Shape and Symmetry of Coordination Polyhedra in Lanthanide Coordination Compounds

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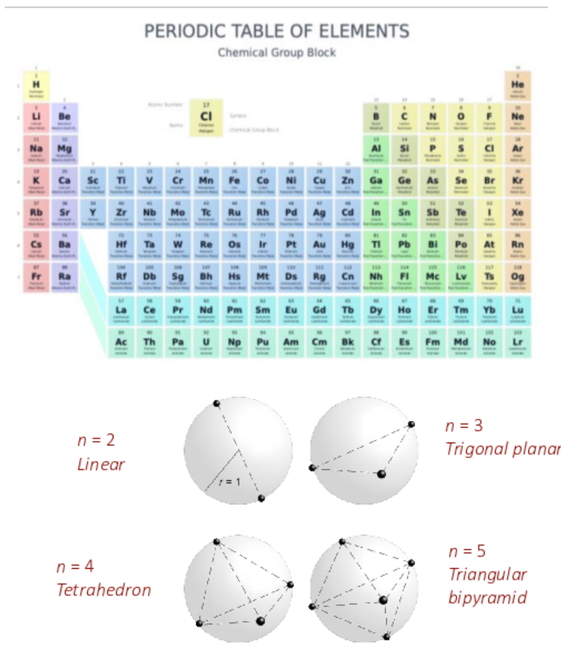
Introduction

Coordination Chemistry studies compounds formed by a central metal atom and ligands bounds to the metal through donor atoms.

***Coordination Polyhedron:** A three-dimensional figure that describes the spatial arrangement of donor atoms around the central metal.

***Thomson problem:** To determine the optimal arrangement of *n* identical electronic charges on the Surface of a sphere such that the electrostatic repulsion between them is minimized.



n = 2 *Linear*

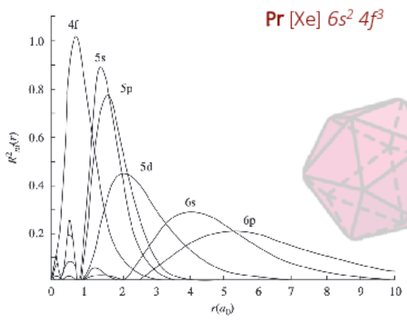
n = 3 *Trigonal planar*

n = 4 *Tetrahedron*

n = 5 *Triangular bipyramid*

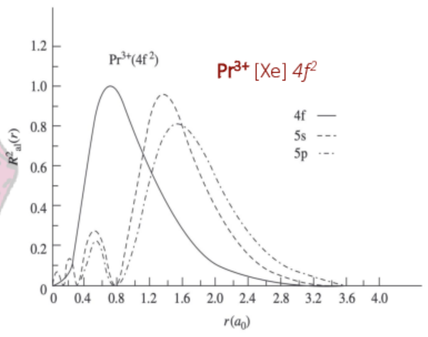
Lanthanide Electronic Structure

Pr [Xe] $6s^2\ 4f^3$

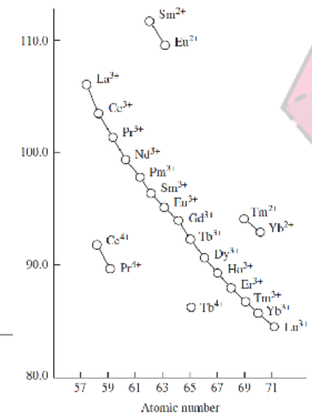


The inner f-electrons are not involved in directional covalent bonding

Pr^{3+} [Xe] $4f^2$



The *5s* and *5p* shells are partially shielded by the f-electrons



Lanthanide contraction

Computational details

Optimizations DFT B3LYP + ECP (Small Core)

ORCA

Analysis of experimental structure available at the CSD (*Cambridge Structural Database*)

CCDC The Cambridge Crystallographic Data Centre + Python Cosymlib library

$[Ln(H_2O)_n]^{3+}$ Models

Study of the stereochemical preferences for each lanthanide as a function of the coordination number

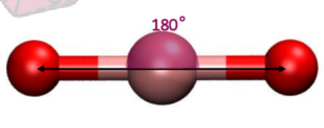
La Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu

How we design our models?

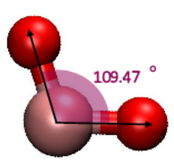
We select a coordination number of interest:

Coordination Number: **2**

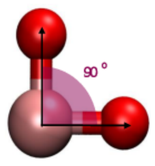
Symmetry types



Linear (L2)



Divacant tetrahedron (vT2)



Tetravacant octahedron (vOC)

We optimize

Search for the M-L distance that minimizes the system's energy

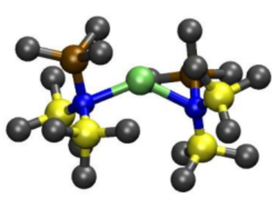
Data analysis and model construction of $[Ln(H_2O)_n]^{3+}$ with optimal M-L distances

Search in the CSD

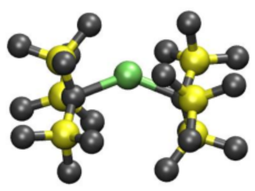
- Search in the CSD for Ln compounds with single, double, triple or quadruple bonds to atoms from groups 14-17 + H
- **Constrains**: Determined 3D coordinates, R ≤ 0.05, no disorder, no errors

Lanthanide: **Yb** Coordination number: **2** CSD Entries: **3**

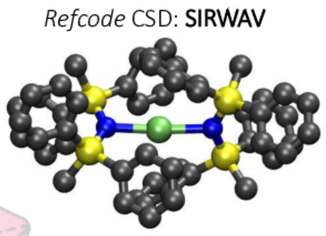
Refcode CSD: **CUBFIO**



Refcode CSD: **YIMZOJ**



Refcode CSD: **SIRWAV**



- ***Cosymlib* structural analysis**

To make the shape measure we consider an arbitrary shape (the CSD structure) $|Q\rangle$ and an ideal reference shape $|P\rangle$

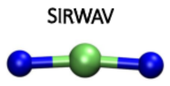
$$S(Q,P) = 100 \cdot \min\left(1 - \frac{\langle Q|P\rangle}{\langle Q|Q\rangle}\right)$$

Superposition between P and Q

Normalization factor

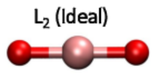
Minimization with respect to the relative position, orientation, and size of Q and P.

SIRWAV



Shape measure $S(L_2)$ = 0.2

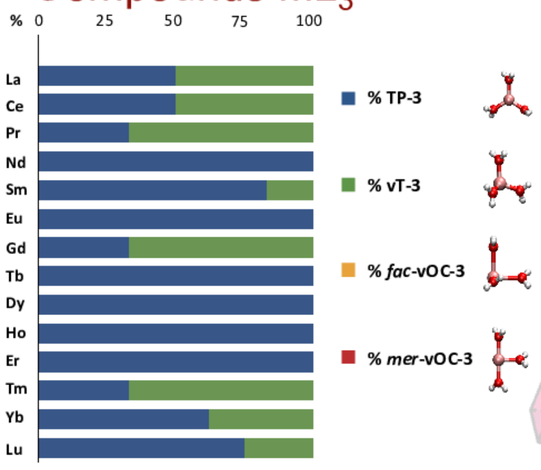
L_2 (Ideal)

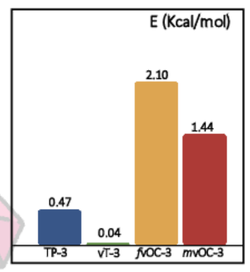


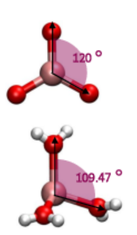
Shape measure $S(L_2)$ = 0.0

Results

Compounds ML_3



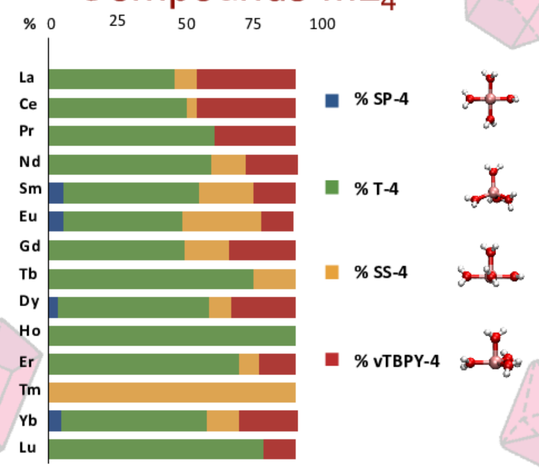


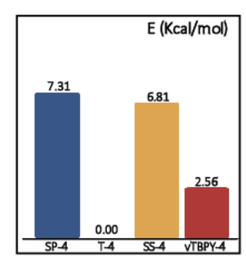


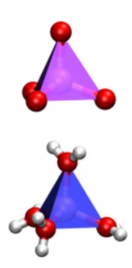
Thomson
TP-3
D_{3h}

$[Eu(H_2O)_3)]^{3+}$
vT-3
C_{3v}

Compounds ML_4



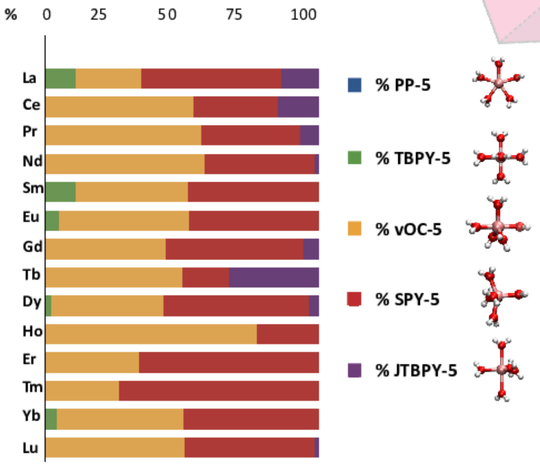


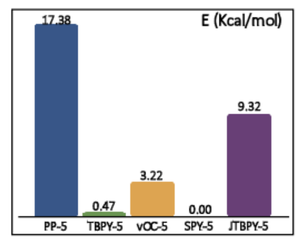


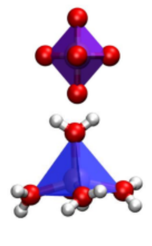
Thomson
T-4
T_d

$[Eu(H_2O)_4)]^{3+}$
T-4
T_d

Compounds ML_5



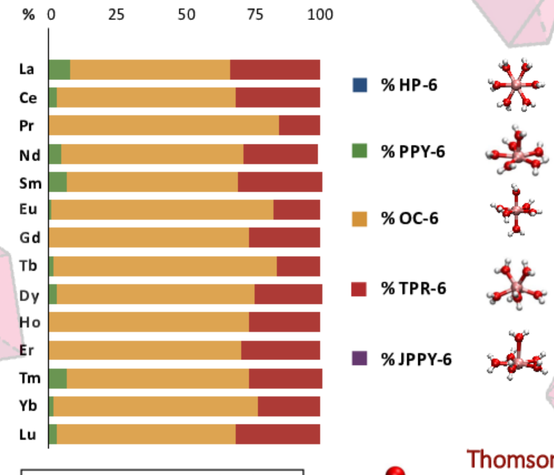


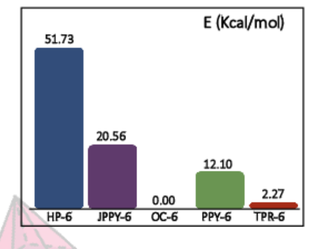


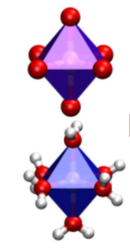
Thomson
TBPY-5
D_{3h}

$[Eu(H_2O)_5]^{3+}$
SPY-5
C_{4v}

Compounds ML_6



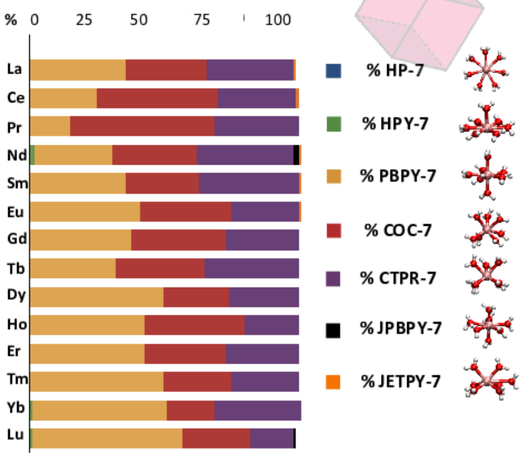


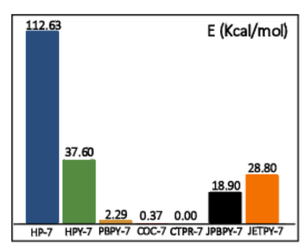


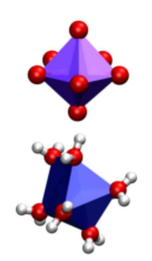
Thomson
OC-6
O_h

$[Eu(H_2O)_6]^{3+}$
OC-6
O_h

Compounds ML_7



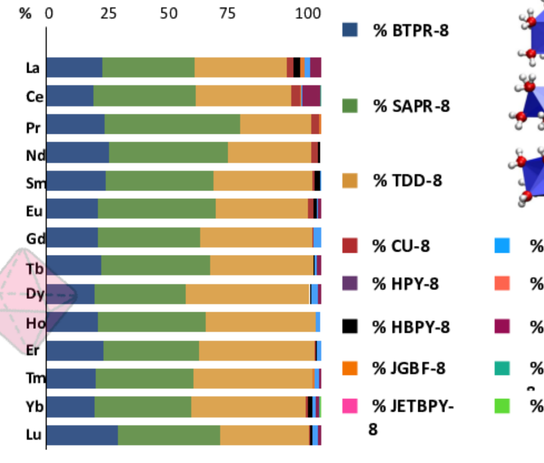


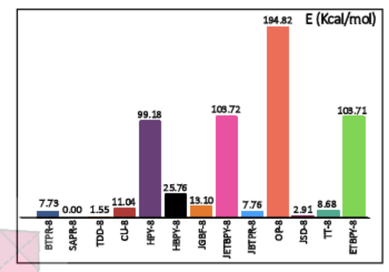


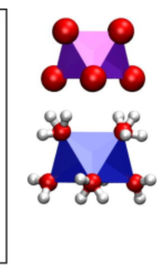
Thomson
PBPY-7
D_{5h}

$[Eu(H_2O)_7]^{3+}$
CTPR-7
C_{2v}

Compounds ML_8



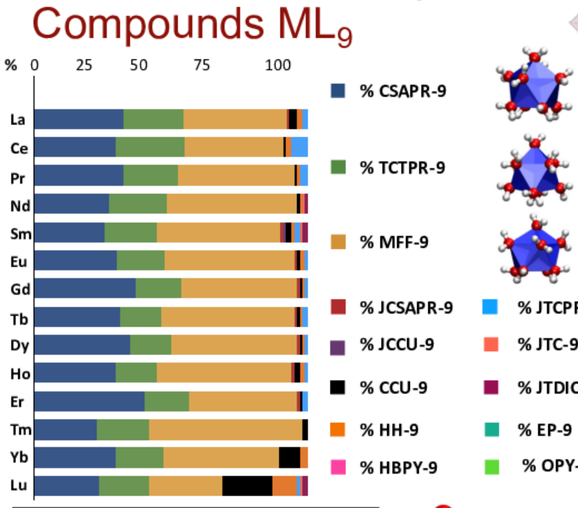


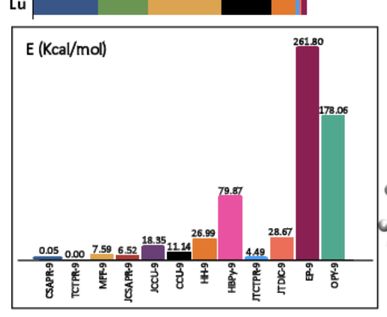


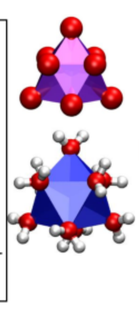
Thomson
SAPR-8
D_{4d}

$[Eu(H_2O)_8]^{3+}$
SAPR-8
D_{4d}

Compounds ML_9







Thomson
TCTPR-9
D_{3h}

$[Eu(H_2O)_9]^{3+}$
TCTPR-9
D_{3h}

Conclusions

- The lanthanide-ligand bond, due to its ionic nature, allows for great variability and a wide range of coordination polyhedra.
- The ionic character increases as one moves along the lanthanide series
- Computational models accurately reproduce the experimentally observed distributions
- For the same coordination number, different polyhedra can exist with energies very close to the minimum, introducing structural variability

Acknowledgements

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