**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**

Using the CSD Python-based applications programming interface (API), we have developed task-specific scripts to search and analyze downloaded CSD structures. Each script entailed the retrieval of structures with three-dimensional structural information from the CSD and the extraction of chemical information from these structures. The first script was to capture structures of Ln complexes with nitrate in the first coordination shell and to analyze different modes of these nitrates in first shell. The second script was to find structures of Ln complexes with water in the first coordination shell. The third script aimed to analyze the ratio of nitrate versus water in the first coordination shell. The fourth script was devised to explore the coordination number of the first coordination shell for Ln complex with nitrate or water like what we did in our scientific report paper. The fifth script was to find the net charge of the first shell.

**Results and Discussion**

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

After the elimination of erroneous entries and those lacking three-dimensional structural. Here we use the same script designed in previous paper to analyze CSD(version 2023) to get our new subset 1 (53370 crystal structures) and subset2 (29891 crystal structures). Based on the new subset2, we used script 1 and script2 to screen out 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).



**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 coordination 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).

**Distribution of complexes with Nitrate or water in first coordination shell**



**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) .

**Coordination number**



**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.

**Ratio of nitrate/water in first coordination shell**



**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.

**Distribution of neutral and non-neutral first shell**

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.

**Net charge of the first coordination shell**

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.

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

**Conclusion**

**Acknowledgments**

This material is based upon work supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, Separation Science program and Materials Chemistry program under Award Number DE-SC00ERKCG21.

**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/nitrate_and_water_in_csd>)

**References**