**Understanding behavior of nitrate and water in first coordination shell of lanthanide complexes from the Cambridge Structure Database**

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**Abstract**

**Introduction**

**Methods**

**Results and Discussion**

**Available complex structures across the lanthanide series**



**Figure 1.** Distribution of the 49472 crystal structures of Subset 1 (all Ln complexes) and the 27858 crystal structures of Subset 2 (mononuclear Ln complexes) from the Cambridge Structural Database over the Ln series.

**Coordination number and first shell distance**

A group of graphs with red and blue lines

Description automatically generated

**Figure 2.** Average coordination number and distance of the first coordination shell of Ln complexes in Subset 1 (green), Subset 2 (red) and Subset 3 (blue; structures in subset 2 but without the cyclopentadienyl ligand; 26156 structures) across the Ln series: (a) Average coordination number for Subsets 1 and 2; (b) Average distance of the first coordination shell for Subsets 1 and 2; (c) Average coordination number for Subset 2 and 3; (d) Average distance of the first coordination shell for Subset 2 and 3. Standard deviations are shown as the error bars. We count the contribution of each cyclopentadienyl ligand to the coordination number as three.

A group of bars with different colors

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**Figure 3.** Distribution of the coordination numbers for each Ln ion of structures in Subset 2 and Subset 3: (a) Pr; (b) Nd; (c) Eu; (d) Dy. The complete set can be found in Figure S1 in the SI.

**Donor types, ligand types, and denticities in the complexes**



**Figure 4.** Breakdown of donor types in the first coordination shell for each Ln element in Subset 2. Other elements include H, P, S, F, Cl, Br, and I.



**Figure 5.** Ligand types in the Ln complexes in Subset 1: complexes with all-organic ligands (purple); complexes with mixed inorganic-organic ligands (green); complexes with all-inorganic ligands (orange).

A graph of different colored lines

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**Figure 6.** Breakdown of the O donor types in the first coordination shell for each Ln element in Subset 2: (a) organic O donors (O-X-R means that an X atom connected to the O donor to Ln); (b) inorganic O donors (POM – polyoxometalate).



**Figure 7.** Breakdown of the O-C-R type of ligands in the first coordination shell for each Ln element in Subset 2.



**Figure 8.** Denticity analysis of ligands in the first coordination shell for each Ln element in Subset 2.

**Distribution of commercial complexants**

A graph of different structures

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**Figure 9**. Ln complexes in Subset 1 with selected commercial complexants: (a) selected commercial complexants; (b) distribution over the ligands; (c) distribution across the Ln series (top 3 complexant types).

A group of molecules with lines and dots

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**Figure 10**. Selected Ln complexes with commercial complexants: (a) Lu complex with a phosphoric acid ligand; (b) Eu complex with a phosphinic acid ligand; (c) Dy complex with a versatic acid ligand.

**Phenanthroline and phenanthroline-based ligands**

In examining the complexes with all-organic ligands and mixed inorganic-organic ligands, we have found many Ln complexes with 1,10-phenanthroline (phen) as a ligand. In addition, phen derivatives are actively explored as new ligands for REE separation processes. Subset 4 (2226 structures in total), created from Subset 1, contains Ln-complexes with at least one phen-based ligand. Figure 11 shows the distribution over the phen ligand types within Subset 4: one can see that the majority (1721 structures or 77%) incorporate the phen ligand itself – highlighting its dominance. A distant second is phen derivatives with imidazo/pyrazino groups that extend the conjugation, followed by substituted phen ligands. We further examined the stoichiometry of the phen ligand or its derivative to the Ln center. As can be seen from Figure 12, the majority of the complexes have 1:1 ligand-to-metal ratio, followed by 2:1; in contrast, 3:1 and 4:1 complexes are rare. This trend is consistent across the Ln series. The dominance of the 1:1 complexes has important implications in designing and employing these ligands for REE separations.

A graph of chemical formulas

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**Figure 11**. Distribution of Ln complexes in Subset 4 based on the types of the phen and its derivatives: (a) phen; (b) imidazo/pyrazino; (c) substituted phen (R = carbon chain or halogen group); (d) amide; (e) carboxylate; (f) triazine/tetrazole; (g) phosphoryl.



**Figure 12.** Distribution of the Ln-complex structures in Subset 4 across the Ln series according to the phenanthroline ligand to the metal center ratio.

**Accuracy of the Ln-complex datasets based on the CSD structures**

**Conclusion**

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**Data and Software Availability**

Python scripts used within the CSD Python API and the resulting datasets from CSD associated with the figures in the text can be found in Github (<https://github.com/sheinlee/Ln-coordination-insights>)

**References**