was considered to be consistent with the UV-Vis titration results.

The second peak was attributed as the carbons adjacent to Eu simultaneously shifted to a higher position with an increase in the amount of ligand [18].

In order to clarify the possible relationship of the complex structure formed in solid state and solution, and to further clarify the coordination environment in greater detail, the Eu : TPTNA complex with a 1 : 1 stoichiometry was studied. Model fitting was performed with back scattering amplitude functions and theoretical phase shifts calculated from models based on the complex structure in single crystal using the code FEFF 8.0. Most of the significant scattering paths (single scattering path for the nearest and next nearest) were taken into consideration in the curve fitting. The resulting coordination numbers obtained from single crystal data were used as fixed values for the fitting. The shell structure divided for the theoretical fitting was defined as: shell 1: Eu–O (amide O), shell 2: Eu–O (NO$_3^-$) and Eu–N, and shell 3: Eu–C, respectively. The bond distance for each shell used as the input parameters in WinXAS software was set as 2.344, 2.576 (Averaged value), and 3.555 Å. Furthermore, multiple scattering may have effect on higher shells. In this study, multiple scattering in the analysis of Eu-N(NO$_3^-$) etc. was neglected, because effective path lengths for multiple scattering were significantly longer. The $\Delta E_0$ values were constrained to be the same values for each fitting. The theoretical fitting results and calculated bond distance, Debye–Waller factor ($\sigma^2$), and energy shift ($\Delta E_0$) are shown in Figure 5 and Table 3. The curve fitting results gave about 2.331 Å for Eu–O (amide O), 2.492 Å for 6 Eu–O (NO$_3^-$) and 3 Eu–N, and 3.525 Å for 8 C, which in a similar trend with the bond distance obtained in single crystal and their differences could be attributed as the equilibrium and thermal vibration in solution state [19]. Although the structure of complex in crystal and MeOH are not expected to be completely identical, the crystallographic data provided similar information and hints to the solution EXAFS data in terms of the coordination behavior and complex structure [20].
Figure 5. The $k^3$-weighted Eu $k$-edge EXAFS spectra (left) and its corresponding Fourier transformation (right).

Table 3. Results of theoretical fitting.

| Complex                  | Shell                      | $S_0^2$ | C.N. | $R_{\text{fitting results}}$ / Å | $\sigma^2$ | $\Delta E_0$ / % |
|--------------------------|----------------------------|---------|------|----------------------------------|-------------|-----------------|
| Eu-TPTNA                 | Eu-O(amide unit)           | 0.9 a   | 1 a  | 2.331(4)                         | 0.0001(2) b | 1.636 c         |
|                          | Eu-O(NO$_3^-$) and Eu-N     | 0.9 a   | 6+3 a| 2.492(6)                         | 0.0048(5) b | 1.636 c         |
|                          | Eu-C (Pyridine groups, alkyl) | 0.9 a   | 8 a  | 3.525(2)                         | 0.0066(4) b | 1.636 c         |

a fixed parameter; b constrained parameter (0.0001 – 0.05); c correlated as same value. The $k$-range for Fourier transformation: 2.5 – 11 Å$^{-1}$; the curve fitting $R$ range: 1 – 3.5 Å; fitting error < 9.8 × 10$^{-5}$.

4. Conclusion

In conclusion, a novel soft N and hard O donor combined ligand including N,N,N',N'-tetrakis(2-pyridylmethyl)-1,3-diaminopropane-2-amide structure (TPTNA) was successfully synthesized. UV-vis titration, X-crystallography, and EXAFS analysis were performed to elucidate the relationship between complex structure in solid state and solution. On the basis of the experiment results, 1 : 1 coordination mode was determined by X-ray crystallography for the crystal structure of Eu$^{3+}$ with TPTNA. It was found that both hard O donor and soft N donors of TPTNA are indispensable in the complexation process. Furthermore, the results of theoretical EXAFS fitting elucidated a similar complex structure in crystal and organic solvent.

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