Relationship Between Structure and Coordination Strength of N and N,O-Hybrid Donor Ligands with Trivalent Lanthanides

Masahiko Nakase a,b, Tohru Kobayashi b, Hideaki Shiwaku b, Shinichi Suzuki b, Travis S. Grimes a, Bruce J. Mincher a, and Tsuyoshi Yaita b

ABSTRACT
To effectively separate lanthanides (Ln(III)) from actinides (An(III)), symmetrical 2,2′-bipyridyl (Bpy), 1,10-phenanthroline (Phen), and unsymmetrical N-methyl-N-tolyl-1,10-phenanthroline-2-carboxamide (MeTol-PTA) were investigated. According to the crystal structures and EXAFS experiments, the decreasing ionic radius from light to heavy Ln led to decreases in the Ln–N (Bpy) and Ln–N (Phen) distances, while log β simply increased due to the electrostatic interaction and the order of Ln–O (MeTol-PTA) < Ln–N (Bpy, Phen) < Ln–N (MeTol-PTA) was obtained. This indicated that the bulky phenanthroline moiety of MeTol-PTA may not allow N (MeTol-PTA) to come close to Ln. Consequently, the log β of MeTol-PTA exhibited a local maximum (around Nd).

KEYWORDS
N,O-hybrid donor; lanthanides; single crystal; EXAFS; stability constants

Introduction
In the treatment of high-level radioactive waste, the separation of trivalent lanthanides (Ln(III)) from trivalent actinides (An(III)) is an effective means of minimizing the burden for vitrification and ultimate deep geological disposal. The separation of f-block elements, namely, An and Ln, has been previously investigated and various ligands have been developed.[1–11] The utilization of synergistic effects and the combination of hydrophilic ligands (masking agents) with hydrophobic ligands (extractants) are also effective for the separation of An and Ln.[12–16] Many computational studies of the structures of complexes and coordination behavior have been reported.[17–20] As the separation of An and Ln has to be performed in a highly radioactive environment, radiolysis and degradation of the ligands have also been extensively studied.[21–24] The difficulty in separating trivalent f-block elements arises from the similarity of their chemical properties, such as ionic radius, ionic charge, and a stable valence state in solution. Recently, substantial progress has been achieved in the separation of hexavalent Am(VI) from trivalent Ln ions. Trivalent Am(III) can be oxidized to Am(VI) by oxidizing agents such as sodium bismuthate and copper(III) periodate prior to treatment with conventional extractants specifically developed for actinide extraction.[25–34] One limitation of this technique is that Am(VI) is reduced on contact with organic compounds. Consequently, there is a need for an improved understanding of Am oxidation chemistry and the development of ligands with high selectivity and fast extraction kinetics to enable the separation of trivalent f-elements. To selectively separate trivalent f-block elements, a greater understanding of the relationship between complex structures and coordination strength is essential. Among the reported ligands for the separation of trivalent actinides and lanthanides, common structures include 2,2′-bipyridine (Bpy) and 1,10-phenanthroline (Phen). Although both symmetrical and unsymmetrical ligand structures are known, the effect of this structural feature remains poorly understood. Therefore, to investigate the relationship between structure and coordination strength, in this study Bpy and Phen were
selected as symmetrical ligands and N-methyl-N-tolyl-1,10-phenanthroline-2-carboxamide (MeTol-PTA, \( R = R’ = \text{methyl} \)) was selected as an unsymmetrical ligand (Fig. 1). The initial study of PTA was reported elsewhere.\(^{35,36}\) The PTA derivative was immobilized into cage-pored mesoporous silica which gave a novel hybrid adsorbent for trivalent lanthanide.\(^{37}\) However, the coordination mechanism of PTA was not yet examined in detail. Bpy consists of two pyridine rings connected through a rotatable C–C bond, whereas Phen consists of two pyridine rings linked by a rigid benzene structure. Therefore, Bpy is more flexible than Phen. In the case of MeTol-PTA (Fig. 1c), the purpose of the \( R \) and \( R’ \) substituents connected to the Phen structure by the amide N is to allow tuning of the electronegativity of the amide O and introduce steric hindrance for the differentiation of 4f/5f elements. In this study, crystallography, extended X-ray absorption fine structure (EXAFS) and UV titration experiments were performed to elucidate the relationship between complex structure and coordination strength and assist in the development of appropriate ligands for specific f-block elements.

**Experimental**

**Crystallography**

The crystallographic experiments were performed as described previously.\(^{38}\) Solutions of the appropriate ligand (10 mmol/L) and Ln nitrate hydroxide (5 mmol/L) were prepared in methanol (1 mL) in 2 mL vials. These solutions were maintained at room temperature without agitation to allow the gradual formation of single crystals at the bottoms of the vials. The formed single crystals were placed on top of a glass capillary and mounted on a goniometer. All of the measurements were performed using a charge-coupled device area detector, graphite-monochromated MoK\(_\alpha\) radiation, and a single-crystal X-ray diffractometer (Saturn 726, Rigaku), and the diffraction spots from the single crystals were analyzed using the appropriate software and methods (CrystalClear, SIR-92, CRYSTALS, and CrystalStructure 3.8.2).\(^{39–42}\) The structural data were visualized using MERCURY and compiled.\(^{43}\) The structure of a general Ln–MeTol-PTA–nitrate complex is shown in Fig. 2 with the key structural parameters indicated.

**EXAFS**

All of the EXAFS experiments were conducted at Super Photon Ring–8 GeV (SPring-8), beamline BL11XU, under the experiment numbers 3508 (2014B, 2015A, 2015B) and 3504 (2016A). For each Ln, the respective K\(_1\) absorption edges were used in the experiments with a silicon (311) surface and an undulator light source. The radial structural functions (RSFs) were handled using WinXAS 3.1, and the theoretical fittings with RSFs were performed using FEFF 8.0.\(^{44,45}\) The first and second peaks of the RSFs were fitted to obtain the coordination numbers, atomic distances, Debye–Waller factors, and values of \( \Delta E_0 \). A series of the theoretical fittings was based on the complex structures in single crystals. The oxygen atoms of the nitrates in the single crystals were replaced with the oxygen atoms of water molecules and the resulting coordination numbers were used as fixed values for the fitting. The shell structure for the fitting was Ln–O (H\(_2\)O, NO\(_3^-\), or amide O), Ln–N, and Ln–C. The \( \Delta E_0 \) values were constrained to be the same values for each fitting.
UV spectroscopic titration

The UV spectroscopic titration experiments and calculation of the acid dissociation constant ($pK_a$) and stability constant ($\log \beta$) were performed as described previously. The complexation equilibria of the Ln ions and respective ligands were obtained by UV spectroscopic titrations in methanol using a UV spectrophotometer (JASCO, V-670), and the temperature of the solutions was maintained at 298.0 ± 0.1 K. Lanthanide chloride hydroxide and hydrochloric acid were used instead of nitric acid (as used in the crystallographic and EXAFS experiments) because nitric acid exhibits an absorption band in the UV range, which would have complicated the spectral interpretation and afforded less reliable fittings. Furthermore, due to the weak interactions of the monovalent nitrate and chloride anions, the effect of the counteranion on the coordination was neglected. To determine the acid dissociation constant ($pK_a$), 10 μL aliquots of 2 mmol/L hydrochloric acid were added to 3 mL of a 50 μmol/L solution of the corresponding ligand. To measure the stability constant ($\log \beta$) of each Ln/ligand pair, 10 μL aliquots of 1–2 mmol/L lanthanide chloride solution were added to 3 mL of a 50 μmol/L solution of the corresponding ligand. Methanol was used as the solvent to dissolve both the metal ion and the ligand. After adding the appropriate aliquots, the methanolic solution was mixed for 1 min using a micro magnetic stirrer to allow the complexation reaction to reach equilibrium. The absorption spectra were measured in the range of 220–400 nm, which corresponds to the absorption bands of the ligands. The $pK_a$ and $\log \beta$ values were calculated by curve fitting to the obtained spectra, including at least 24 data points for each fit, using the software HYPERQUAD. To calculate the stability constants, Eqs. (1)–(5) were used:

$$[Ln] + [\text{ligand}] \Rightarrow [Ln(\text{ligand})] \quad (1)$$

$$[Ln] + 2[\text{ligand}] \Rightarrow [Ln(\text{ligand})_2] \quad (2)$$

$$K_a = [\text{ligand}][H^+]/[(\text{ligand})H^+] \quad (3)$$

$$b_{Ln(\text{ligand})} = [Ln(\text{ligand})]/[Ln][\text{ligand}] \quad (4)$$

$$b_{Ln(\text{ligand})_2} = [Ln(\text{ligand})_2]/[Ln][\text{ligand}]^2 \quad (5)$$

To calculate $\log \beta$ for Ln–Bpy, Ln–Phen, and Ln–MeTol-PTA, both 1:1 and 1:2 coordinated species were considered because the structures of the single crystals consisted of one Ln ion and two ligands (i.e., Ln:ligand = 1:2), and this produced the best fit to the experimental data. The uncertainty of less than 5% was considered to arise from the experimental and computational errors.
**Ligand synthesis**

Bpy and Phen were purchased from Sigma-Aldrich and used without further purification. MeTol-PTA was synthesized and purified in our laboratory. First, 2-methyl-1,10-phenanthroline was synthesized and oxidized in two steps using different oxidants.\(^{47,48}\) 8-Aminoquinoline (30.0 g, 0.207 mol) and sodium iodide (0.297 g, 1.98 mmol), were added to 70 wt % sulfuric acid (75 mL). This mixture was then heated to 110°C using an oil bath and crotonaldehyde (24.2 g, 0.345 mol) was added dropwise with magnetic stirring. After refluxing at 110°C for 5 h, the solution was cooled down and then neutralized by the addition of concentrated sodium hydroxide solution. The water was evaporated and the product was extracted several times using dichloromethane. After evaporation of the dichloromethane, the crude material was purified by column chromatography using ethyl acetate as the eluent to afford 2-methyl-1,10-phenanthroline (9.26 g, 23.0% yield).

2-Methyl-1,10-phenanthroline (9.26 g, 0.048 mol) and selenium dioxide (13.2 g, 0.119 mol, Wako Chemicals) were added to 1,4-dioxane (200 mL, Wako Chemicals) containing 4 wt % water, and reacted under reflux at 105°C for 3 h. The hot solution was then filtered through Celite and allowed to cool to form a precipitate of 2-aldehyde-1,10-phenanthroline. Nitric acid solution (180 mL, 61 wt %) was then added and reacted under reflux at 105°C for 3 h. The reaction solution was directly poured over ice to afford 1,10-phenanthroline-2-carboxylic acid as a pale yellow precipitate (8.74 g, 0.039 mmol, 81.2% yield).

The subsequent synthesis of MeTol-PTA from 1,10-phenanthroline-2-carboxylic acid was almost identical to that reported elsewhere.\(^{35,36}\) 1,10-Phenanthroline-2-carboxylic acid (3.95 g, 0.0176 mol) was chlorinated using 10 equiv of thionyl chloride (12.7 mL, 0.176 mol) under reflux for 2 h. After removal of the excess thionyl chloride under reduced pressure, the crude acid chloride was dissolved in dichloromethane (30 mL). N-Methyl-p-toluidine (2.13 g, 0.0176 mol, 1.0 equiv) and triethylamine (2.94 mL, 0.0211 mol, 1.2 equiv) were then added dropwise at 5°C, and the solution was stirred overnight at ambient temperature. The dichloromethane layer was successively washed three times with sodium hydroxide (30 mL, 1 mol/L), three times with hydrochloric acid (30 mL, 1 mol/L), and once with distilled water (30 mL) and subsequently dried over sodium nitrate (Kanto Kagaku) and evaporated. The residue was purified by column chromatography using chloroform as the eluent, to afford the final MeTol-PTA (1.97 g, 0.60 mmol, 34.2% yield).\(^1\)H NMR (400 MHz, CDCl\(_3\), \(\delta\) in ppm): 2.10 (3H, s), 3.56 (3H, s), 6.88 (2H, d, \(J = 7.2\) Hz), 7.10 (2H, d, \(J = 7.2\) Hz), 7.45 (1H, d, \(J = 7.6\) Hz), 7.63 (2H, m), 7.69 (1H, d, \(J = 8.0\) Hz), 8.01 (1H, d, \(J = 7.6\) Hz), 8.16 (1H, d, \(J = 8.0\) Hz), 9.16 (1H, d, \(J = 3.2\) Hz).\(^1\)C NMR (400 MHz, CDCl\(_3\), \(\delta\) in ppm): 168.6, 154.1, 149.9, 145.6, 144.9, 141.0, 136.2, 135.7, 129.3, 128.5, 128.2, 127.7, 127.1, 126.8, 125.7, 122.8, 121.9, 37.6, 20.5.

**Results and discussion**

**Crystal structures and stability constants**

All of the crystal structures discussed in this manuscript are accessible from the Cambridge Structural Database (see the Acknowledgments). In this study, [Ln(Bpy)\(_2\)(NO\(_3\))\(_3\)] and [Ln(Phen)\(_2\)(NO\(_3\))\(_3\)] were investigated, as depicted in Fig. 3. In both cases, each Ln ion is coordinated by the four nitrogen atoms of two Bpy or Phen ligands and the six oxygen atoms of three nitrate units. The crystallographic data for [Ln(Bpy)\(_2\)(NO\(_3\))\(_3\)] and [Ln(Phen)\(_2\)(NO\(_3\))\(_3\)] are summarized in Tables 1 and 2; the single asterisks on some of the element symbols indicate that the data could not be obtained in these cases owing to limitations of the single crystals, such as being too small or fragile. The space groups and Z values were the same throughout the Ln series, the lattice parameters were very similar, and the quality of the crystals was good. In both the cases of Bpy and Phen, total coordination numbers were 10 for every crystal.

In the case of MeTol-PTA, the composition ratios differed depending on the size of the Ln ion, as depicted in Fig. 4 and summarized in the crystal data listed in Table 3. The double asterisk in Table 3 indicates that the crystal quality was not good but remained usable. When the ionic radius was large, as
in the case of Ce, 6 nitrate oxygens (i.e., three bidentate nitrates) coordinated to form \([\text{Ce}(\text{PTA})_2(\text{NO}_3)_3]\), namely, the total coordination number was 12, but for the other heavier Ln ions except Nd, 4 nitrate oxygens (i.e., two bidentate nitrates and one monodentate nitrate) coordinated with Ln to form \([\text{Ln}(\text{PTA})_2(\text{NO}_3)_2]\), namely, the total number of coordination was 10. This difference makes the space group of the Ce complex distinct from the others. In the case of Nd, \([\text{Nd}(\text{PTA})_2(\text{NO}_3)_2]\) and \([\text{Nd}(\text{PTA})(\text{NO}_3)_4]\) complexes were packed in the same crystal, namely, the total coordination number for both complexes were 11. This may also be attributable to the ionic size. From the stoichiometry of the

![Figure 3. Structures of complexes in single crystals: (a) Ln–Bpy–nitrate and (b) Ln–Phen–nitrate.](image)

| Table 1. Crystallographic data for the Ln–Bpy–nitrate complexes. |
|---------------------------------------------------------------|
| **Composition ratio**                                       |
| Ln | Ligand | Nitrate | Space group | Z value | a [Å] | b [Å] | c [Å] | R₁ | wR₂ |
|-----|--------|---------|-------------|---------|-------|-------|-------|----|-----|
| La* | 2      | 1       | 3           | Pbcn    | 4     | –     | –     | –  | –   |
| Ce* | –      | –       | –           | –       | –     | –     | –     | –  | –   |
| Pr  | 16.976 | 9.199   | 15.024      | 0.0322  | 0.0139|
| Nd  | 16.915 | 9.175   | 14.987      | 0.0238  | 0.0473|
| Sm  | 16.826 | 9.1759  | 15.038      | 0.0304  | 0.0774|
| Eu* | –      | –       | –           | –       | –     | –     | –     | –  | –   |
| Gd* | –      | –       | –           | –       | –     | –     | –     | –  | –   |
| Tb  | 16.699 | 9.155   | 15.034      | 0.0232  | 0.0332|
| Dy  | 16.670 | 9.154   | 15.049      | 0.0355  | 0.0526|
| Ho  | 16.639 | 9.143   | 15.035      | 0.0253  | 0.0297|
| Er  | 16.602 | 9.1376  | 15.049      | 0.0224  | 0.0190|
| Tm  | 16.551 | 9.024   | 14.984      | 0.0214  | 0.0230|
| Yb  | 16.544 | 9.1086  | 15.066      | 0.0213  | 0.0387|
| Lu* | –      | –       | –           | –       | –     | –     | –     | –  | –   |

| Table 2. Crystallographic data for the Ln–Phen–nitrate complexes. |
|---------------------------------------------------------------|
| **Composition ratio**                                       |
| Ln | Ligand | Nitrate | Space group | Z value | a [Å] | b [Å] | c [Å] | β [°] | R₁ | wR₂ |
|-----|--------|---------|-------------|---------|-------|-------|-------|-------|----|-----|
| La | 2      | 1       | 3           | C2/c    | 4     | 11.360| 18.39 | 13.26 | 100.17| 0.0796 | 0.1479 |
| Ce | 11.207 | 18.151 | 13.123      | 100.564 | 0.0227 | 0.0607|
| Pr | 11.205 | 18.098 | 13.104      | 100.549 | 0.0684 | 0.1109|
| Nd | 11.194 | 18.072 | 13.088      | 100.540 | 0.0451 | 0.0926|
| Sm | 11.226 | 18.068 | 13.110      | 100.629 | 0.0299 | 0.0318|
| Eu | 11.181 | 17.995 | 13.056      | 100.589 | 0.0765 | 0.1669|
| Gd*| –      | –       | –           | –       | –     | –     | –     | –  | –   |
| Tb*| –      | –       | –           | –       | –     | –     | –     | –  | –   |
| Dy*| –      | –       | –           | –       | –     | –     | –     | –  | –   |
| Ho | 11.149 | 17.877 | 13.000      | 100.606 | 0.0575 | 0.1003|
| Er*| –      | –       | –           | –       | –     | –     | –     | –  | –   |
| Tm | 9.463  | 15.538 | 17.079      | 93.435  | 0.0278 | 0.0320|
| Yb*| –      | –       | –           | –       | –     | –     | –     | –  | –   |
| Lu*| –      | –       | –           | –       | –     | –     | –     | –  | –   |
complexes, it is clear that larger ions can allow more oxygen atoms to coordinate, but for smaller Ln, there is not sufficient surface area to coordinate with six oxygens. These differences should have an impact on the coordination strength, that is, the stability constant (log $\beta$).

### Table 3. Crystallographic data for the Ln–MeTol–PTA–nitrate complexes.

| Composition ratio | Ln | Ligand | $\text{NO}_3^-$ (2-O) | $\text{NO}_3^-$ (1-O) | Space group | $Z$ value | $a$ [Å] | $b$ [Å] | $c$ [Å] | $\alpha, \beta, \gamma$ [°] | $R_1$ | wR$_2$ |
|-------------------|----|--------|-----------------------|-----------------------|-------------|-----------|--------|--------|--------|---------------------|-------|-------|
| $\text{La}^*$    | 1  | –      | –                     | –                     | –           | –         | –      | –      | –      | –                   | –     | –     |
| $\text{Ce}$      | 1  | 2      | 3                     | 0                     | $P21/c$     | 4         | 12.741 | 21.980 | 15.182 | $\beta$: 89.071  | 0.1357 | 0.3505 |
| $\text{Pr}^*$    | 1  | –      | –                     | –                     | –           | –         | –      | –      | –      | –                   | –     | –     |
| $\text{Nd}^{**}$ | 1  | 1      | 4                     | 0                     | $P-1$       | 4         | 14.998 | 17.240 | 18.908 | $\alpha$: 63.592  | 0.1465 | 0.3996 |
|                   | 1  | 2      | 2                     | 0                     |             |           |        |        |        | $\beta$: 66.995  |       |       |
| $\text{Sm}$      | 1  | 2      | 2                     | 0                     | $P-1$       | 2         | 13.018 | 13.719 | 13.722 | $\gamma$: 66.012 | 0.1419 | 0.1508 |
| $\text{Eu}$      | 1  | 2      | 2                     | 0                     | $P-1$       | 2         | 13.072 | 13.769 | 13.769 | $\alpha$: 91.181  | 0.0766 | 0.1987 |
| $\text{Gd}$      | 1  | 2      | 2                     | 0                     | $P-1$       | 2         | 13.010 | 13.683 | 13.680 | $\beta$: 106.761 | 0.0661 | 0.1769 |
| $\text{Tb}$      | 1  | 2      | 2                     | 0                     | $P-1$       | 2         | 13.042 | 13.726 | 13.719 | $\gamma$: 91.461  | 0.0694 | 0.1823 |
| $\text{Dy}$      | 1  | 2      | 2                     | 0                     | $P-1$       | 2         | 13.133 | 13.806 | 13.801 | $\alpha$: 91.459  | 0.0826 | 0.0986 |
| $\text{Ho}^*$    | –  | –      | –                     | –                     | –           | –         | –      | –      | –      | –                   | –     | –     |
| $\text{Er}^*$    | –  | –      | –                     | –                     | –           | –         | –      | –      | –      | –                   | –     | –     |
| $\text{Tm}^*$    | –  | –      | –                     | –                     | –           | –         | –      | –      | –      | –                   | –     | –     |
| $\text{Yb}^*$    | –  | –      | –                     | –                     | –           | –         | –      | –      | –      | –                   | –     | –     |
| $\text{Lu}^*$    | –  | –      | –                     | –                     | –           | –         | –      | –      | –      | –                   | –     | –     |

Figure 4. Structures of the Ln–MeTol–PTA–nitrate complexes: (a) three nitrates coordinating via two oxygens each, (b) two nitrates coordinating via two oxygens each and one nitrate coordinating via one oxygen, and (c) mixture of 1:1 and 1:2 complexes for Nd.
Figure 5 shows the dependences of the bonding distances in the crystal states (first y axis) and the stability constants for the complexes with a 1:2 Ln-ligand ratio (second y axis) on the Ln ionic radius. For fitting the UV spectra, the log $\beta$ values for the 1:1 and 1:2 complexes were used and those for the 1:3 complexes were not used, because these conditions afforded the best fit for all ligands. In the figures, only the log $\beta$ values for the 1:2 Ln-ligand complexes are shown, since the log $\beta$ values for the 1:1 Ln-ligand complexes showed the same trend as for the 1:2 complexes but the values were much smaller. For Bpy and Phen, the Ln–N distance decreased with decreasing Ln ionic radius, regardless of the ligand. The changes in the Ln–N(Bpy) and Ln–N(Phen) distances were almost the same as the change in the ionic size. Simultaneously, the value of log $\beta$ increased with decreasing Ln ionic radius. This indicates that the interactions between Bpy or Phen and Ln can be mainly ascribed to electrostatic interactions based on the ionic size. In contrast, MeTol-PTA showed a different tendency. For lighter Ln ions such as Ce, the Ce–N (MeTol-PTA) and Ce–O (MeTol-PTA) distances were greater than expected for those for intermediate and heavier Ln ions. This can be explained by the ionic radius; while six oxygens from three nitrates and two oxygens from two MeTol-PTA and four nitrogen from two MeTol-PTA (total coordination number; 12) are able to coordinate with Ce due to the larger ionic surface, the smaller sizes of the intermediate and heavier Ln ions can only accommodate four oxygens from nitrates and two oxygens from MeTol-PTA and four nitrogen from two MeTol-PTA (total coordination number; 10) due to the smaller ionic surface. When a larger number of O atoms coordinate with Ce, the environment around the Ce becomes congested and the atoms cannot come closer to due to the complexity, which results in increased bonding distance and weaker interaction of Ce–O and Ce–N. Nd–MeTol-PTA crystal consisted of two different stoichiometries of complexes (total coordination number for the both stoichiometries were 11) as shown in Fig. 4b.

The order of atomic distances in the crystals was Ln–O (MeTol-PTA) < Ln–N (Bpy) < Ln–N (Phen) < Ln–N (MeTol-PTA). For MeTol-PTA, the Ln–O distances were shorter than the Ln–N distances owing to the difference in the ionic radii of O and N, and the change in Ln–N (MeTol-PTA) was more gradual than the change in Ln ionic radius (lanthanide contraction). In addition, the change in Ln–O (MeTol-PTA) was steeper than the change in Ln–N (Bpy) and Ln–N (Phen). As already mentioned, the Ln–N distances in the symmetrical Bpy and Phen decreased with the decreasing Ln ionic radius, and correspondingly the value of log $\beta$ increased. However, the log $\beta$ of MeTol-PTA showed a local maximum, unlike Bpy and Phen, indicating a selectivity for certain Ln ions. This is because the Ln–O (MeTol-PTA) coordination is stronger and the N cannot come closer as in the case of Bpy and Phen, due to the bulkiness of the rigid phenanthroline moiety unsymmetrically connected to the amide structure. From the following results, it was determined that there is an optimum arrangement that leads to the highest affinity with a specific Ln (in the case of MeTol-PTA, Nd exhibits the highest selectivity).

Figure 6 shows the relationships between the Ln ionic radius and (a) the N–Ln–N and N–Ln–O angles and (b) the Py–Py dihedral angle for Bpy and the O–C–N–C and O–C–C–N dihedral angles for MeTol-PTA (as indicated in Fig. 2). The unsymmetrical ligand MeTol-PTA and the symmetrical ligands Bpy and Phen exhibited slightly different tendencies. As shown in Fig. 6a, the N–Ln–N angles for Bpy and Phen simply increased with decreasing Ln ionic radius. For MeTol-PTA, the N–Ln–N angles were smaller than those for Bpy and Phen throughout the Ln series, because of the order of atomic distance, that is, Ln–N (Bpy, Phen) < Ln–N (MeTol-PTA).

As shown in Fig. 6b, the dihedral angle of the two pyridine rings in Bpy decreased almost linearly with decreasing Ln ionic radius to make the two pyridine rings flat. This indicates that Bpy can coordinate with Ln ions of different sizes by twisting the Py–Py dihedral angle, as depicted in Fig. 7a. As shown in Fig. 5a, a large change in log $\beta$ was observed during the transition from light to heavy Ln ions. The magnitude of this change in log $\beta$ was much greater for Bpy than for Phen. This may be attributable to the higher rotational freedom of the single C–C bond between the pyridine rings. In contrast, the dihedral angle of MeTol-PTA suggested that steric hindrance played an important role due to the bulkiness of the Phen and tolyl moieties, especially for Ln ions with large ionic radii (i.e., light Ln), as shown in Fig. 7b. In addition, local maxima were observed for both of the dihedral
angles in MeTol-PTA (O–C–N–C and N–C–C–O). The Ln ions with intermediate sizes exhibited a more twisted structure and the highest stability constants, as shown in Figs. 5b and 6b. Due to the additional degrees of freedom in the MeTol-PTA structure, its structural changes are not simple as in
the case of Bpy, but the detection of a local maximum dihedral angle indicates that there is an optimum arrangement of donor atoms in the molecule. To fully understand the relationship between the local maximum stability constants and dihedral angles, further studies such as DFT calculations may be needed. By substituting the functional groups in PTA (R and R’, Fig. 1c), it should be possible to tune the electronegativity of the donor atoms and the level of steric hindrance, allowing many factors to be altered. A systematic comparison of the complex structures and stability constants would then provide insights into the optimum molecular design and detailed mechanisms for the selective recognition and separation of specific f-block elements.

**Complex structure in solution by EXAFS measurements**

Figure 8 shows the RSFs for Bpy–Eu and MeTol-PTA–Eu in methanol with various Eu:ligand stoichiometric ratios. Eu and the ligands were mixed in a stoichiometric ratio of 1:4 to cause most of the complex to form a 1:2 stoichiometry, and theoretical fitting was then performed based on crystals of the 1:2 complexes. In the case of Bpy, the first peak of the RSF possessed an almost symmetrical shape as shown in Fig. 8a, which indicates a symmetrical complex structure. As a result of the replacement of
oxygen from the water of hydration with N (Bpy), the first peak was slightly shifted to a higher position due to the difference in ionic radius between O (water) and N (Bpy). The intensity of the second peak increased with an increasing amount of ligand, which indicated that this peak corresponded to the carbons adjacent to the pyridine nitrogens. In contrast, in the RSFs for MeTol-PTA, the shape of the first peak became unsymmetrical with an increasing amount of ligand in the methanol mixture, as shown in Fig. 8b, which indicated the different distances of Eu–N (MeTol-PTA) and Eu–O (MeTol-PTA). To elucidate the solution structures of the complexes in greater detail, the Ln:ligand complexes with a 1:2 stoichiometry were studied (Ln: Ce, Eu, Dy; ligand: Bpy, Phen, MeTol-PTA). The EXAFS oscillations in k-space and the RSFs are shown in Supplemental Information. The results of the theoretical fittings based on the crystal structures of the 1:2 complexes and the raw data for the Bpy–Eu, Phen–Eu, and MeTol-PTA–Eu complexes are presented in Fig. 9, while the coordination number, atomic distance, Debye–Waller factor ($\sigma^2$), and energy shift ($\Delta E_0$) calculated from the theoretical fitting are summarized in Table 4. According to the theoretical fittings, the same trends in terms of atomic distances were obtained: Ln–O (MeTol-PTA) < Ln–N (Bpy, Phen) < Ln–N (MeTol-PTA). In addition, the atomic distances in the single crystal are tabulated in Table 5 (numbers were extracted from Fig. 5a–b). By comparison of atomic distances in solution and crystal, atomic distances in solution were slightly longer than those in crystals due to the more intense thermal vibration in solution. Although the structures of complexes in crystals and organic solvents are not expected to be completely identical, the crystallographic data provided similar information to the solution EXAFS data in terms of the coordination behavior and complex structures.

**Conclusions**

To develop selective ligands for specific f-block elements, the relationships between complex structures and coordination strength were examined using crystallography, EXAFS, and UV spectroscopic titration. The structures of the Ln–ligand complexes in crystals and solution (methanol) were determined by crystallography and EXAFS, respectively, and the coordination strengths were estimated by measuring the stability constants ($\log \beta$ for Ln:ligand 1:2 complexes) by UV spectroscopic titration in methanol. In this study, two symmetrical N-donor ligands (2,2′-bipyridyl (Bpy) and 1,10-phenanthroline (Phen)) and an unsymmetrical N,O-hybrid donor ligand (N-methyl-N-tolyl-1,10-phenanthroline-2-carboxamide (MeTol-PTA)) were investigated. First of all, the difference in total coordination number was seen; 10 for every Bpy–Ln and Phen–Ln, 12 for MeTol-PTA–Ce, 11 for MeTol-PTA–Nd, and 10 for heavier
Lanthane than Nd. It was found that a decreasing Ln ionic radius led to decreases in the N−Ln (Bpy) and N−Ln (Phen) distances for both the single crystals and methanol solution samples. At the same time, log β increased linearly. This tendency was attributed to simple electrostatic interactions between Ln and Bpy or Phen. In contrast, MeTol-PTA showed more complex behavior. With decreasing Ln ionic radius, the change in the O−Ln (MeTol-PTA) distance was steeper and the N−Ln (MeTol-PTA) distance was greater. Furthermore, MeTol-PTA showed a local maximum in terms of log β (Nd), which indicates the selective recognition of a specific Ln. This was attributed to the stronger interaction of O and the bulky Phen moiety of MeTol-PTA, which did not allow the Ln ions to interact in a closer

![Radial structural functions Ln:ligand complexes with a stoichiometry of 1:2 (Ln: Ce, Eu, Dy; ligand: (a) Bpy, (b) Phen, (c) MeTol-PTA).](image)

Table 4. Results of theoretical fitting.

| Complex      | Shell                          | C.N. | R/Å  | σ²    | ΔE₀   |
|--------------|--------------------------------|------|------|-------|-------|
| Ce−Bpy       | Ce−O(NO₃ or H₂O)                | 6    | 2.52 | 0.0047| 9.2   |
|              | Ce−N(Bpy)                      | 4    | 2.67 | 0.0001| 9.2   |
|              | Ce−C(Bpy)                      | 8    | 3.58 | 0.0093| 9.2   |
| Ce−Phen      | Ce−O(NO₃ or H₂O)                | 6    | 2.52 | 0.1057| 7.4   |
|              | Ce−N(Phen)                     | 4    | 2.68 | 0.0020| 7.4   |
|              | Ce−C(Phen)                     | 8    | 3.57 | 0.0055| 7.4   |
| Ce−MeTol-PTA | Ce−O(PTA, NO₃, or H₂O)         | 8    | 2.53 | 0.0105| 5.3   |
|              | Ce−N(MeTol-PTA)                | 4    | 2.69 | 0.0022| 5.3   |
|              | Ce−C(MeTol-PTA)                | 10   | 3.55 | 0.0106| 5.3   |
| Eu−Bpy       | Eu−O(NO₃ or H₂O)                | 6    | 2.45 | 0.0053| 12.4  |
|              | Eu−N(Bpy)                      | 4    | 2.61 | 0.0022| 12.4  |
|              | Eu−C(Bpy)                      | 8    | 3.53 | 0.0065| 12.4  |
| Eu−Phen      | Eu−O(NO₃ or H₂O)                | 6    | 2.44 | 0.0020| 11.4  |
|              | Eu−N(Phen)                     | 4    | 2.60 | 0.0005| 11.4  |
|              | Eu−C(Phen)                     | 8    | 3.52 | 0.0060| 11.4  |
| Eu−MeTol-PTA | Eu−O(PTA, NO₃, or H₂O)         | 6    | 2.46 | 0.0067| 12.6  |
|              | Eu−N(MeTol-PTA)                | 4    | 2.63 | 0.0015| 12.6  |
|              | Eu−C(MeTol-PTA)                | 10   | 3.51 | 0.0082| 12.6  |
| Dy−Bpy       | Dy−O(NO₃ or H₂O)                | 6    | 2.41 | 0.0039| 10.7  |
|              | Dy−N(Bpy)                      | 4    | 2.57 | 0.0001| 10.7  |
|              | Dy−C(Bpy)                      | 8    | 3.47 | 0.0056| 10.7  |
| Dy−Phen      | Dy−O(NO₃ or H₂O)                | 6    | 2.41 | 0.0069| 8.3   |
|              | Dy−N(Phen)                     | 4    | 2.55 | 0.0001| 8.3   |
|              | Dy−C(Phen)                     | 8    | 3.44 | 0.0054| 8.3   |
| Dy−MeTol-PTA | Dy−O(PTA, NO₃, or H₂O)         | 6    | 2.40 | 0.0061| 10.4  |
|              | Dy−N(MeTol-PTA)                | 4    | 2.58 | 0.0012| 10.4  |
|              | Dy−C(MeTol-PTA)                | 10   | 2.46 | 0.0061| 10.4  |
position to the N as in the case of Bpy and Phen. The same trends in terms of atomic distances were observed by crystallography and EXAFS: Ln–O (MeTol-PTA) < Ln–N (Bpy, Phen) < Ln–N (MeTol-PTA). This result strongly supported the discussion earlier. In terms of dihedral angles, Bpy could coordinate with Ce by twisting its pyridine–pyridine dihedral angle to accommodate the ionic size, but MeTol-PTA exhibited a local maximum dihedral angle, which also demonstrates the existence of an optimum arrangement of donor atoms and steric structure in the ligands for specific Ln recognition. To further elucidate the relationship between the structure and coordination strength of these complexes, additional ligands with a variety of structures should be examined, and DFT calculations may be effective. A systematic comparison of the structures and stability constants should provide detailed insights into the optimum molecular design and coordination mechanism to enable the selective recognition and separation of specific f-block elements.

Acknowledgments

The EXAFS experiments were performed at SPring-8, beamline BL11XU, research number 3508 (2014B, 2015A, 2015B) and 3504 (2016A).

“*The crystal structures discussed in this study can be obtained from the Cambridge Structural Database under the following entries: 1817238–1817244, 1817244–1817244, 1818234–181824.

Funding

This research was supported by the Japan Society for the Promotion of Science through a Grant-in-Aid for JSPS Fellowship (research number: 26-202), a Grant-in-Aid for Young Researchers (B) (16K18351), and a Grant-in-Aid for Overseas Research (H404).

ORCID

Masahiko Nakase http://orcid.org/0000-0002-3748-0373
Bruce J. Mincher http://orcid.org/0000-0003-3108-2590

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| Table 5. Atomic distance in single crystals. |
| Ln-N | Phen | Bpy | MeTol-PTA (short) | MeTol-PTA (long) |
| Ln-O | MeTol-PTA |
| Ce | 2.64 | – | 2.78 | 2.82 | 2.61 |
| Eu | 2.57 | – | 2.65 | 2.66 | 2.39 |
| Dy | – | 2.516 | 2.62 | 2.65 | 2.36 |
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