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Molecular modelling of lanthanide(III) chloride complexes with the nitrogen ligand DPA: AIM/NCI analysis and ligand conformational search

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Introduction

Geometry optimizations were performed on the crystal structure asymmetric units as determined for the novel lanthanide coordination compounds: $LaCl_3(DPA)_2$, μ-Cl_2-$[PrCl_2(H_2O)(DPA)]_2$, $[LnCl_2(DPA)_2]Cl$ (Ln = Nd,Dy & Y).

Lanthanide complexes are known to be stereochemically labile, with variable coordination numbers ranging from 2-12. This is due to the localization of f-electrons near the core region of the metal nucleus and the associated ligand-to-metal ionic bonding. The conformation of the ligands would therefore be highly dependent on their respective environment, i.e. on the strength of both intra- and intermolecular interactions. [1]

This study will focus mainly on identifying and characterizing intramolecular interactions that contribute to the overall stability of the geometry of the complexes, in the gas-phase (*in vacuo*). Hydrogen bonding being one of the most important examples of stabilizing interactions.

Theoretical methods

All geometry optimisations were carried out with the *Gaussian 09* [2] software package.

The geometry optimisation calculations, of the lanthanide complexes, were performed using density functional theory (DFT) at the M06-D3/aug-cc-pVTZ/RECP level. For each lanthanide metal center the 'core' electrons were represented by a small-core (28 electron) Stuttgart-Dresden (SDD) quasi-relativistic effective core potential (ECP), while the remaining 'valence' electrons (incl. f-electrons) were explicitly modelled using the energy-optimized (14s13p10d8f6g)/ [6s6p5d4f3g] atomic natural orbital (ANO) Gaussian valence basis sets of Cao and Dolg .[3]
Atoms-in-molecules (AIM) electron density topological analysis [4], shown in Fig. 1, and non-covalent interaction (NCI) analysis [5], shown in **Fig. 2**, were performed on the energy minimized structures, using the software package Multiwfn [6].

Initial optimizations on DPA were performed using the M06-D3/6-311++G(d,p) level, followed by the larger aug-cc-pVTZ basis set.

Ligand conformational search

The ligand geometry optimizations were successfully performed on 621 initial geometries, which were generated by identifying all unique permutations of four principle dihedral angles, in 60° increments, found in the N-donor ligand *bis*(pyridin-2-ylmethyl)amine (*DPA*). The total number of input geometries were reduced by accounting for the inherent symmetry present in the *DPA* molecule, in order to prevent the redundant optimisation of equivalent initial geometries.

AIM/ NCI analysis

One of the principle components of the atoms-in-molecules (AIM) approach involves locating stationary points in space where the curvature of electron density are characterised according to the following four categories [10], see **Fig.1**:

- Nuclear critical points [NCPs, (3, -3)]
- Bond critical points [BCPs, (3, -1)]
- Ring critical points [RCPs, (3, +1)]
- Cage critical points [CCPs, (3, +3)]

Non-covalent interaction (NCI) analysis supplements the aforementioned approach, particularly where weak interactions may exist in the absence of BCPs. [5] This approach identifies regions in space where attractive interactions ($sign(\lambda_2)\rho<0$) or repulsive interactions ($sign(\lambda_2)\rho>0$) dominate, see **Fig. 2**.

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HPC content

All geometry optimisations were carried out with the *Gaussian 09* [2] software package, installed on the Lengau Cluster at the CHPC. The electron density data, used for AIM/NCI analysis, were extracted from the self-consistent field (SCF) output generated by *Gaussian 09*. Isosurfaces were generated using the visualisation server *chpcviz1*, for the visual representation of real space functions (such as electron density).

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