# Novel Separation System of Trivalent Actinides-combined Effects of Substituted Tris(2-pyridylmethyl)amine Ligand and Hydrophobic Counter-anion

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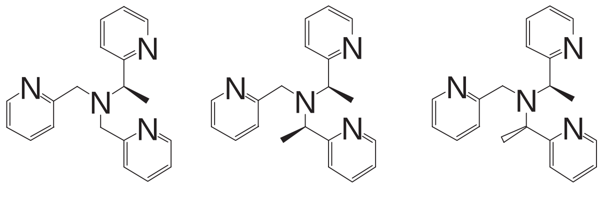
Stereochemical substitution on tripod ligand significantly offered efficient separation of trivalent actinides from trivalent lanthanides. Liquid–liquid extraction using chiral tris(2-pyridylmethyl)amine ligands as an extractant exhibited high efficiency and selectivity for trivalent actinides. A combination of chiral ligand and 2-bromodecanoic acid further enhanced extraction performance for trivalent actinides.

In biological systems, a cation is precisely recognized by a ligand such as a natural ionophore in which chiral substituents on the ligand give effective conformation for coordinating to a specific cation.[1] Thus, designing a bio-inspired ligand as a cation-specific ionophore has promising possibilities in developments of ion sensing as well as the precise separation.[2]

Some synthetic chiral ionophores have successfully demonstrated that the chirality of the ligand well operated in recognition of achiral anions and metal cations. Tridentate pyridine podands, bis(2-pyridylmethyl) 2,6-pyridinedicarboxylate derivatives, which have chirality on the methylene group of the terminal pyridyl groups, exhibited the enhanced stability constants for the Ag(I) complexation.[3] The chiral tris(pyridylmethyl)amines (Figure 1) also offered the luminescence enhancement of Eu(III) and Tb(III).[4]

Separation of trivalent actinides [An(III)] from trivalent lanthanides [Ln(III)] is one of the most challenging endeavors in analytical and separation science, because of the similarity of their chemical properties. One promising approach is to use a soft-donor ligand based on its preferable coordination to softer An(III). Some sulphur donor ligands significantly separated An(III) from Ln(III), and nitrogen-donor ligands further have practical advantage due to their combustibility.[5–8]

Tripodal pyridine ligand is one of the promising ligand systems for effective separation of An(III). For example, liquid–liquid extraction with tris(pyridylmethyl)amine (**tpa**) and tris(pyrazylmethyl)amine (**tpza**) was reported to exhibit the selectivity of An(III) over Ln(III).[9] Taking the advantage of chiral nitrogen-donor ligands for the separation of An(III) from Ln(III), we develop below the liquid–liquid extraction of An(III) from Ln(III) using chiral tris(pyridylmethyl)amines, (*R*)-**1**, (*R*,*R*)-**2**, and (*R*,*S*)-**2**, as shown in Figure 1.[10] This novel separation system remarkably exhibited high selectivity to the An(III) over Ln(III) driven by chiral ligands and hydrophobic counter anions.



(*R*)-**1** (*R*, *R*)-**2** (*R*, *S*)-**2**

**Figure 1.** Structures of chiral tripod ligands.

**Table 1.** Distribution ratio of Am(III) and Eu(III) with chiral ligands and various counter anions[a]

| Counter anion | Ligand | pH | Distribution ratio | |
|---|---|---|---|---|
| | | | Am(III) | Eu(III) |
| **Pic** | (*R*)-**1** | 4.73 | 1.86 | 0.23 |
| | (*R*,*R*)-**2** | 4.73 | 0.077 | 0.0068 |
| | (*R*,*S*)-**2** | 4.71 | 0.0048 | 0.00037 |
| **Dec** | (*R*)-**1** | 4.70 | 0.12 | 0.011 |
| | (*R*,*R*)-**2** | 4.70 | 0.019 | 0.0011 |
| | (*R*,*S*)-**2** | 4.74 | 0.044 | 0.0018 |
| **Br-Dec** | (*R*)-**1** | 4.76 | 52.3 | 5.42 |
| | (*R*,*R*)-**2** | 4.78 | 14.2 | 0.67 |
| | (*R*,*S*)-**2** | 4.76 | 26.8 | 0.95 |

[a] $1.0 \times 10^{-2}$ M of ligand, $1.0 \times 10^{-2}$ M of picric acid, $1.0 \times 10^{-2}$ M of decanoic acid, $1.0 \times 10^{-2}$ M of 2-bromodecanoic acid in nitrobenzene and $I = 1.0 \times 10^{-1}$ M $NaNO_3$.

To assess the effects of the ligand substitution on the separation of An(III),[11] a combination of tripod ligands with three different types of counter anions, picric acid (**Pic**), decanoic acid (**Dec**), and 2-bromodecanoic acid (**Br-Dec**), were investigated which are highly hydrophobic enough to promote liquid–liquid extraction. Table 1 shows the distribution ratios of Am(III) and Eu(III) with chiral tripod ligands in conjunction with three hydrophobic counter anions. In each case, the distribution ratio of Am(III) was higher than that of Eu(III). This tendency reflects the fact that these chiral tripod ligands favour Am(III) to Eu(III). It was observed that the distribution ratio of Am(III) and Eu(III) with the mono-substituted (*R*)-**1** was higher than those with di-substituted (*R*,*R*)-**2** and (*R*,*S*)-**2**. Since the distribution ratio of Eu(III) with **tpa** and **dec** was remarkably high, 0.25, at pH 5.18 under a similar condition to Table 1, the ligand substitution would depress the extractability of An(III) and Ln(III). It was reported that the stability constants of lanthanide complexes with these substituted ligands were almost the same.[4c] The difference in distribution ratios, therefore, might be due to solvation or solubility of extracted complexes in the organic phase. When **Pic** or **Dec** was used, the distribution ratios were relatively small, but the increased distribution ratio was observed with **Br-Dec**. Since it was reported that the three ligands

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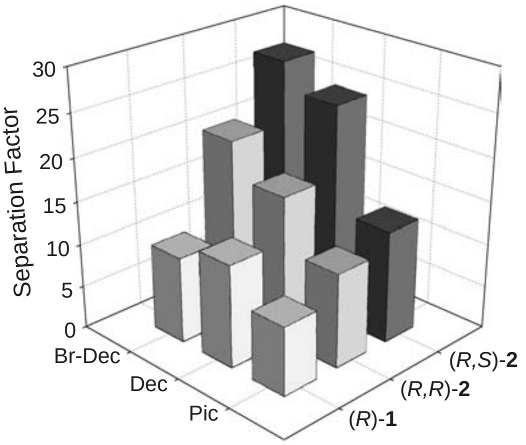

**Figure 2.** Separation factors between Am(III) and Eu(III).

participated in the extraction of An(III) and Ln(III) by means of **tpa** and **Br-Dec**, similar extraction equilibria of An(III) and Ln(III) were presumed in these substituted ligand systems.[9] These suggest that an optimum separation system could be composed by the combination of substituted ligands and counter anions.

Figure 2 shows the comparison of the separation factors (SFs)[12] between Am(III) and Eu(III) with chiral tripod ligands, which are higher than 10 in all the cases. Since SFs with **tpa** and **tpza** were reported as 1.9 and 10, these chiral ligand systems are auspicious to separate An(III) from Ln(III). The SFs observed with (*R*,*R*)-**2** and (*R*,*S*)-**2** are much higher than that with (*R*)-**1** in the presence of three counter anions. In particular, meso isomer of di-substituted tris(pyridylmethyl)amine, (*R*,*S*)-**2**, reduced the extractability of An(III) and Ln(III), but remarkably enhanced the selectivity to An(III) over Ln(III). The ligand substitution apparently provided a favorable coordination to Am(III) than to Eu(III). The extractability of the di-substituted ligand was improved by the proper choice of counter anions. The SFs increased in order as follows: **Pic** < **Dec** < **Br-Dec**. Since **Br-Dec** was the most efficient counter anion for selective extraction of Am(III), a proper combination of highly substituted nitrogen donor ligand and hydrophobic counter anion offered efficient separation system of An(III) from Ln(III). Further experiments on the elucidation of the liquid–liquid extraction of An(III) and Ln(III) and structural studies of extracted complexes are in progress.

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10 Synthesis and characterization of these chiral ligands: see Ref. 4c. Their stereochemical purity was determined to be >95%.

11 A general procedure for liquid–liquid extraction: Am(III) and Eu(III) were used for evaluation of separation as a representative of An(III) and Ln(III), respectively, because of experimental convenience. An aqueous solution containing both ca. $10^{-8}$ mol dm$^{-3}$ $^{241}$Am(III) and $^{152}$Eu(III) and $(1.0–4.0) \times 10^{-2}$ mol dm$^{-3}$ counter anion was shaken with an equal volume of organic solution containing $(1.0–20) \times 10^{-2}$ mol dm$^{-3}$ tris(pyridylmethyl)amines ligand ((*R*)-**1**, (*R*,*R*)-**2**, or (*R*,*S*)-**2**) for 10 min at pH 4.70–4.78 and $25.0 \pm 0.5$ °C. The adjustment of ionic strength ($I$) of the aqueous phase was kept constant at $1.0 \times 10^{-1}$ mol dm$^{-3}$ using sodium nitrate. After phase separation, the pH of the aqueous phase was measured with a glass electrode. An aliquot of each phase was taken out and the $\gamma$ activity was measured at 59.6 keV for $^{241}$Am and 122 keV for $^{152}$Eu with a high purity Ge detector. The distribution ratio ($D$) of Am(III) and Eu(III) was calculated from the counting rates.

12 The separation factor is defined by $D_{\mathrm{Am}}/D_{\mathrm{Eu}}$.

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