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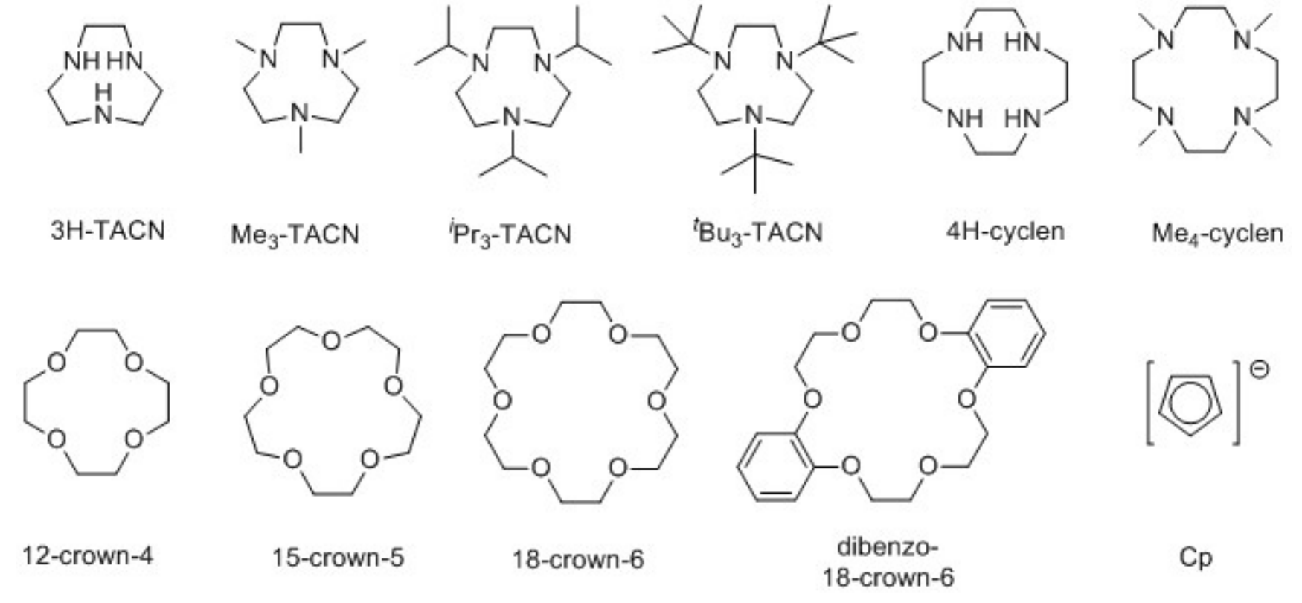
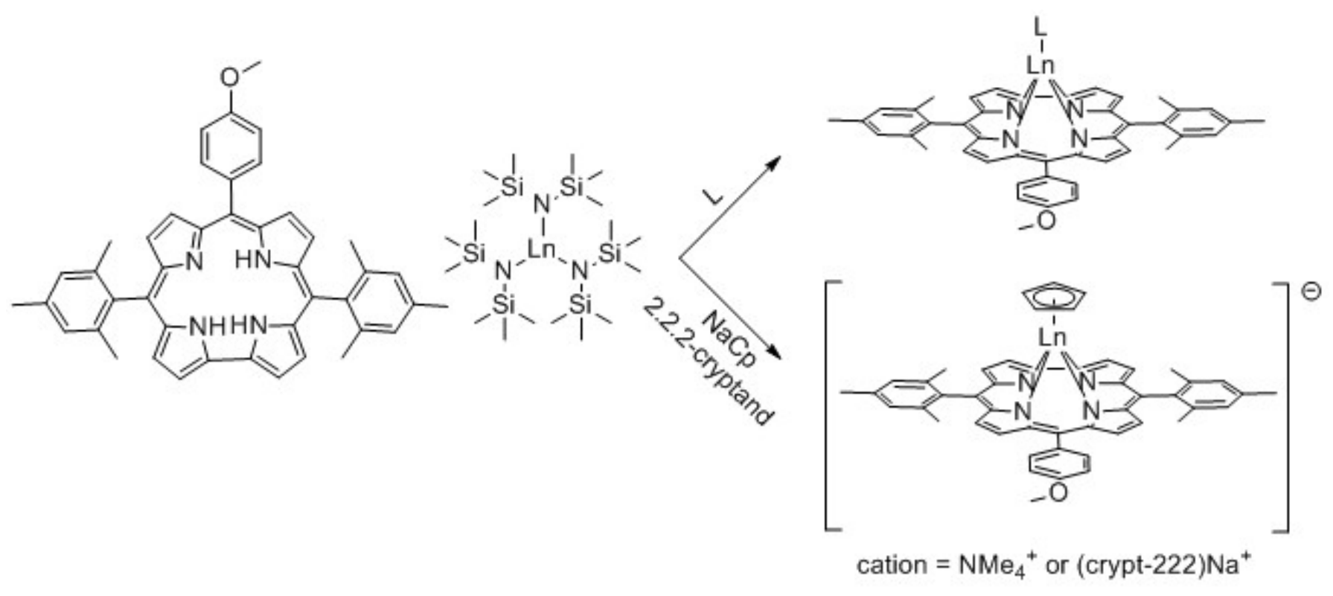


Above: all capping ligands that have been investigated by this project
Below: scheme for synthesis of complexes under investigation



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Lanthanide Contraction: A Systematic Study of Corrole Complexes

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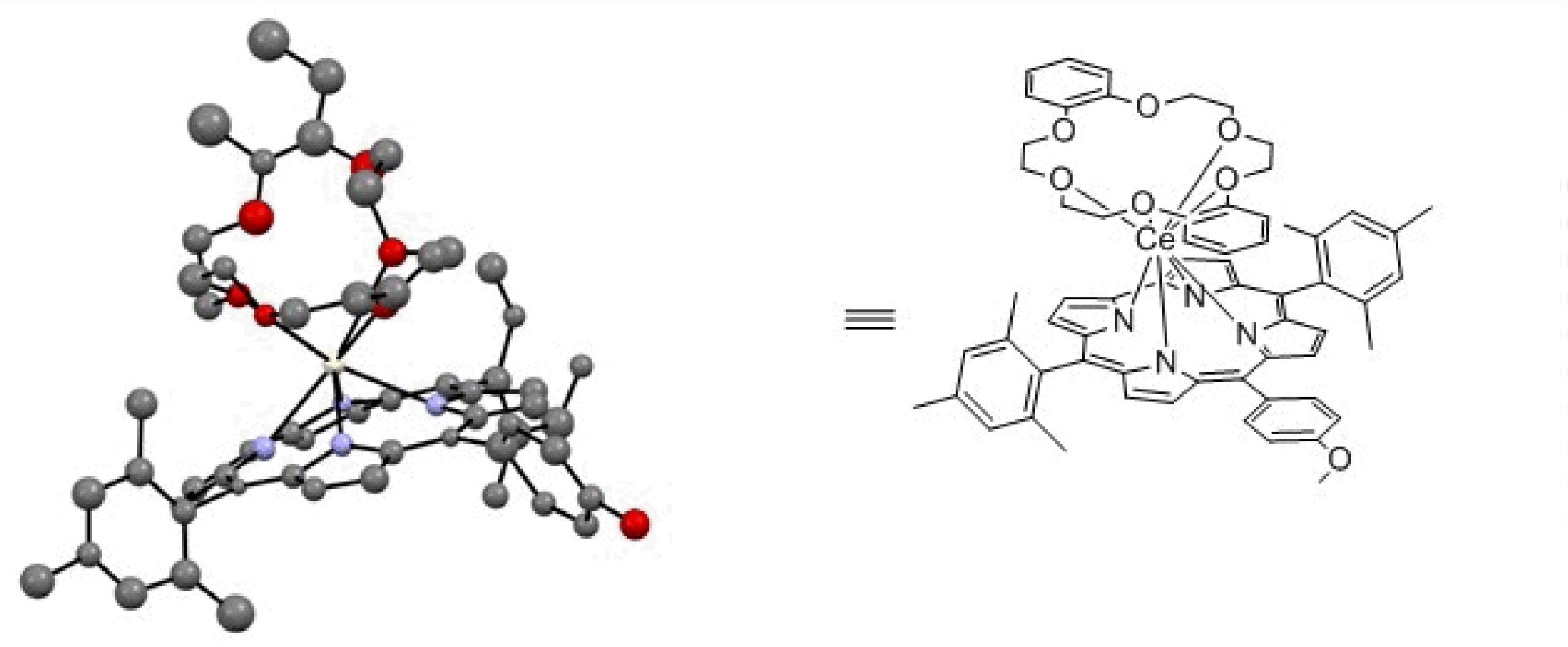
Abstract

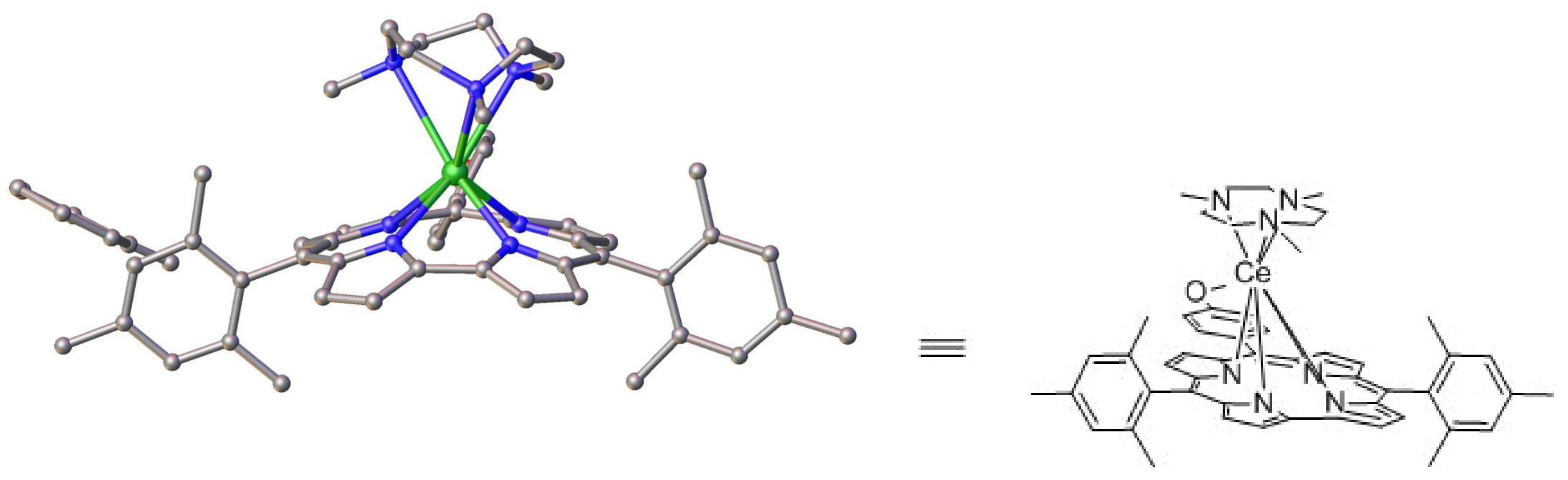
An investigation of the lanthanide contraction trend in lanthanide corrole complexes is proposed.

Introduction

Compounds of the lanthanides—the period 6 *f*-block elements—are used in various fields; their applications include contrast agents in medical imaging and NMR, in bulk magnetism as permanent magnets and in quantum computing due to their molecular magnetic properties. The synthesis and characterization of lanthanide complexes is therefore of interest both scientifically and industrially, since a more complete understanding of such complexes may reveal new applications. Lanthanide contraction is a periodic trend in which an atypically steep decrease in atomic radius is observed across the lanthanides to the diffuse geometry of the *f* subshell, giving the outermost 6*s* electrons poor shielding. Corroles are aromatic macrocycles which are similar to porphyrins in structure and denticity but typically adopt a trianionic coordination mode—ideal for lanthanides, for which +3 is the most common oxidation state.

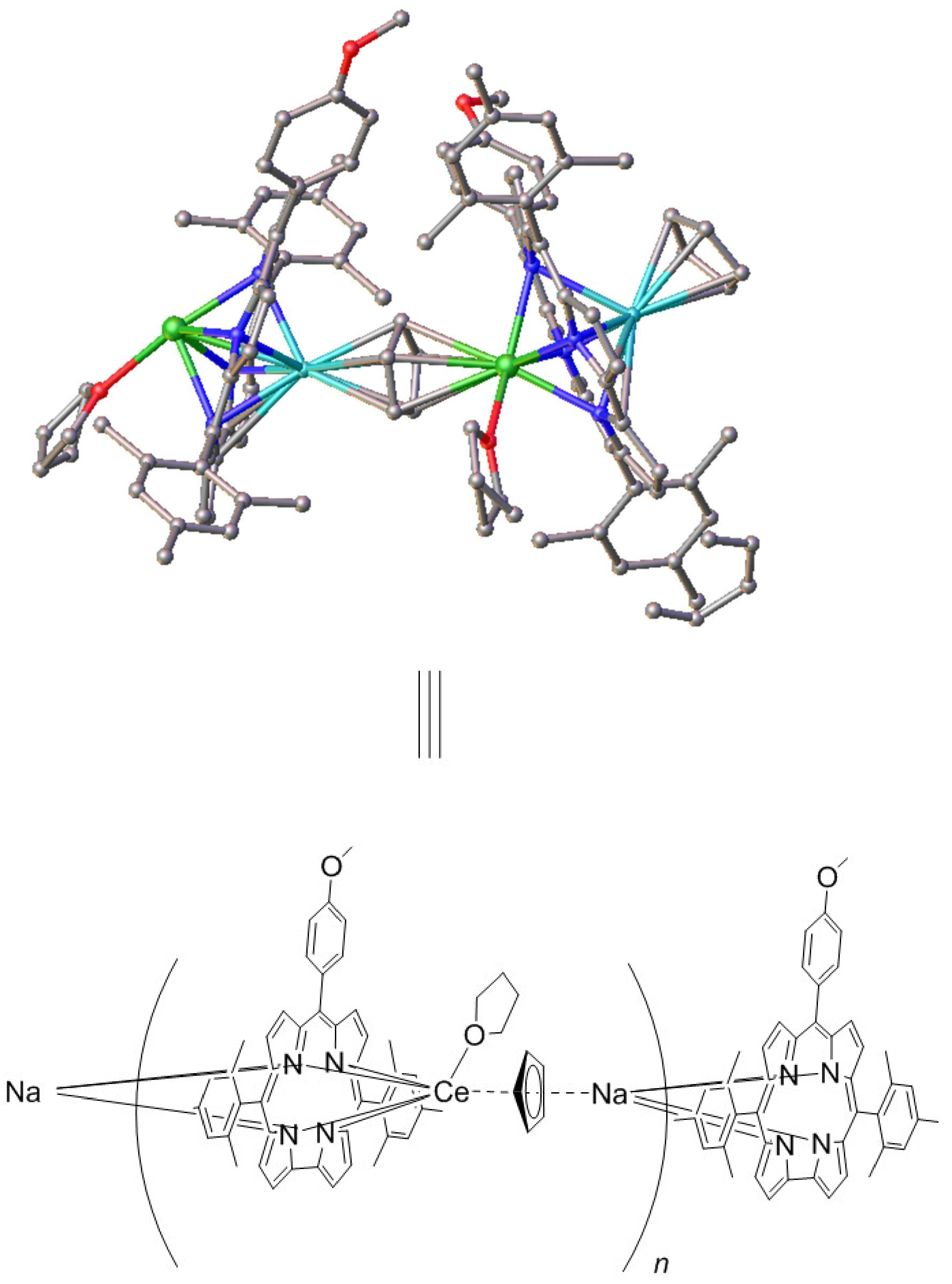
A systematic investigation into the structures of these complexes across the thirteen stable lanthanide nuclei is novel. The goal of this project is to characterize all thirteen complexes, especially through single-crystal X-ray diffraction (SC-XRD) to determine dimensions relevant to evaluation of the lanthanide contraction trend. The primary complication to this goal has been the presence of crystallographic disorder in the capping ligand; such disorder hinders our ability to draw conclusions from crystallographic data.





Results

X-ray diffraction data show that the desired monomeric complex has been isolated in four cases with four different capping ligands. All these structures suffered from the aforementioned disorder; additionally, the crystal structure for the dibenzo-18-crown-6 analog was found to coordinate via a tetradentate mode instead of the desired hexadentate. The structure of a halide-bridged cerium trimer has also been solved. Most recently, a structure has been obtained of a metal-organic framework (MOF) consisting of alternating cerium and sodium atoms linked by alternating corrole and Cp molecules. The Cp capping ligand in this latest structure suffers from minimal crystallographic disorder.



Experimental

Each lanthanide complex is prepared from 5,15-bis(mesityl)-10-anisylcorrole and the corresponding tris(bis(trimethylsilyl)amino)lanthanide(III), followed by addition of capping ligand, according to a published procedure.[1] Crystals suitable for SC-XRD are then grown from a toluene solution by vapor diffusion with hexanes or by concentration under vacuum. All crystal structures collected thus far have been of cerium complexes.

Future directions

Present research is concerned with isolating a monomeric lanthanide complex capped by Cp. 2.2.2-cryptand will be used to sequester sodium ions into the outer coordination sphere, hopefully preventing the bridging of corrole-Ln-Cp units. Although necessary, use of coordinating solvent will be minimized to reduce the chance of forming Ln-solvent adducts as was observed in the most recent structure. Other avenues of research include the investigation of the catalytic activity of the corrole-Ln-Cp-Na MOF and isolation of a Ln-corrole MOF by reaction in a non-coordinating solvent. Due to the redox activity of the corrole ligand and the redox innocence of Cp, we are also interested in exploring the electrochemistry of these complexes. The redox activity of other transition metal corroles has been previously explored (example CV below);[2] no electrochemical studies of lanthanide corroles have been reported to date.

References

1. Chem. Commun. 2013, **49**, 3104-3106.
2. Polyhedron 2006, **25** (7), 1519-1530.