

# Enumeration and visualization of various subspaces of the octahedral complex space

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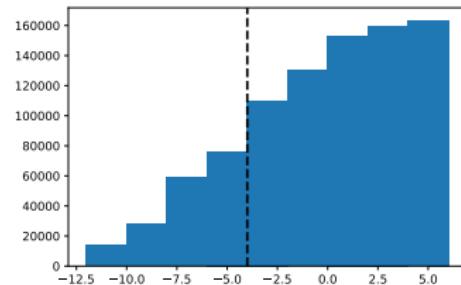
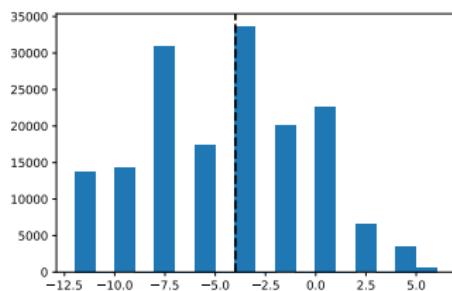
# Subsets of octahedral space

The sizes of the selected subsets of octahedral space.

| Set                     | description                                   | size                        |
|-------------------------|---|-----------------------------|
| Homoleptics             | $\text{eq} = \text{ax}$                       | 553                         |
| "5+1" symmetric         | $\text{eq} = \text{ax}_1 \neq \text{ax}_2$    | 163,620                     |
| "4+2" symmetric         | $\text{eq}_1 \neq \text{eq}_2 = \text{ax}$    | 185,376                     |
| Strongly symmetric      | $\text{eq} \neq \text{ax}$                    | 245,316                     |
| Equatorially asymmetric | $\text{eq}_1 \neq \text{eq}_2 \neq \text{ax}$ | 15,924,796                  |
| Weakly symmetric        | $\text{eq} \neq \text{ax}_1 \neq \text{ax}_2$ | 45,077,310                  |
| Complete Heteroleptics  | $L_i \neq L_j$                                | $\approx 5.9 \cdot 10^{12}$ |
| Octahedral Space        | all   | $> 1.8 \cdot 10^{14}$       |

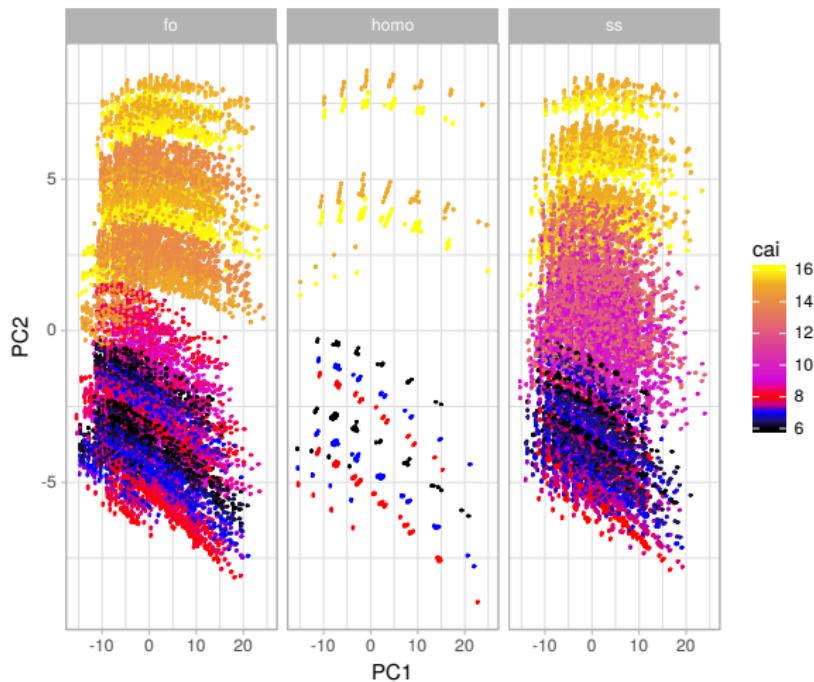
# Properties of the sets

- Reduce space to facilitate sampling from non-homoleptics
- Example: strongly symmetric, monodentate ligand fields (163,620)
- Exclude all with charge smaller than -4, which results in 87,150 ligand fields (53 %).



# Principal Component Analysis

The homoleptics (ho) span the strong symmetry (ss) and "5+1" (fo) set.



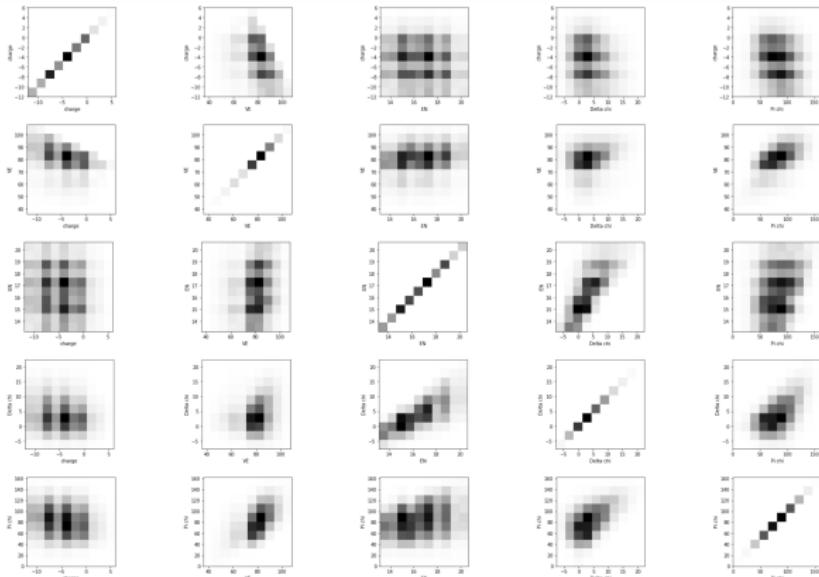
# Footprint and Entropy calculation

We use five properties to characterize the ligand field and generate a five dimensional distribution:

- total charge
- total valence electrons
- electronegativity of the connecting atom
- $\chi_{\text{ax,eq}}^{\text{lc}} = \sum EN_{\text{CA}} \cdot EN_i$
- $\chi'_{\text{ax,eq}}^{\text{lc}} = \sum EN_{\text{CA}} - EN_i$

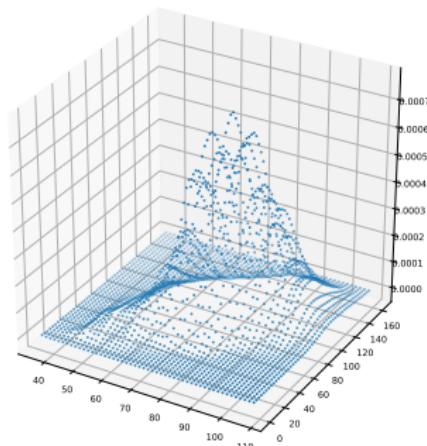
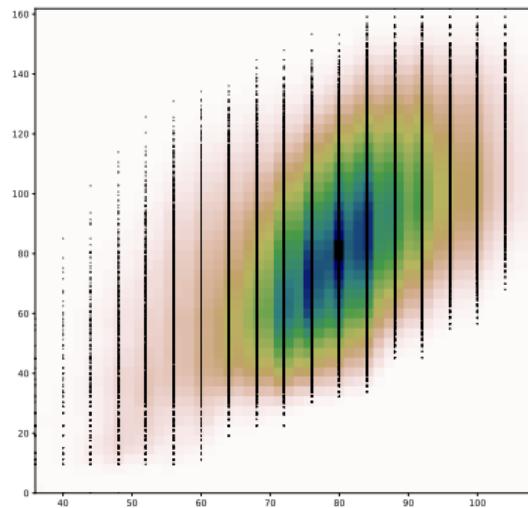
We then calculate the entropy,  $H_{\text{KDE}}$ , of the Kernel Density Estimated distribution.

# Correlation analysis for strongly symmetric monodentates



# Example of KDE slice

Dimensions  $\frac{lc}{ax, eq} \chi_1$  vs. charge in  $H_{KDE}$  for strongly symmetric monodentates.

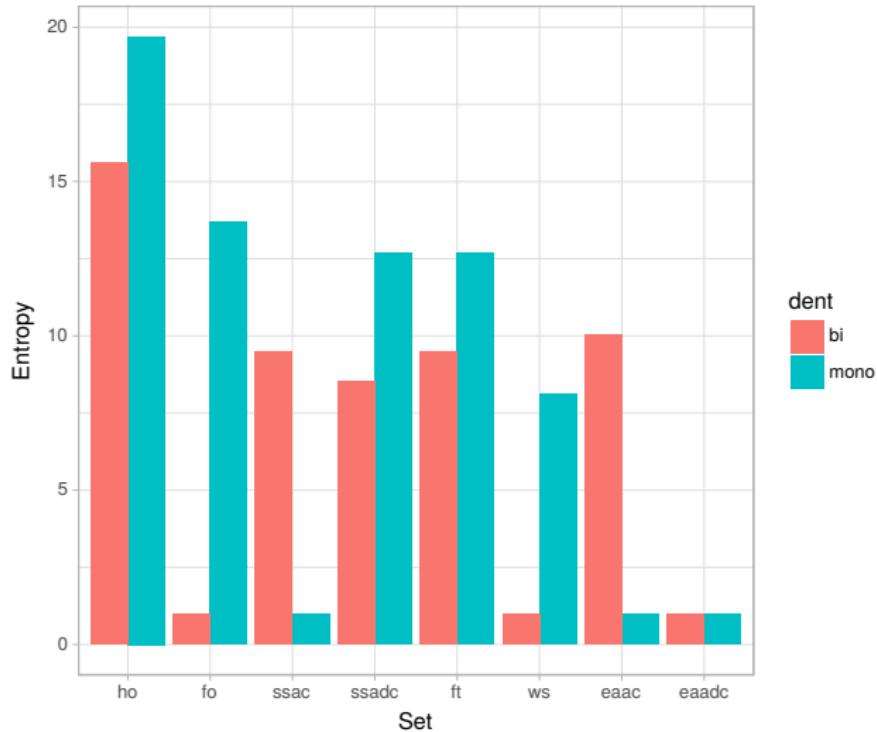


# Monodentate Footprints

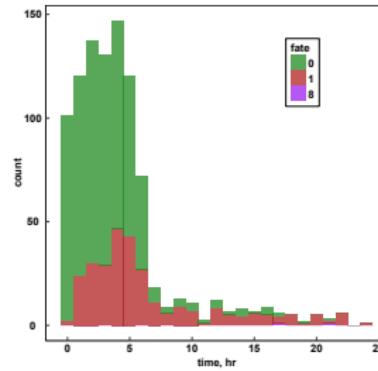
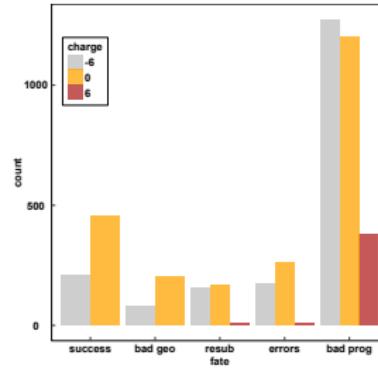
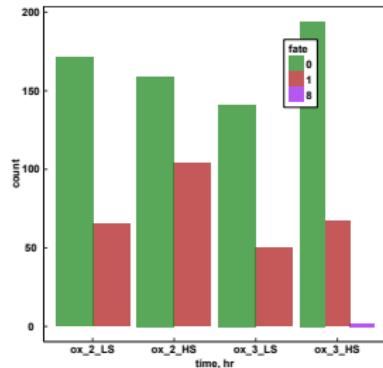
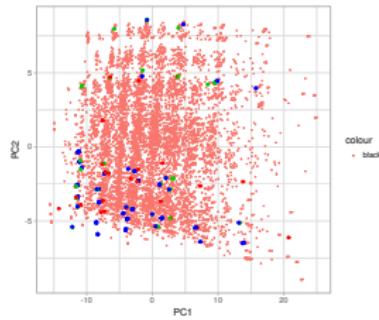
Table : Entropic footprint

| Set                         | $H_{\text{KDE}}^{\text{monodent}}$ | $H_{\text{KDE}}^{\text{bident}}$ |
|-----------------------------|------------------------------------|----------------------------------|
| Homoleptics                 | 19.7                               | 15.63                            |
| "5+1" symmetric             | 13.7                               | -                                |
| Strongly symmetric AC       | -                                  | 9.47                             |
| Strongly symmetric ADC      | 12.70                              | 5.53                             |
| "4+2" symmetric             | 12.70                              | 9.47                             |
| Weakly symmetric            | 8.1                                | 7.7                              |
| Equatorially asymmetric AC  | -                                  | 10.04                            |
| Equatorially asymmetric ADC |                                    |                                  |

# Entropy histogram



# Actual calculations



- 0:  $[NH_3]$ ,  $[N]\#[N]$ ,  $[C+]\#[O^-]$ ,  $[C+]\#[NH^-]$ ,  $[N]\#[CH]$
- 1:  $[CH_+] = [CH_3^-]$ ,  $[NH] = [O]$ ,  $[CH_+] = [OH^-]$ ,  $[CH_2^+] - [OH_2^-]$
- 8:  $[OH_2^-] - [PH^+]$ ,  $[P^+] = [OH^-]$ ,  $[PH^+] - [OH_2^-]$ ,  $[NH_2^-] = [CH^+]$