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

Shicheng Li,1 Santa Jansone-Popova,2 and De-en Jiang1,\*

1Department of Chemical and Biomolecular Engineering, Vanderbilt University, Nashville, Tennessee 37235, United States

2Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, United States

\*To whom correspondence should be addressed. E-mail: de-en.jiang@vanderbilt.edu

**Abstract**

**Introduction**

**Methods**

**Results and Discussion**

**Available complex structures with nitrate or water in first coordination shell across the lanthanide series**



**Figure 1.** Distribution of 29891 crystal structures of subset2 (mononuclear Ln complexes), 8991 crystal structures of subset2w (Ln complexes with water in first shell) and 4209 crystal structures of subset2n (Ln complexes with nitrate in first shell).

**Modes of nitrate in first shell**



**Figure 2.** Distribution of 3673 crystal structures of subset2n\_org\_1 (nitrates in first shell have only mode: bidentate) and 167 crystal structures of subset2n\_org\_2 (nitrates in first shell have both two modes: monodentate and bidentate).

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



**Figure 3.** Distribution of 2905 crystal structures of subset2n\_no\_w\_org (nitrates but no water in first shell); 935 crystal structures of subset2n\_w\_org (both nitrates and water in first shell) ; 7509 crystal structures of subset2w\_no\_n\_org (water but no nitrates in first shell) .



**Figure 4.**  Average coordination number of the first coordination shell of Ln complexes in subset2n (blue) and subset2w (red) across the Ln series; Standard deviations are shown as the error bars.



**Figure 5.** Average ratio of nitrate/water in first coordination shell in subset2n\_w\_org across the Ln series; Standard deviations are shown as the error bars.

A comparison of different colored bars

Description automatically generated

**Figure 6.** Distribution of neutral first shell and non neutral first shell in (a)subset2n and (b)subset2w.

A group of red lines

Description automatically generated

**Figure 7.** Average net charge in first shell of Ln complexes in (a)subset2n (b)subset2w (c)subset2n\_non\_neutral (d)subset2w\_non\_neutral across the Ln series; Standard deviations are shown as the error bars.

**Distribution of commercial complexants**

**Phenanthroline and phenanthroline-based ligands**

**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**