

## Abstract

Synthesis of heterometallic complexes containing  $3d$  and  $4f$  metal ions can be undertaken by the utilisation of various strategies like cationic–template method, anion–template method, metalloligand method and ligand controlled hydrolytic method. Choice of ligands for such synthesis is governed by the preference of  $3d$  metal ions to bind soft donors and that of  $4f$  ions towards hard donors in line with HSAB theory. The preparation of higher nuclearity molecules often relies on ligand–controlled self–assembly under the hydrolytic method. Complexes synthesised by this strategy makes use of serendipity and trial and error tactics to arrive at the appropriate reaction conditions and such complexes are often termed as coordination aggregates or coordination clusters. Limited hydrolysis of metal bound water and solvent molecules under ligand control lead to well defined structures, formed with the help of so generated  $\text{OH}^-$ ,  $\text{OMe}^-$ ,  $\text{O}^{2-}$ , etc. bridging anions serving as ancillary ligands, rather than intractable precipitates. Other ancillary ligands such as carboxylates also play an important role in supporting the primary ligand both in terms of providing structural stability and limiting hydrolysis. A major drawback of this methodology is the lack of control over the structure of the final molecule together with the metal ion coordination geometry which further complicates prediction of desirable magnetic and other useful properties. Understanding the underlying processes of aggregation of these extremely complex systems is thus of utmost importance for development of a more planned synthetic approach although progress has been slow over the past decade. In this thesis a systematic approach of variation of the ligand backbone has been undertaken to investigate the coordination behaviour of related ligand systems towards  $\text{Co}_2(\mu\text{-OH}_2)(\text{O}_2\text{CCMe}_3)_4(\text{HO}_2\text{CCMe}_3)_4$  and  $\text{Ln}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$  along with  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  in one instance in the formation of  $\text{Co}^{\text{II/III}}\text{-}4f$  complexes of varying nuclearity exhibiting unique topologies. Use of a rigid Schiff base ligand containing thioether donor give rise to a uniquely distorted octahedral  $\text{Co}^{\text{II}}$  center best described as being locked in transition between *facial* and *meridional* geometric isomers in a dinuclear  $\text{Co}^{\text{II}}\text{-}4f$  complex. Increasing the flexibility of the ligand backbone through introduction of alcohol arm lead to increase in nuclearity forming heptanuclear  $\text{Co}^{\text{II}}\text{-}4f$  coordination clusters accompanied by literature unknown lanthanide(III)–pivalate–based counter anions. MeCN solvent induced structural transformations to hexanuclear and decanuclear aggregates open up a viable synthetic route for accessing new structural types. Such transformations along with mass spectrometric investigations shed light on the aggregation pathways. Introduction of multiple alcohol arms in the ligand backbone lead to unique pentanuclear  $\text{Co}^{\text{II/III}}\text{-}4f$  complexes bearing resemblance with the structure of OEC in PSII. Photocatalytic water oxidation studies are carried out with these complexes. Use of two primary ligands in the synthesis of tetranuclear and pentanuclear aggregates highlights the effect of lanthanide contraction and sequence of ligand addition on the nuclearity and structure of the final molecule. Magnetic studies reveal SMM like behaviour in some of the aggregates as well as highlighting the limitations of theoretical methodologies in predicting the magnetic behaviour.

**Keywords:** Schiff base; heterometallic polynuclear complexes;  $\text{Co}^{\text{II/III}}\text{-}4f$  coordination aggregates, ancillary ligands; ligand–controlled self–assembly; X–ray crystal structure; magnetic susceptibility; CASSCF calculations; photocatalytic water oxidation; mass spectrometry.