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Lanthanide Hydroxide Cluster Complexes via Ligand-Controlled Hydrolysis of the Lanthanide Ions

Zhonghao Zhang, Yanan Zhang, and Zhiping Zheng

Abstract We survey in this chapter the lanthanide hydroxide cluster complexes since the publication of the comprehensive review on the same subject (Handbook of physics and chemistry of rare earths 40:109–240, 2010). Specifically, polynuclear complexes with carboxylate, diketonate, phosphate, sulfonate, and polyoxometalate (POM) ligands featuring polyhedral cluster-type lanthanide-hydroxo (Ln-OH) core motifs are summarized. The synthetic procedures leading to the production of the cluster species and the unique cluster core motifs are the focus of the discussion. Within each ligand family, we organize the cluster complexes according to their nuclearity with the intention to demonstrate the formal assembly of higher-nuclearity complexes using smaller and recognizable motifs as secondary building units. It is clear that a number of such motifs are prevalent and are shared by cluster complexes with ligands that are structurally and functionally distinct. With the work reviewed previously and the rapidly increasing number of polynuclear lanthanide hydroxide complexes, we hope to validate that once a synthetic serendipity, the chemistry of lanthanide hydroxide complexes is now a legitimate new paradigm of lanthanide coordination chemistry that is of fundamental interest and potential useful applications.

Keywords Cluster • Hydrolysis • Hydroxide • Ligand • Nuclearity

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1 Introduction

Polynuclear lanthanide hydroxide clusters are a class of fundamentally interesting and practically significant substances. They are attracting widespread current interest because of their appealing structures, synthetic challenges, and, most importantly, their potential applications. Continuous development of this burgeoning class of lanthanide complexes will help define a new paradigm of coordination chemistry of these unique metal elements. These fundamental efforts will also lead to the development of advanced materials of practical applications. For example, some lanthanide hydroxide clusters have been used as precursors for oxide-based electrical and optical materials [1], while others have been incorporated into polymers to prepare hybrid materials with enhanced mechanical properties [2]. In addition, intriguing molecule-based magnetic phenomena have been observed in lanthanide hydroxide clusters, potentially useful for quantum computing, magnetic information storage [3], and environmentally friendly magnetic refrigeration [4]. Some lanthanide hydroxide cluster complexes have been found to catalyze chemical transformations including hydrolytic cleavage of nucleic acids [5]. Some cluster complexes have also been proposed as potentially more efficient contrast-enhancing agents in biomedical imaging [6]. Indeed, molar relaxivities greatly surpassing those of current working force of contrast agents in magnetic resonance imaging (MRI) have been demonstrated in the laboratories. Moreover, fixation of atmospheric CO_2 by lanthanide hydroxide complexes has recently been reported, which bears significant environmental ramifications [7]. These exciting and useful applications of lanthanide hydroxide cluster complexes are probably the main driving force for the presently widespread interest in this special class of lanthanide-containing substance, and the extensive research activities, some of which being reviewed below, are consistent with this assessment.

In order to put the materials reviewed here in the developmental context and to help the readers who are interested in this research topic but not necessarily working in the field, the following explanatory notes are warranted:

1. Should Cotton's original definition [8] of a metal cluster be strictly followed, few of these polynuclear lanthanide hydroxide complexes may be qualified as

"clusters" simply because metal–metal bonding or electronic/magnetic interactions between individual metal centers are insignificant in these species. The use of the term is thus for the description of an assembly of metal atoms bridged by ligands from a mere structural perspective.

2. Lanthanide cluster compounds have been obtained by two major routes, one involving organometallic syntheses that typically generate moisture and/or air-sensitive species and the other under hydrolytic conditions but not necessarily in aqueous solutions. We limit our discussion to the cluster-type polynuclear lanthanide hydroxide complexes prepared by the latter means with a note that similar products have also been isolated but generally unexpectedly from some organometallic procedures.
3. As the chemistry of lanthanide hydroxide clusters has been enjoying a rapid development, there are now a large number of such compounds in the literature, with the number still growing at a fast pace. If species containing both lanthanides and other metal elements are included, this number is even bigger. We therefore limit our discussion to only new lanthanide-exclusive species since the publication of the 2010 review on a similar topic in the *Handbook of Physical and Chemistry of the Rare Earth Elements* [9].

2 Ligand-Controlled Lnathanide Hydrolysis

The lanthanide ions, prevalently trivalent, are hard Lewis acids that prefer O-based ligands with aqua coordination being most revealing. Lewis acid-activation of the coordinated water molecule renders the complex susceptible to hydrolysis, and if the pH condition is not carefully controlled, intractable product mixture consisting of lanthanide hydroxides and/or oxides are typically obtained. In fact, except for certain multiply charged chelating ligands such as ethylenediaminetetraacetate (EDTA), lanthanide complexes are generally prepared under highly acidic conditions. However, adventitious hydrolysis does occur with the production of lanthanide complexes characterized by the unexpected presence of hydroxo and/or, much less frequently, oxo groups in the cluster-type core structures. Though interesting, reports of such species were sporadic and reproducibility was problematic prior to the systematic work by Zheng and coworkers [10].

Attracted by the structural aesthetics and tempted by the potential of developing rational synthesis of such otherwise synthetically elusive species, we set out almost two decades ago to explore a systematic approach in which deliberate hydrolysis of the lanthanide ions is carried out in the presence of ligands capable of limiting the degree of hydrolysis of the lanthanide ions [11, 12]. Three considerations went into our hypothesis. First, adventitious hydrolysis was commonly accepted as being responsible for the unexpected production and isolation of the hydroxo/oxo complexes. But can such unintended hydrolysis be exploited in a deliberate and, more importantly, reproducible manner? Second, the presence of the primary ligand, with respect to the "secondary" hydroxo/oxo ligand, is probably critical in arresting or

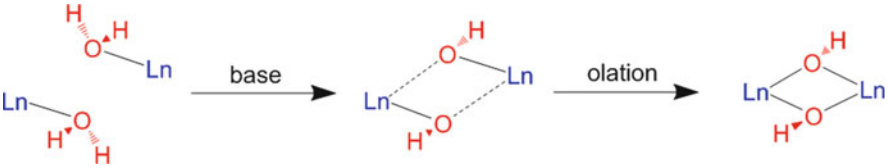


Fig. 1 Ligand-controlled hydrolytic approach to the assembly of lanthanide hydroxide clusters

limiting the otherwise extensive hydrolysis of the lanthanide ion to prevent the formation of the eventual precipitate products. If so, are there any specific structural and functional features required for such ligands? Third, despite the different lanthanide ions and/or ligands used, a number of these unexpected hydroxo cluster complexes share some prevalent Ln-OH core motifs. This suggests that a common reaction pathway may exist for the assembly of the cluster core. In other words, a systematic synthetic approach to these new lanthanide hydroxide complexes may be developed. Then, what is the scope of such a new paradigm of lanthanide coordination chemistry in terms of the nature of the lanthanide ions and any applicable supporting ligands?

These thoughts are reflected in the approach of “ligand-controlled hydrolysis” schematically shown in Fig. 1. Key to the success of this approach is the pre-occupation of part of the lanthanide coordination sphere by the supporting ligands, leaving only a limited number of sites available for aqua coordination. Deprotonation of the lanthanide-activated aqua ligands upon base addition is thus limited, and so is olation – the aggregation of the resulting lanthanide-hydroxo (Ln-OH) species via sharing of the hydroxo groups – leading eventually to cluster species rather than intractable precipitates of lanthanide oxides/hydroxides.

Significant progress in this new chemistry of lanthanide coordination has been made through our own efforts and those of others [9] since our first report of a pentadecanuclear europium cluster complex assembled by using tyrosine as the hydrolysis-limiting ligand [11]. With almost two decades of development, ligand-controlled hydrolysis has become a time-honored approach to the synthesis of lanthanide hydroxide/oxide clusters [9, 10].

The survey of the new cluster species and related discussion in this chapter are organized according to the type of ligands used for hydrolysis control (Table 1). Within each type of ligands, clusters are presented and discussed in ascending order of the cluster’s nuclearity. A brief summary will be provided at the conclusion of the chapter in which the authors’ personal perspective of what future directions this research may head toward is offered.

2.1 *Carboxylates*

Carboxylates are time-honored ligands for lanthanide coordination. These include simple carboxylates such as formate and acetate [13–16], (poly)amino(poly)

Table 1 Abbreviations of ligands

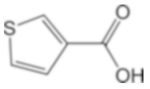
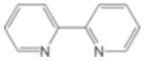
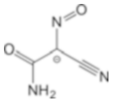
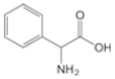
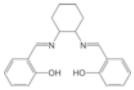
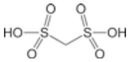
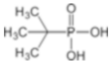
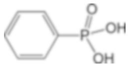
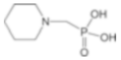
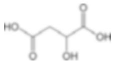
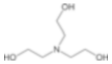
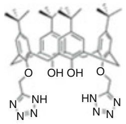
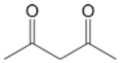
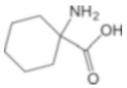
3-TCAH	Thiophene-3-carboxylic acid	Fig. 10	
bipy	2,2′-Bipyridine	Fig. 5 Fig. 9	
ccnm	Carbamoylcyanonitrosomethanide	Fig. 48	
D-PhGly	D-Phenyl glycine	Fig. 28	
H_2L_6	*N*,*N*′-bis(salicylidene)-1,2-Cyclohexanediamine	Fig. 25	
H_2mds	Methylenedisulfonic acid	Fig. 38	
$H_2O_3P^t$Bu	*Tert*-butyl phosphonic acid	Fig. 11 Fig. 34 Fig. 35	
H_2PhPO_3	Phenylphosphonic acid	Fig. 37	
H_2pmp	*N*-Pipe-ridinomethane-1-phosphonic acid	Fig. 36	
H_3mal	Malic acid	Fig. 43	
H_3tea	Triethanolamine	Fig. 21	
H_4**1**	Tetrazole-functionalized calixarene	Fig. 13	
H_8TBC8A	*p*-*Tert*-butylcalix[8]arene	Fig. 37	See Fig. 37
Hacac	Acetylacetone	Fig. 22 Fig. 25 Fig. 31 Fig. 32	
HAcc	1-Amino-cyclohexanel-carboxylic acid	Fig. 2 Fig. 7	

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Table 1 (continued)

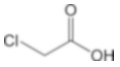
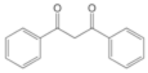
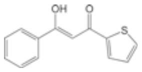
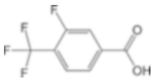
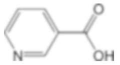
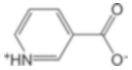
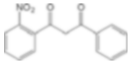
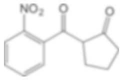
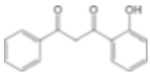
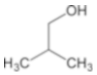
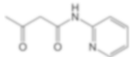
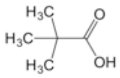
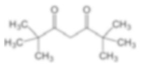
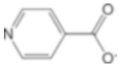
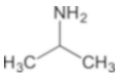
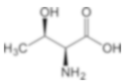
HCAA	Chloroacetic acid	Fig. 16	
Hdbm	Dibenzoylmethane	Fig. 24 Fig. 28 Fig. 33	
Hhtp	(Z)-3-Hydroxy-3-phenyl-1-(thiophen-2-yl)prop-2-en-1-one	Fig. 26 Fig. 27	
HL	3-Fluoro-4-(trifluoromethyl)benzoic acid	Fig. 5 Fig. 9	
Hnic	Niconitic acid	Fig. 15 Fig. 17	
Hnic	Pyridinium nicotinate	Fig. 3	
Hnmc	*Ortho* ring-functionalized 1-phenylbutane-1,3-dione ligand 1	Fig. 23	
HO-Hdbm	*Ortho*-hydroxydibenzoylmethane	Fig. 29	
Hnpd	*Ortho* ring-functionalised 1-phenylbutane-1,3-dione ligand 2	Fig. 23	
HO^iBu	Isobutyl alcohol	Fig. 35	
Hpaa	*N*-(2-pyridyl)-acetoacetamide	Fig. 21	
HO_2C^tBu	Pivalic acid	Fig. 6 Fig. 11 Fig. 34 Fig. 35	
Hthd	2,2,6,6-Tetramethylheptane-3,5-dione	Fig. 30	
ina	Isonicotinate	Fig. 4 Fig. 12 Fig. 14	
$^iPrNH_2$	Isopropylamine	Fig. 35	
L-thre	L-Threonine	Fig. 18	

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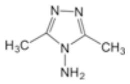
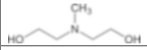
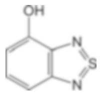
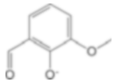
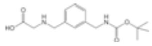
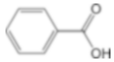
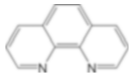
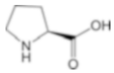
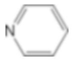
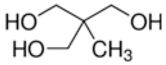
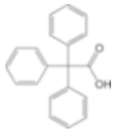
Table 1 (continued)

L_8	4-Amino-3,5-dimethyl-1,2,4-triazole	Fig. 47	
$mdeaH_2$	*N*-Methyldiethanolamine	Fig. 6	
O-btd	4-Hydroxo-2,1,3-benzothiadiazolate	Fig. 24	
o-van	3-Methoxysalicylaldehydato anion	Fig. 6 Fig. 12	
$PepCO_2H$	2-[{3-(((*tert*-butoxycarbonyl)amino)methyl)benzyl}-amino]acetic acid	Fig. 33	
$PhCO_2H$	Phenylcarboxylic acid	Fig. 13	
phen	1,10-Phenanthroline	Fig. 48	
proline	L-Proline	Fig. 42	
py	Pyridine	Fig. 4	
$thmeH_3$	Tris(hydroxymethyl)ethane	Fig. 8	
tpaH	Triphenylacetic acid	Fig. 8	

carboxylates [10], and those that are structurally and functionally more sophisticated [17]. It should be noted that lanthanide carboxylate complexes have traditionally been prepared under highly acidic conditions (pH 3–4) due exactly to the hydrolysis concern alluded to above. It was Zheng et al. who explored the otherwise well-established lanthanide coordination chemistry with α-amino acids under pH conditions that are 2–3 orders of magnitude higher than the commonly accepted acidic conditions that uncovered the wealth of the "high-pH" coordination chemistry of the lanthanides [10–12]. Polynuclear lanthanide complexes characterized by the presence of polyhedral lanthanide-oxo/hydroxo core motifs have been obtained with the amino acid ligands serving as hydrolysis-limiting and structure-supporting ligands. It is believed that the presence of amino group and other hydrophilic functional group(s) helps enhance the water solubility of the complexes formed at a lower pH, allowing subsequent deprotonation of any available aqua ligand(s) or hydrolysis to occur upon addition of a base. It is understandable that not all carboxylate ligands can be used to support the hydroxide complexes due to the fact that many lanthanide complexes with such ligands are insoluble and precipitate out before the pH of the reaction mixture may be enhanced. Equally possible is that researchers, wary of the formation of intractable lanthanide oxide/hydroxide precipitates, were simply trying to avoid any high-pH conditions.

This ligand-controlled hydrolytic approach has since become a standard method for the preparation of lanthanide hydroxide cluster complexes. Understandably, drastically different cluster species have been obtained depending sensitively on the supporting ligands used. The structure of the resulting cluster is also dependent on other reaction conditions such as the presence of any additional ligands or reactants, although these species may not eventually be incorporated into the final cluster products.

2.1.1 Tetra-, Penta-, and Heptanuclear Clusters

Long et al. reported two tetranuclear lanthanide hydroxide cluster complexes $[Ln_4(\mu_3\text{-}OH)_4(Acc)_6(H_2O)_7(ClO_4)]\cdot(ClO_4)_7\cdot 11H_2O\cdot(Ln = Dy,\ Yb)\cdot(HAcc = 1\text{-}$amino-cyclohexanel-carboxylic acid) by using amino acid-like ligand HAcc to control the lanthanide hydrolysis [18]. The cluster core, now a well-established motif in the literature, consists of four Ln^{3+} ions and four triply bridging hydroxo groups occupying the alternating vertices of a distorted cubane. Each edge of the Ln_4 tetrahedron is bridged by a carboxylate group of the organic ligand. The coordination spheres are completed by aqua ligands and for one of them, a monodentate perchlorate (Fig. 2a). It is of note that the reactions using two lighter lanthanide ions La^{3+} and Nd^{3+} under otherwise identical conditions produced trinulcear complexes of the common formula $[Ln_3(Acc)_{10}(H_2O)_6]\cdot(ClO_4)_9\cdot 4H_2O\cdot(Ln = La,\ Nd)$ in which three lanthanide ions are in a linear arrangement with neighboring Ln^{3+} ions being bridged by four carboxylate groups from different Acc^- ligands. Each of the terminal Ln^{3+} ions is further coordinated by three aqua ligands and a carboxylate group, one being monodentate and the other, chelating (Fig. 2b). Formation of different products probably reflects the influences of the size and/or Lewis acidity of the lanthanide ions: The lighter and larger lanthanide ions (La^{3+} and Nd^{3+}) may not be as adequately Lewis acidic to be hydrolyzed as the heavier and smaller, and therefore more acidic Dy^{3+} and Yb^{3+}.

Using nicotinic acid in a similar capacity, Zheng et al. obtained and structurally characterized isostructural tetranuclear complexes of the formula $[Ln_4(\mu_3\text{-}OH)_4(Hnic)_5(H_2O)_{12}](ClO_4)_8\cdot(Ln = Eu,\ Gd;\ Hnic = \text{pyridinium nicotinate})$ [19]. The cluster core is the same as the aforementioned distorted cubane. However,

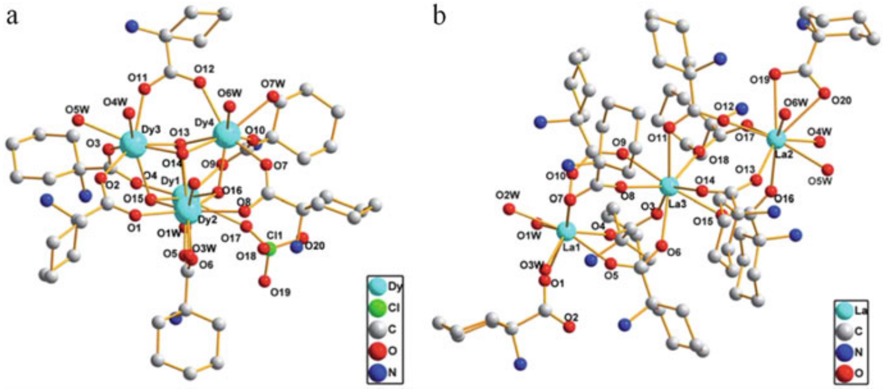


Fig. 2 Structure of: (**a**) $[Dy_4(\mu_3\text{-}OH)_4(Acc)_6(H_2O)_7(ClO_4)]^{7+}$ and (**b**) $[La_3(Acc)_{10}(H_2O)_6]^{9+}$. Reprinted with the permission from [18] Copyright 2011 Royal Society of Chemistry

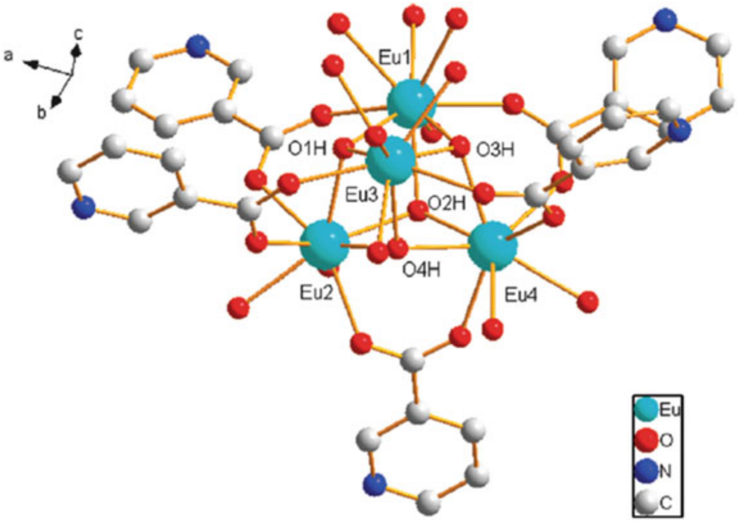


Fig. 3 Structure of the $[Eu_4(\mu_3\text{-}OH)_4(Hnic)_5(H_2O)_{12}]^{8+}$. Reprinted with the permission from [19] Copyright 2009 American Chemical Society

only five of the six edges of the Ln_4 tetrahedron are bridged by the carboxylate group of the zwitterionic ligand; the coordination of the two unique lanthanide ions is made up for by using additional aqua ligands (Fig. 3).

When hydrolysis was carried out with the use of isonicotinate (ina) as supporting ligand, a tetranuclear complex formulated as $[Dy_4(\mu_3\text{-}OH)_4(ina)_6(py)(CH_3OH)_7](ClO_4)_2{\cdot}py{\cdot}4CH_3OH$ (py = pyridine) was obtained [20]. Its core structure is the same as the one when nicotinic acid was used [19]. In addition to the bridging by in a carboxylate group, seven methanol molecules and one pyridine molecule help

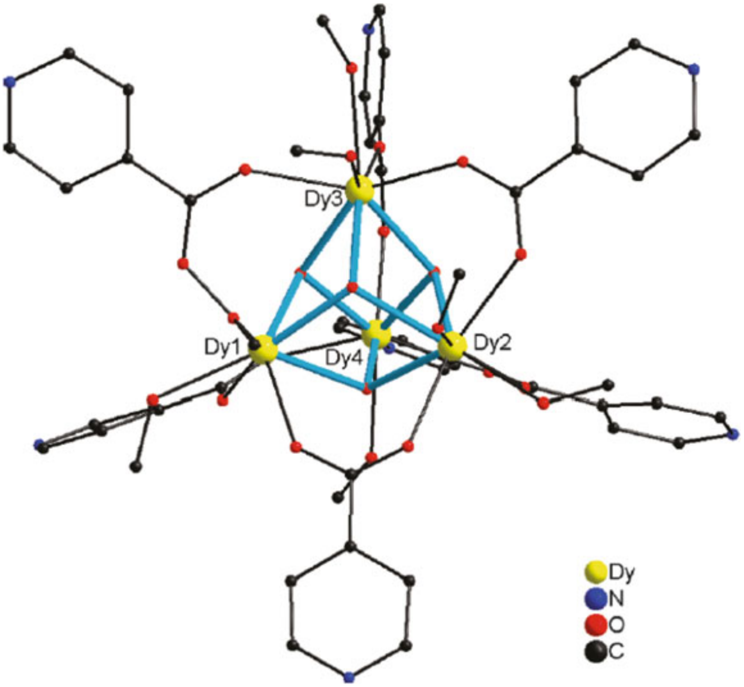


Fig. 4 Structure of $[Dy_4(\mu_3\text{-}OH)_4(ina)_6(py)(CH_3OH)_7]^{2+}$. Reprinted with the permission from [20] Copyright 2009 American Chemical Society

complete the metal coordination (Fig. 4). This cluster complex was shown to display properties characteristic of a single-molecule magnet.

In ligand-supported assembly of hydroxide clusters, the use of organic co-ligand (s) other than coordinating solvent(s) is a common practice. For example, Zhao et al. reported a tetranuclear complex $[Dy_4(\mu_3\text{-}OH)_2(L)_{10}(bipy)_2(H_2O)_2]$ (HL = 3-fluoro-4-(trifluoromethyl)benzoic acid; bipy = 2,2′-bipyridine) in which the metal coordination is achieved by both L and the chelating bipy, in addition to the hydroxo and aqua ligands [21]. The parallelogram-shaped cluster core consists of four coplanar lanthanide atoms connected by two μ_3-OH groups, one on each opposite sides of the plane. This motif is also frequently encountered in lanthanide hydroxide complexes. Two of the four edges of the parallelogram are each bridged by two carboxylate groups from different L ligands, while the other two are each bridged by one carboxylate group and one μ_2-H_2O molecule. The coordination sphere is completed by either a bipy or a monodentate L ligand (Fig. 5).

Two additional series of tetranuclear hydroxide clusters featuring the same core motif were reported. Murray et al. reported the isostructural complexes $[Ln_4(\mu_3\text{-}OH)_2(o\text{-van})_4(O_2C^tBu)_4(NO_3)_2]\cdot CH_2Cl_2\cdot 1.5H_2O\cdot$(Ln = Gd, Dy; *o*-van = 3-methoxysalicylaldehydato anion; O_2C^tBu = pivalate or $(CH_3)_3CCO_2^-$) [22], while Powell et al. reported five isostructural complexes of the common formula $[Ln_4(\mu_3\text{-}OH)_2(mdeaH)_2(O_2C^tBu)_8]$ ($mdeaH_2$ = *N*-methyldiethanolamine; Ln = Tb,

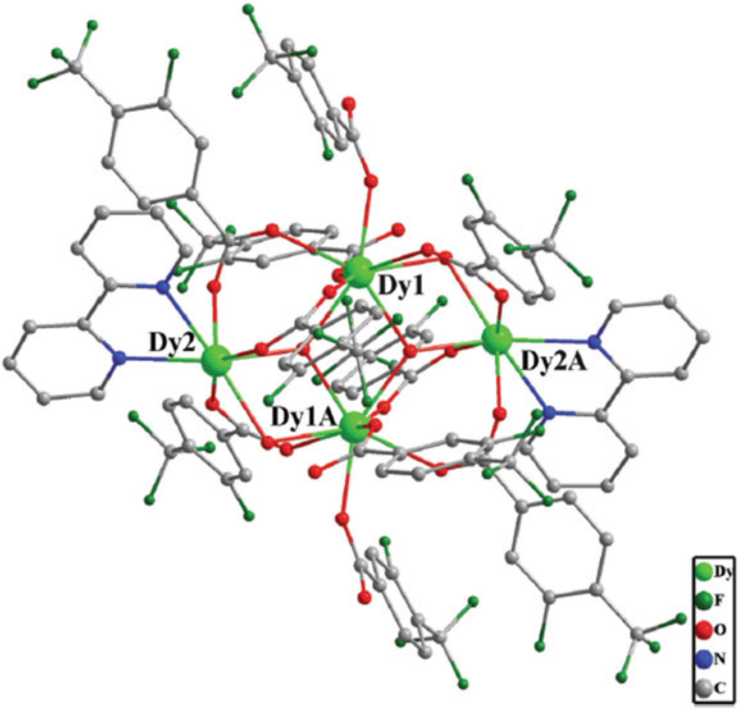


Fig. 5 Structure of $[Dy_4(\mu_3\text{-}OH)_2(L)_{10}(bipy)_2(H_2O)_2]$. Reprinted with the permission from [21] Copyright 2014 Royal Society of Chemistry

Dy, Ho, Er, Tm) [23]. Together with *o*-van in the former and mdeaH in the latter, pivalate serves in both series to stabilize the cluster core. Crystal structures of the complexes representing the two series are shown in Fig. 6.

With the use of 1-amino-cyclohexanel-carboxylic acid (Acc), Long et al. isolated $[Dy_5(\mu_3\text{-}OH)_6(Acc)_6(H_2O)_{10}]\cdot Cl_9\cdot 24H_2O$ [24] when $DyCl_3$ was used, which differs sharply from the tetranuclear species when $Dy(ClO_4)_3$ was used as the starting lanthanide salt [18]. The profound anion-template effects on the cluster nuclearity have previously been established [25], but we note that the anions do not participate in the metal coordination in either of these two complexes. Thus, the exact roles played by the anions in dictating the outcome of the reactions carried out under otherwise identical conditions remain to be understood.

In the cluster core, the five Dy^{3+} ions are organized into a trigonal bipyramidal geometry. Alternatively, it may be viewed as two distorted cubanes joined together by sharing a trimetallic face. Each triangular metal face is capped by a μ_3-OH group, while each non-equatorial metal edge is bridged by an Acc carboxylate group. The coordination sphere of each Dy^{3+} ion is completed by two aqua ligands (Fig. 7).

Collison et al. reported two isostructural heptanuclear complexes $[Ln_7(OH)_6(thmeH_2)_5(thmeH)(tpa)_6(MeCN)_2](NO_3)_2\cdot(Ln = Gd,\ Dy;\ thmeH_3 =$ tris

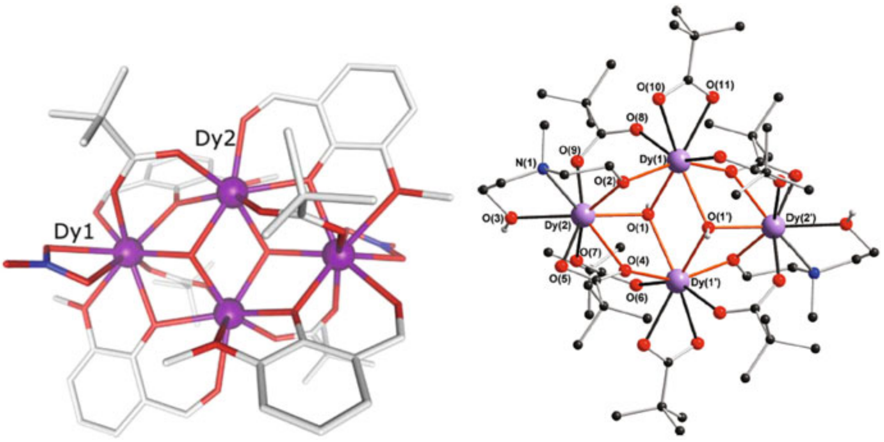


Fig. 6 Structures of [$Dy_4(\mu_3\text{-}OH)_2$(*o*-van)$_4(O_2C^tBu)_4(NO_3)_2$] (*left*) and [$Dy_4(\mu_3\text{-}OH)_2(mdeaH)_2(O_2C^tBu)_8$] (*right*). Reprinted with the permission from [22] Copyright 2011 Royal Society of Chemistry and [23] Copyright 2010 American Chemical Society

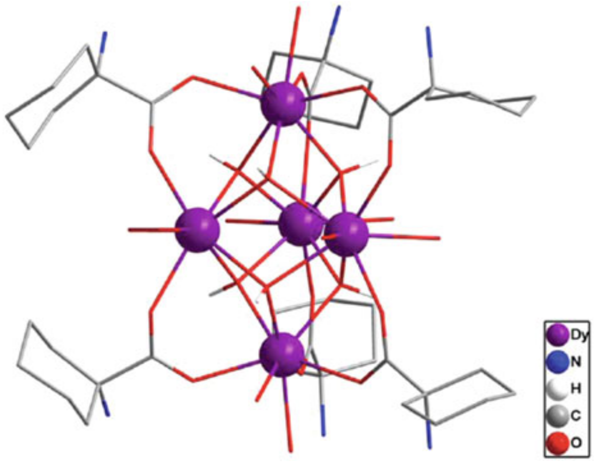


Fig. 7 Structure of $[Dy_5(\mu_3\text{-}OH)_6(Acc)_6(H_2O)_{10}]^{9+}$. Reprinted with the permission from [24] Copyright 2012 American Chemical Society

(hydroxymethyl)ethane; tpaH = triphenylacetic acid) [26]. The synthesis was carried out under solvothermal conditions using a mixture of lanthanide nitrate hydrates, thmeH$_3$, tpaH, and triethylamine in acetonitrile. The cluster core consists of seven coplanar Ln^{3+} ions organized into a disc-like hexagon with six peripheral Ln^{3+} ions occupying the vertices of the hexagon and the remaining Ln^{3+} ion sitting at the center of hexagon and connecting the peripheral metal ions through six μ_3-OH groups. Alternatively this cluster core can be viewed as two of the coplanar tetranulcear units, such as those shown in Figs. 5 and 6, joined together by two μ_3-OH groups. In effect, the six μ_3-OH groups are alternatingly above and below the

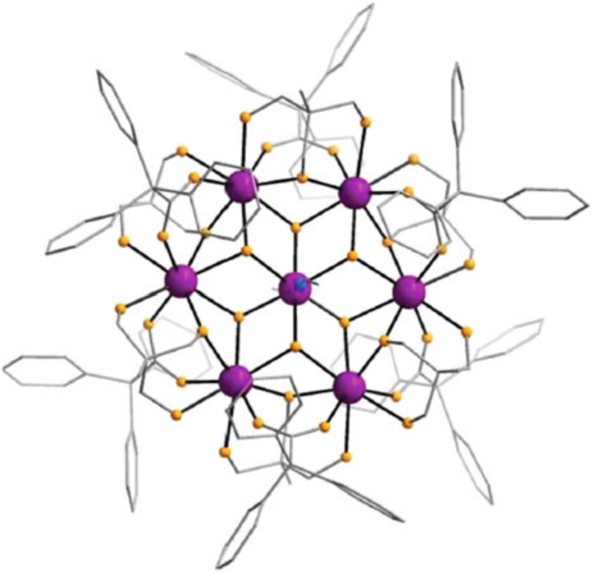


Fig. 8 Structure of [$Ln_7(\mu_3\text{-}OH)_6(thmeH_2)_5(thmeH)(tpa)_6(MeCN)_2]^{2+}$ (color code: *purple*, Ln; *yellow*, O; *blue*, N; and *skeletal*, C). Reprinted with the permission from [26] Copyright 2011 Royal Society of Chemistry

disc plane. In addition to the coordination by these OH groups, the central lanthanide ion is further coordinated with two *trans*-disposed acetonitrile molecules. Each edge of the lanthanide hexagon is bridged by one tpa carboxylate group and one $thmeH_2^-$ or $thmeH_2^-$ ligand (Fig. 8).

2.1.2 Decanuclear and Higher-Nuclearity Clusters

An increasing number of lanthanide hydroxide complexes of even higher nuclearities have also appeared in the literature, although their assembly generally cannot be predicted. A number of factors may be responsible for the formation of such giant cluster species. These include the nature of the ligands, the lanthanide ions, available anionic templates, as well as pH condition. For example, in the aforementioned work by Zhao and coworkers in which tetranuclear cluster complexes were obtained, a decanuclear complex $[Dy_{10}(\mu_3\text{-}OH)_8(L)_{22}(bipy)_2(H_2O)_2]\cdot 5H_2O\cdot$(L = 3-fluoro-4-(trifluoromethyl)benzoate) was also isolated when the reaction pH was adjusted to 10 with NaOH prior to the hydrothermal treatment [21]. The complex structure as shown in Fig. 9 has a formal crystallographic center symmetry. The Dy^{3+} ions are connected by eight μ_3-OH groups and the L carboxylate groups. The coordination spheres are further fulfilled by either chelating bipy or aqua ligands.

It should be noted that a gadolinium complex $[Gd_{10}(\mu_3\text{-}OH)_8(3\text{-}TCA)_{22}(H_2O)_4]\cdot$ (3-TCAH = thiophene-3-carboxylic acid) with a similar decanuclear core (Fig. 10) had been reported by Bu and his coworkers, but the primarily supporting ligand is different [27]. In addition, no co-ligand was utilized.

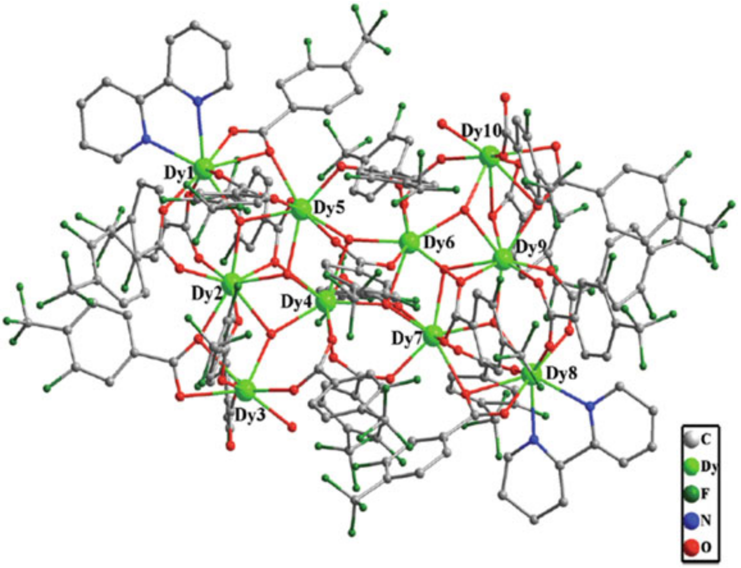


Fig. 9 Structure of $[Dy_{10}(\mu_3\text{-}OH)_8(L)_{22}(bipy)_2(H_2O)_2]$(L = 3-fluoro-4-(trifluoromethyl)benzoate. Reprinted with the permission from [21] Copyright 2014 Royal Society of Chemistry

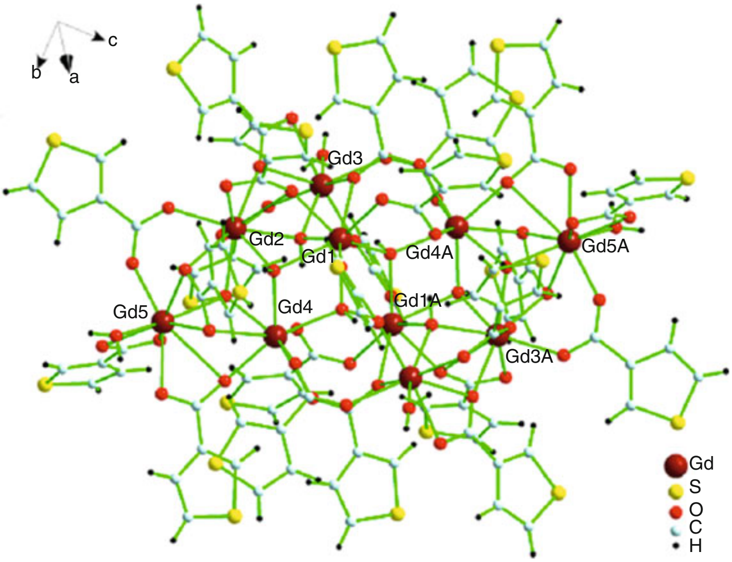


Fig. 10 Structure of $[Gd_{10}(\mu_3\text{-}OH)_8(3\text{-}TCA)_{22}(H_2O)_4]$. Reprinted with the permission from [27] Copyright 2013 American Chemical Society

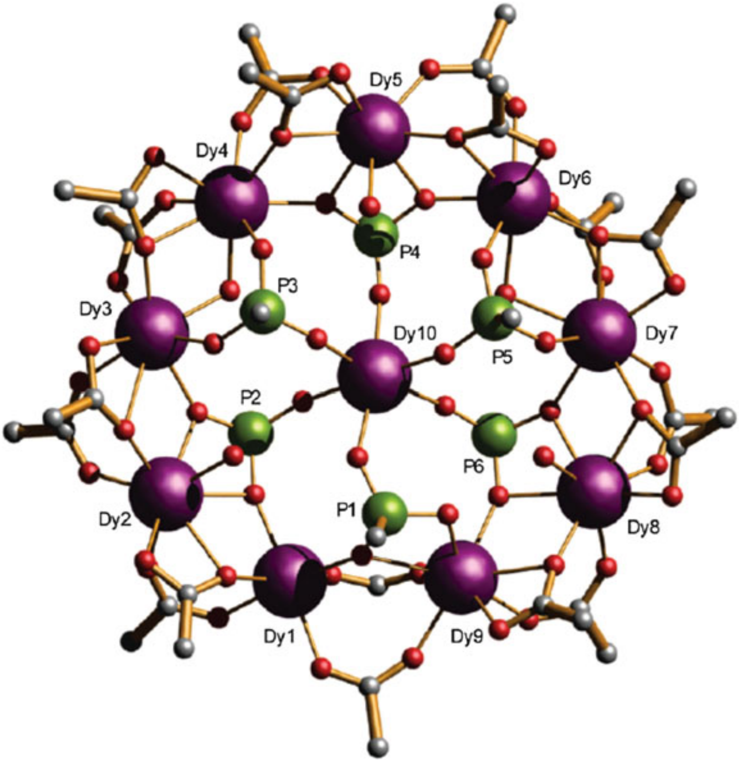


Fig. 11 Structure of $[Dy_{10}(O_2C^tBu)_{18}(O_3P^tBu)_6(OH)(H_2O)_4]^-$. Reprinted with the permission from [28] Copyright 2014 Royal Society of Chemistry

Distinctly different from the above compounds, two lanthanide complexes of the common formula $[Co_3(\mu_3\text{-}O)(O_2C^tBu)_6(py)_3][Ln_{10}(O_2C^tBu)_{18}(O_3P^tBu)_6(OH)(H_2O)_4]$ (Ln = Dy, Gd) reported by Winpenny et al. possess a decanuclear cluster core that features a nine-metal ring surrounding a central metal atom in the complex anion [28]. The lanthanide ions are essentially coplanar with those in the ring occupying at the vertices of a nearly regular nonagon, each connecting the central lanthanide ion via an O of the O_3P^tBu ligand. Connection between neighboring metal atoms in the ring is achieved by O_3P^tBu, O_2C^tBu, and bridging aqua and/or OH ligands (Fig. 11).

With isonicotinic acid (Hina) and *o*-vanillin as protecting ligands, Murray et al. obtained a decanuclear complex $[Dy_{10}(\mu_4\text{-}O)_2(\mu_3\text{-}OH)_6(o\text{-}van)_6(ina)_{13}(H_2O)_2](NO_3)$ that can be viewed as two pentanuclear complex units bridged by one ina carboxylate group [29]. This pentanuclear cluster core has the structure of a distorted trigonal bipyramid similar to the one discussed above [24]. Within each pentanuclear unit, the metal ions are bridged by one μ_4-O group, three μ_3-OH groups, the ina carboxylate, and the O atom of the deprotonated

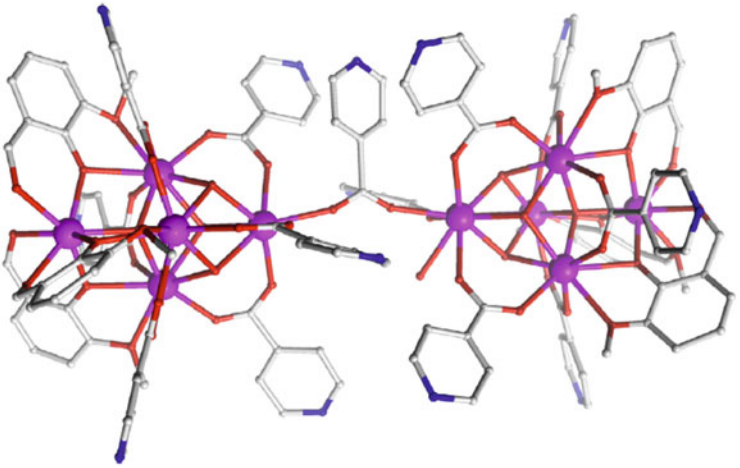


Fig. 12 Structure of $[Dy_{10}(\mu_4\text{-}O)_2(\mu_3\text{-}OH)_6(o\text{-van})_6(ina)_{13}(H_2O)_2]^+$ cluster. Reprinted with the permission from [29] Copyright 2013 Elsevier

phenol groups of the *o*-van ligands. The coordination sphere is completed by the OH and MeO groups of the *o*-van ligand and aqua ligands (Fig. 12).

With the combined use of structurally or functionally more sophisticated ligands, lanthanide hydroxide complexes of even higher nuclearities can be obtained. For example, Ogden et al. reported the use of a tetrazole-functionalized calixarene (**1**) in combination with acetic acid or phenylcarboxylic acid in the controlled assembly of lanthanide cluster complexes [30]. The synthesis was carried out by using a mixture of ligand **1**, $Dy(NO_3)_3(DMSO)_3$, and ammonium acetate or ammonium benzoate in H_2O/ethanol. With the sterically more hindered phenylcarboxylate, they obtained a dodecanuclear complex $[Dy_{12}(\mathbf{1}\text{-}3H)_3(\mathbf{1}\text{-}2H)_3(PhCO_2)_5(\mu_3\text{-}OH)_{16}(H_2O)_{21}]$ (**1**-3H and **1**-2H represent, respectively, triply and doubly deprotonated ligand **1**), whereas with acetate, they isolated a nonadecanuclear complex $[Dy_{19}(\mathbf{1}\text{-}3H)(\mathbf{1}\text{-}2H)_{11}(CH_3CO_2)_6(\mu_3\text{-}OH)_{26}(H_2O)_{30}]$. The cluster core of $[Dy_{12}(OH)_{16}]$ in the smaller complex can be viewed as two trigonal bipyramids and one distorted tetrahedron joined together by sharing vertices (Fig. 13a, top) with each of the triangular Dy3 faces being capped by a μ_3-OH group. The cluster core is encapsulated by the organic protecting sphere formed by both the carboxylate and the calixarene ligands (Fig. 13a, bottom). In the larger complex, the core of $[Dy_{19}(\mu_3\text{-}OH)_{26}]$ can be conveniently viewed as being elongated by adding one trigonal bipyramid and one distorted tetrahedron to the dodecanuclear core. Alternatively the core may be more straightforwardly viewed as three trigonal bipyramids being sandwiched by two distorted tetrahedra with neighboring polyhedra being joined together by sharing a Dy-vertex (Fig. 13b, top). Corresponding to the larger and elongated cluster core, there are 26 μ_3-OH groups, each capping a triangular metal face. This hydroxide cluster core is protected in an organic sphere composed of acetate ligands and the tetrazole groups of the

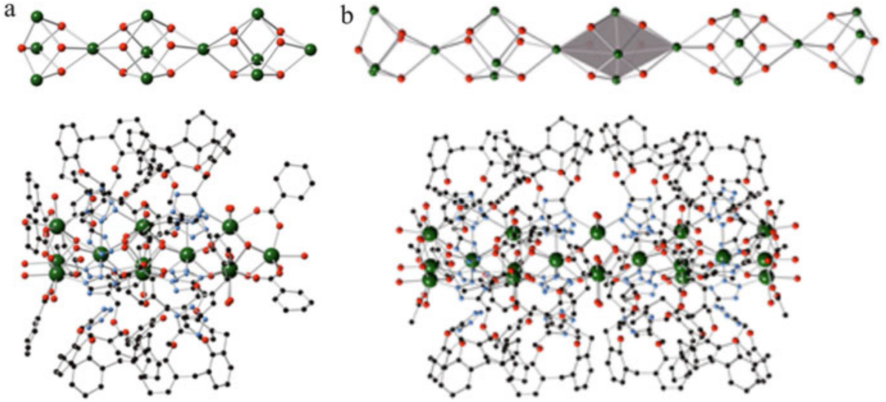


Fig. 13 Structures of the cluster core (*top*) and the complex (*bottom*) of: (**a**) $[Dy_{12}(\mathbf{1}\text{-}3H)_3(\mathbf{1}\text{-}2H)_3(PhCO_2)_5(OH)_{16}(H_2O)_{21}]$ and (b) $[Dy_{19}(\mathbf{1}\text{-}3H)(\mathbf{1}\text{-}2H)_{11}-(CH_3CO_2)_6(OH)_{26}(H_2O)_{30}]$. Reprinted with the permission from [30] Copyright 2014 American Chemical Society

calixarene ligand (Fig. 13b, bottom). In both complexes, aqua ligands fulfill the rest of the metal coordination sphere.

Even larger lanthanide hydroxide clusters have also been reported, generally as unintended outcome of reactions originally aiming at different synthetic targets. As an example, three 26-metal lanthanide hydroxide cluster complexes were reported by two different groups. They are $[Er_{26}I(\mu_3\text{-}OH)_{20}(\mu_3\text{-}O)_6(NO_3)_9(ina)_{33}(OH)_3(H_2O)_{33}]$ reported by Xue et al. [31] and $[Ho_{26}(ina)_{28}(CH_3COO)_4(CO_3)_{10}(OH)_{26}(H_2O)_{18}]\cdot 20H_2O$ and $[Er_{26}(ina)_{29}(CH_3COO)_3(CO_3)_{10}(OH)_{26}(H_2O)_{19}]\cdot 26H_2O$ by Xu and his coworkers [32]. The first member of the three was isolated from a hydrothermal reaction using a mixture of Er_2O_3, AgI, isonicotinic acid, and HNO_3, whereas the others were obtained, also under hydrothermal conditions, using a mixture of Ln_2O_3, $Mn(OAc)_2\cdot 4H_2O$, isonicotinic acid, and formic acid.

Surprisingly, despite the different synthetic procedures and the compositions of the final product, the polyhedral arrangement of the core metal atoms is actually the same with the difference being only in the type and the number of bridging ligands. As such, only the representative structure of $[Er_{26}I(\mu_3\text{-}OH)_{20}(\mu_3\text{-}O)_6(NO_3)_9(ina)_{33}(OH)_3(H_2O)_{33}]$ is shown in Fig. 14. All three complexes have the same number (26) of triply bridging oxo/hydroxo groups. Furthermore, in each of the lanthanide-oxo/hydroxo cores there are a total of 42 bridging ligands that connect adjacent lanthanide atoms. These bridging ligands are all O-based with ina being common in all three clusters. The remaining bridging ligands are either inorganic (NO_3^-, CO_3^{2-}) or acetate ion. Coordination of the lanthanide ions is completed by aqua and other small-entity ligands that do not alter the overall complex structures.

In addition to the essential presence of bridging hydroxo group, anion species including O^{2-}, N_3^-, NO_3^-, halides, CO_3^{2-}, and ClO_4^- have frequently been

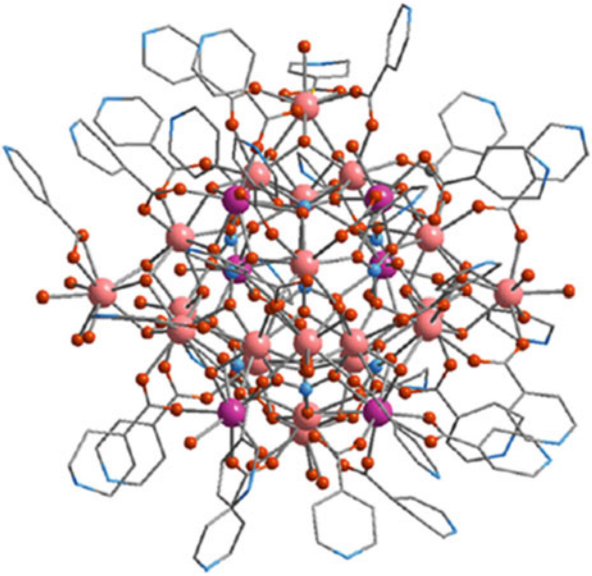


Fig. 14 Structure of $[Er_{26}I(\mu_3\text{-}OH)_{20}(\mu_3\text{-}O)_6(NO_3)_9(ina)_{33}(OH)_3(H_2O)_{33}]$. Reprinted with the permission from [31] Copyright 2008 Elsevier

observed in high-nuclearity lanthanide hydroxide clusters wherein such anions serve presumably to template the assembly of the giant clusters. We note that the genesis of these anions (if they are not from the starting materials) and/or their role(s) constitute an active research topic for which definitive answers remain unclear. In the work reported by Hong et al., two 36-metal cluster complexes formulated as $[Ln_{36}(nic)_{36}(OH)_{49}(O)_6(NO_3)_6(N_3)_3(H_2O)_{20}]\cdot Cl_2\cdot 28H_2O\cdot(Ln = Gd, Dy)$ were obtained from a hydrothermal reaction using a mixture of lanthanide chloride, NaN_3, nicotinic acid, and HNO_3 [33]. Structural studies by single-crystal X-ray diffraction revealed 36 Ln^{3+} ions organized into a cage-like structure featuring coordination by bridging OH^-, O^{2-}, N_3^-, and NO_3^- groups (Fig. 15a). The distorted cubane units of $[Ln_4(\mu_3\text{-}OH)_4]^{8+}$ are easily recognizable in the core structure, together with other types of Ln-OH motifs that link these cubane units. The Ln^{3+} coordination sphere is completed by aqua ligands, carboxylate O atoms, as well as the nic chelating carboxylate groups (Fig. 15b).

Tong et al. reported two high-nuclearity complexes $[Gd_{38}(\mu\text{-}O)(\mu_8\text{-}ClO_4)_6(\mu_3\text{-}OH)_{42}(caa)_{37}(H_2O)_{36}(EtOH)_6](ClO_4)_{10}\cdot(OH)_{17}\cdot 14DMSO\cdot 13H_2O$ and $[Gd_{48}(\mu_4\text{-}O)_6(\mu_3\text{-}OH)_{84}(caa)_{36}(NO_3)_6(H_2O)_{24}(EtOH)_{12}(NO_3)Cl_2]Cl_3\cdot 6DMF\cdot 5EtOH\cdot 20H_2O$ (Hcaa = chloroacetic acid) [34]. The profound influence of the nature of the anions on the structure of the resulting clusters is clearly shown here. While the reaction of a mixture containing chloroacetic acid, gadolinium perchlorate, and NaOH in a water/ethanol/DMSO mixed solvent produced the 38-metal cluster complex, the use of gadolinium nitrate or chloride hydrate in place of gadolinium perchlorate afforded the 48-metal complex under nearly identical reaction conditions.

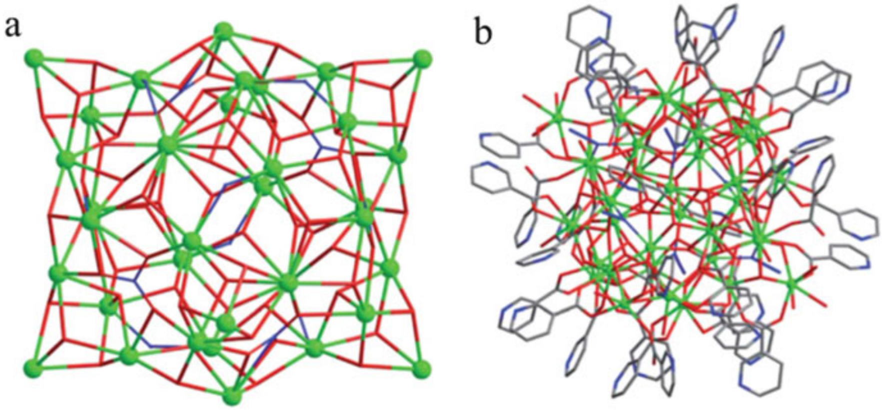


Fig. 15 Structure of: (**a**) $[Ln_{36}(nic)_{36}(OH)_{49}(O)_6(NO_3)_6(N_3)_3(H_2O)_{20}]^{2+}$ and (**b**) the hydroxide cluster core. Reprinted with the permission from [33] Copyright 2013 Royal Society of Chemistry

The 38 Gd^{3+} ions in the smaller complex are organized into a cage-like structure featuring twelve vertex-sharing $\{Gd_4\}$ tetrahedra with the metals joined together by one μ-O, μ_8-ClO_4^-, μ_3-OH, and caa carboxylate groups. The coordination sphere is completed by aqua and ethanol ligands (Fig. 16a). In comparison, the 48 metal atoms in the larger complex are connected by six μ_4-O anions, 84 μ_3-OH groups, and caa carboxylate groups into a barrel-like structure. One NO_3^- anion and two Cl^- anions are imbedded inside the void of the barrel through hydrogen bonding. Aqua and ethanol ligands as well as NO_3^- anions complete the lanthanide coordination (Fig. 16b).

Although nicotinic acid was used, a very similar hydroxide cluster core as in the work by Tong et al. [34] with an identical arrangement of 48 lanthanide ions was reported by Hong and coworkers [35]. Specifically, using a mixture of NaN_3, nicotinic acid, $NaNO_3$, and erbium chloride, a hydrothermal reaction produced $\{[Cl_2\&(NO_3)]@[Er_{48}(nic)_{44}(OH)_{90}(N_3)(H_2O)_{24}]\}\cdot 6Cl\cdot 35H_2O$ wherein the occlusion of two Cl^- and one NO_3^- ions (Fig. 17b) is also observed. The barrel-like cluster core may alternatively be viewed as an $\{Er_{12}\}$ ring being sandwiched between two $\{Er_{18}\}$ wheels (Fig. 17a). The assembly of the two almost identical cluster cores suggests that this cluster motif, though obtained in different reactions, may be a common one in the family of lanthanide hydroxide complexes.

The significant templating roles played by small anions are further exemplified in the assembly of $[Er_{60}(\text{L-thre})_{34}(\mu_6\text{-}CO_3)_8(\mu_3\text{-}OH)_{96}(\mu_2\text{-}O)_2(H_2O)_{18}]Br_{12}(ClO_4)_{18}(H_2O)_{40}$ (L-thre = L-threonine) by Zheng and his coworkers. This giant complex was prepared by the hydrolysis of Er^{3+} using L-threonine as supporting ligand [36]. The 60 Er^{3+} ions are arranged into a discrete sodalite cage (Fig. 18a) with each of its 24 vertices being occupied by an $[Er_4(\mu_3\text{-}OH)_4]^{8+}$ cubane unit (Fig. 18b). Alternatively, the cage structure can be viewed as being built by using two different yet related cubane-wheel second-building units (SBUs), one being dodecanuclear (composed of four vertex-sharing cubanes) and the other

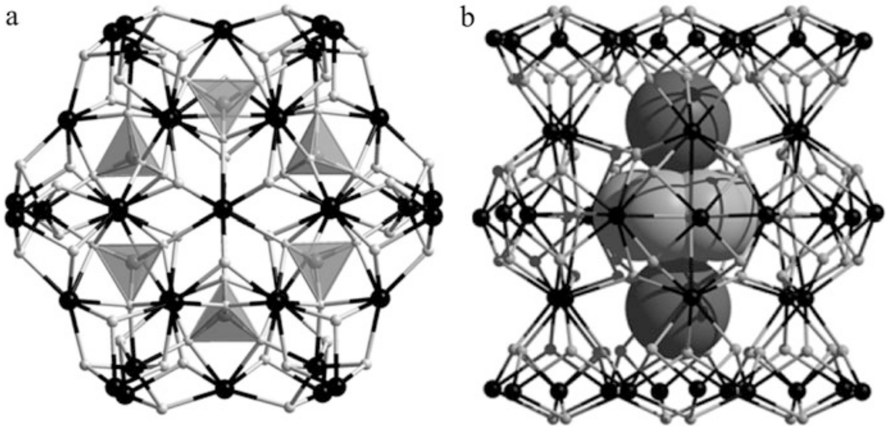


Fig. 16 Structure of: (**a**) $\{Gd_{38}(O)(ClO_4)_6(OH)_{42}\}^{64+}$ and (**b**) $\{Gd_{48}(\mu_4\text{-}O)_6(\mu_3\text{-}OH)_{84}Cl_2(NO_3)\}$. Reprinted with the permission from [34] Copyright 2013 Wiley-VCH Verlag GmbH & Co

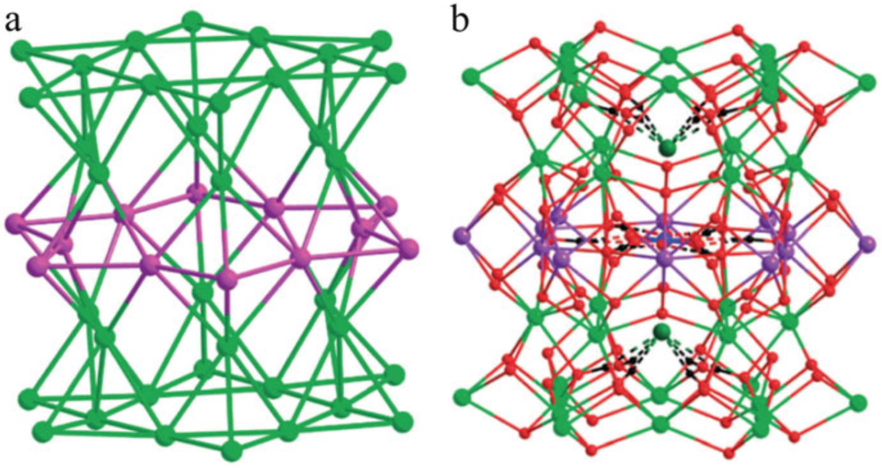


Fig. 17 Structure of: (**a**) the cluster core of $\{[Cl_2\&(NO_3)]@[Er_{48}(nic)_{44}(OH)_{90}(N_3)\text{-}(H_2O)_{24}]\}$ $6Cl{\cdot}35H_2O$ with the encapsulated anions and bridging atoms displayed and (**b**) the metallic backbone of the cluster core. Reprinted with the permission from [35] Copyright 2013 Royal Society of Chemistry

octadecanuclear (consisting of six vertex-sharing cubanes) with the latter being templated by a $\mu_6\text{-}CO_3{}^{2-}$ ion. The lanthanide hydroxide cluster core is encapsulated by L-thre$^-$ ligands (Fig. 18c).

More recently, three isostructural cluster complexes with a record-high 104 lanthanide atoms were reported by Long and his coworkers [37]. These complexes, formulated as $[Nd_{104}(ClO_4)_6(CH_3COO)_{60}(\mu_3\text{-}OH)_{168}(\mu_4\text{-}O)_{30}(H_2O)_{112}]$ $(ClO_4)_{18}{\cdot}(CH_3CH_2OH)_8{\cdot}xH_2O$ and $[Ln_{104}(ClO_4)_6(CH_3COO)_{56}(\mu_3\text{-}OH)_{168}$

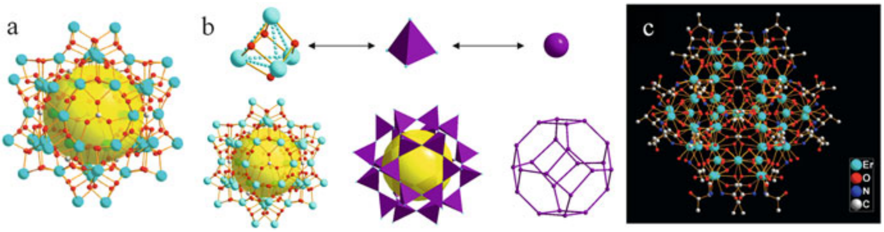


Fig. 18 (**a**) Structure of the 24-cubane cluster core in $[Er_{60}(\text{L-thre})_{34}(\mu_6\text{-}CO_3)_8(\mu_3\text{-}OH)_{96}(\mu_2\text{-}O)_2(H_2O)_{18}]^{30+}$; (**b**) formal assembly of a discrete sodalite cage by using cluster cubane units as SBUs; and (**c**) structure of the cationic 60-metal complex. Reprinted with the permission from [36] Copyright 2009 American Chemical Society

$(\mu_4\text{-}O)_{30}(H_2O)_{112}]\cdot(ClO_4)_{22}\cdot(CH_3CH_2OH)_2\cdot xH_2O$ (Ln = Nd, Gd), were obtained from the reaction of *N*-acetyl-D-glucosamine, $Co(CH_3COO)_2\cdot 4H_2O$, and lanthanide perchlorate in ethanol under either solvothermal or ambient-pressure conditions. It is of note that Co^{2+} was not incorporated into the product, but replacing the transition metal acetate for sodium acetate did not lead to the same cluster species; the role of the transition metal ion remains unclear. The 104 metal ions are organized into an aesthetically pleasing four-shell cage structure with an ideal cubic symmetry (Fig. 19a). An alternative way of looking at the structure is that it can be built by 24 square pyramidal $[Ln_5(\mu_4\text{-}O)(\mu_3\text{-}OH)_4]^{9+}$ and 8 $[Ln(\mu_3\text{-}OH)_6]^{3-}$ units. Every four adjacent units of $[Ln_5(\mu_4\text{-}O)(\mu_3\text{-}OH)_4]^{9+}$ are joined together by centering around one $\mu_4\text{-}O^{2-}$ anion to form an $[Ln_{16}(\mu_4\text{-}O)_5(\mu_3\text{-}OH)_{20}]^{18+}$ wheel that occupies one vertex of a perfect octahedron (Fig. 19b). The Ln^{3+} ions are further connected by acetate ligands (Fig. 19c). Water molecules and 6 ClO_4^- anions are encapsulated within the void of the nanoscopic cluster. The 104-Gd complex has been shown to possess one of the largest magnetocaloric effects measured for all lanthanide-exclusive clusters reported. These magnetic lanthanide clusters are of interest in developing energetically more efficient and more environmentally friendly cooling technologies.

2.2 Diketonates

Equally extensively utilized in lanthanide coordination chemistry are diketonate-based ligands [38–43]. Recent years have seen their increasing use in supporting the assembly of lanthanide hydroxide cluster complexes [44, 45]. A number of cluster core motifs have been reported and are collected in Fig. 20 with the planar tetranuclear and square pyramidal pentanuclear motifs being more frequently observed than the rest. We note that lanthanide hydroxide clusters supported by carboxylate-based ligands exhibit a much greater structural variety than those with diketonate ligands.

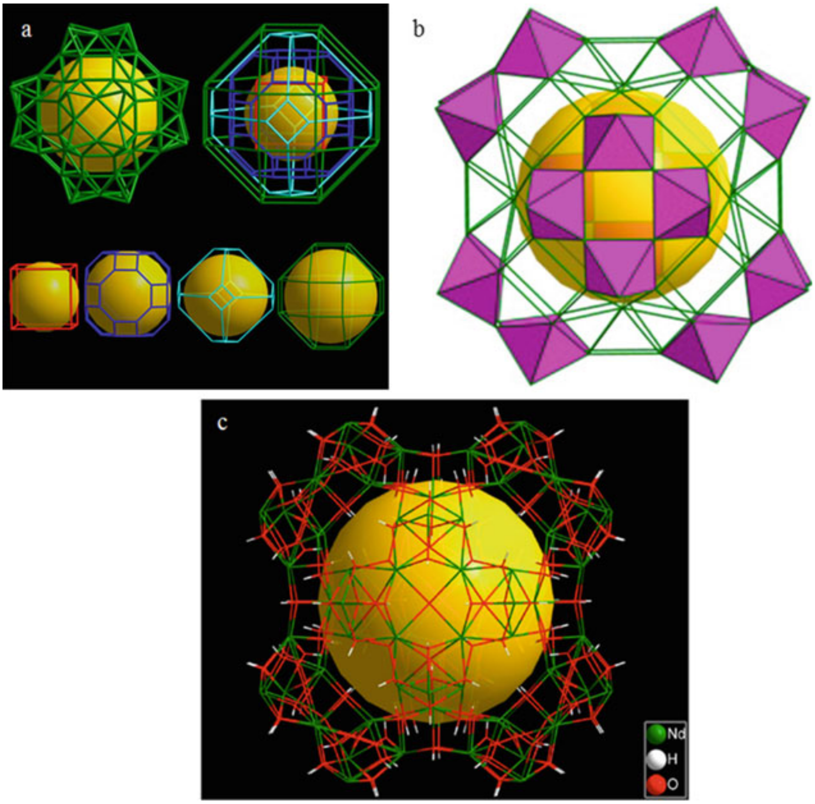


Fig. 19 (**a**) Four-shell organization of the 104 lanthanide atoms; (**b**) building the cluster core by using square pyramidal SBUs; and (**c**) structure of the cationic complex $[Ln_{104}(\mu_3\text{-}OH)_{168}(\mu_4\text{-}O)_{30}]^{84+}$ showing the coordination/passivation of the cluster core by acetate ligands. Reprinted with the permission from [37] Copyright 2014 American Chemical Society

2.2.1 Clusters with Nuclearity Smaller Than Nine

Trinuclear lanthanide hydroxide cluster complexes are not common. [46] One recent example is $[Dy_3(OH)(teaH_2)_3(paa)_3]Cl_2{\cdot}MeCN{\cdot}4H_2O$ ($teaH_3$ = triethanolamine; paaH = *N*-(2-pyridyl)-acetoacetamide) wherein deprotonated $teaH_3$ and paaH were used together to support a cuboidal or incomplete cubane core of $[Dy_3(\mu_3\text{-}OH)]$ [29]. The three Dy^{3+} ions together with the μ_3-OH group form a pyramid that is encapsulated by the diketonate ligands. Each of the three Dy…Dy edges is bridged by one ethanoxide O atom of one $teaH_2$ ligand that also uses its N atom and the remaining two ethanol OH groups to coordinate the same lanthanide ion. Each lanthanide ion is also chelated by two ketonate O atoms of a paa ligand (Fig. 21).

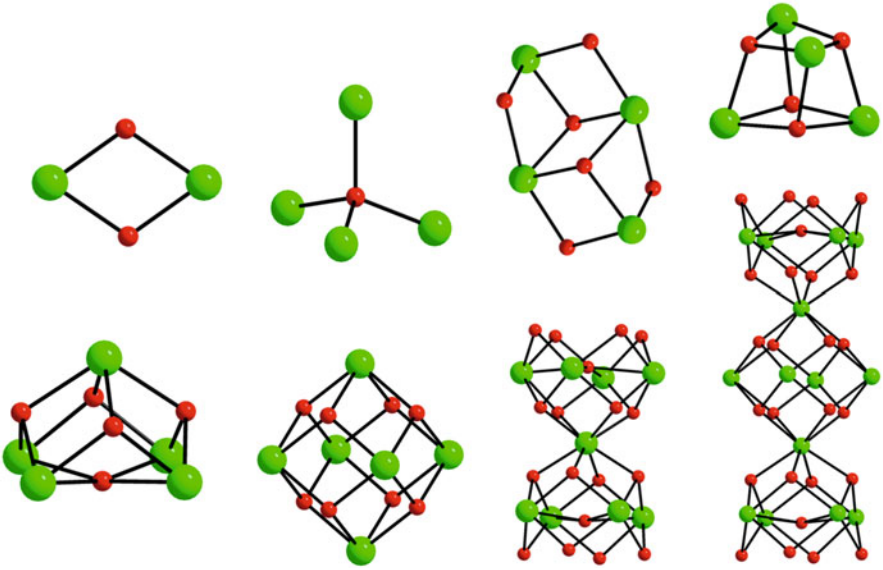


Fig. 20 Structure of representative core motifs in lanthanide-oxo/hydroxo cluster complexes supported by diketonate-based ligands

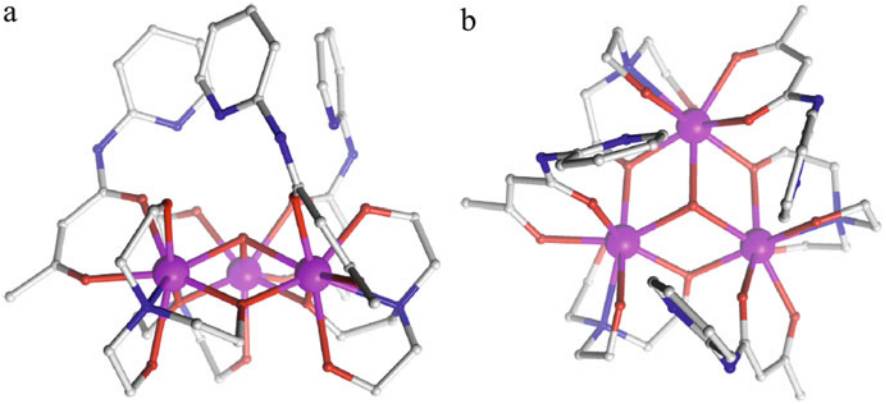


Fig. 21 *Side view* (**a**) and *top view* (**b**) of $[Dy_3(OH)(teaH_2)_3(paa)_3]^{2+}$. Reprinted with the permission from [29] Copyright 2013 Elsevier

Tetranuclear cluster motifs are either a distorted cubane or a planar arrangement of 4 lanthanide ions with two μ_3-OH groups. Both motifs, already discussed above, have seen frequent occurrence in the literature.

Zheng et al. conducted a systematic study on utilizing acetylacetonate (acac) as protecting ligand to support the assembly of hydroxide cluster complexes in organic solution. A structure representing the isostructural tetranuclear complexes $Ln_4(\mu_3\text{-}OH)_2(\mu_3\text{-}OCH_3)_2(CH_3OH)_2(acac)_8$ (Ln = Nd, Sm) is shown in Fig. 22 [47]. The

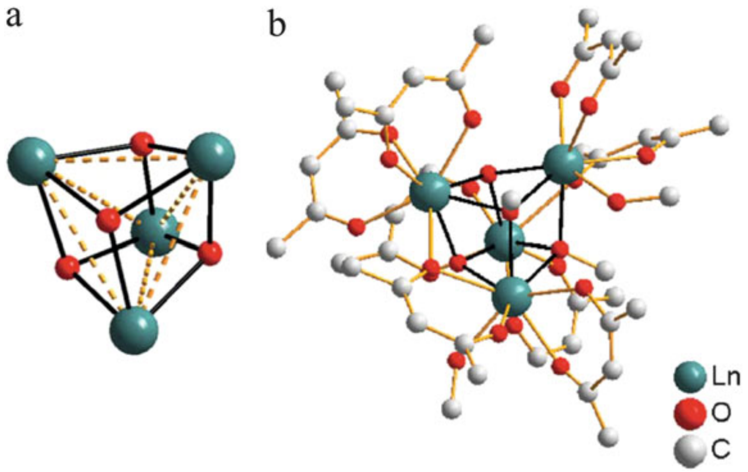


Fig. 22 Structures of: (**a**) the cubane cluster core and (**b**) $[Ln_4(\mu_3\text{-}OH)_2(\mu_3\text{-}OCH_3)_2(CH_3OH)_2(acac)_8]$ [47]. Reprinted with the permission from [47] Copyright 2011 Royal Society of Chemistry

cubane cluster core of $[Ln_4(\mu_3\text{-}OH)_2(\mu_3\text{-}OCH_3)_2]^{8+}$ features coordination by two μ_3-OH and two $\mu_3\text{-}OCH_3^-$ groups (Fig. 22a). Each Ln^{3+} ion is chelated by two acac ligands with two of the lanthanide ions being also coordinated with one methanol molecule (Fig. 22b).

Using *ortho* ring-functionalized 1-phenylbutane-1,3-dione ligands bearing nitro (Hnpd and Hnmc), methoxy (Hmmc), or fluoro (Hfpp) groups, MacLellan et al. reported a series of tetranuclear hydroxide cluster complexes $[Er_4(\mu_3\text{-}OH)_4(H_2O)_2(npd)_8]$, $[Ln_4(\mu_3\text{-}OH)_4(nmc)_8]\cdot(Ln = Gd, Tb, Dy \text{ and } Er)$, $[Er_4(\mu_3\text{-}OH)_4(mmc)_8]$, and $[Er_4(\mu_3\text{-}OH)_4(H_2O)_2(fpp)_8]$ [48]. These complexes were prepared in methanol using a reaction mixture containing lanthanide chloride hydrates, one of the diketone ligands, and trimethylamine; the organic base is responsible for promoting the hydrolysis of the lanthanide hydrates.

All of these complexes contain the same cubane cluster core, and the structures of $[Er_4(\mu_3\text{-}OH)_4(H_2O)_2(npd)_8]$ and $[Er_4(\mu_3\text{-}OH)_4(nmc)_8]$ are shown in Fig. 23. In both complexes, each of the Er^{3+} ions is chelated by two diketonate ligands (either npd or nmc). In $[Er_4(\mu_3\text{-}OH)_4(H_2O)_2(npd)_8]$, two of the four Er^{3+} ions are also each coordinated by one aqua ligand in addition to two chelating diketonate ligands (Fig. 23a).

A number of tetranuclear complexes with different diketonate ligands but bearing the same planar cluster motif have been reported. Shown in Fig. 24 are the structures of $[Er_4(dbm)_6(O\text{-}btd)_4(\mu_3\text{-}OH)_2]$ and $[Er_4(dbm)_4(O\text{-}btd)_6(\mu_3\text{-}OH)_2]$ (dbm = dibenzoylmethanide; O-btd = 4-hydroxo-2,1,3-benzothiadiazolate) [49]. In both clusters, the planar rhomboid cluster core is encapsulated by a combination of the bridging–chelating O-btd ligands and chelating-only dbm ligands.

Using a combination of Hacac and $H_2L_6 = N,N'$-bis(salicylidene)-1,2-cyclohexanediamine, Sun et al. obtained four isostructural complexes of the

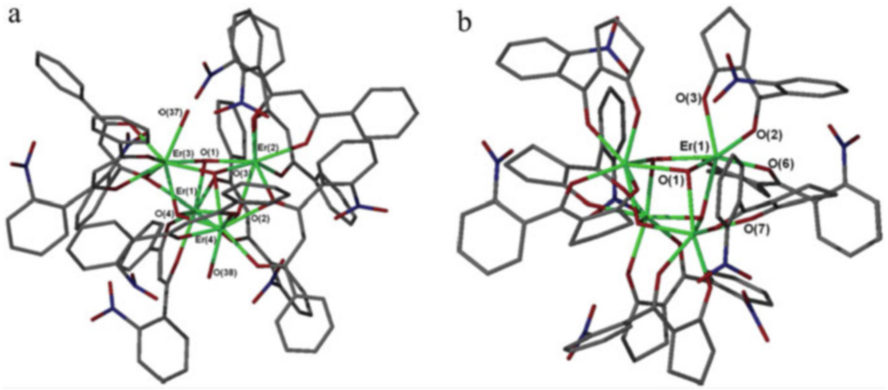


Fig. 23 Structure of: (**a**) $[Er_4(\mu_3\text{-}OH)_4(H_2O)_2(npd)_8]$ and (**b**) $[Er_4(\mu_3\text{-}OH)_4(nmc)_8]$. Reprinted with the permission from [48] Copyright 2011 Royal Society of Chemistry

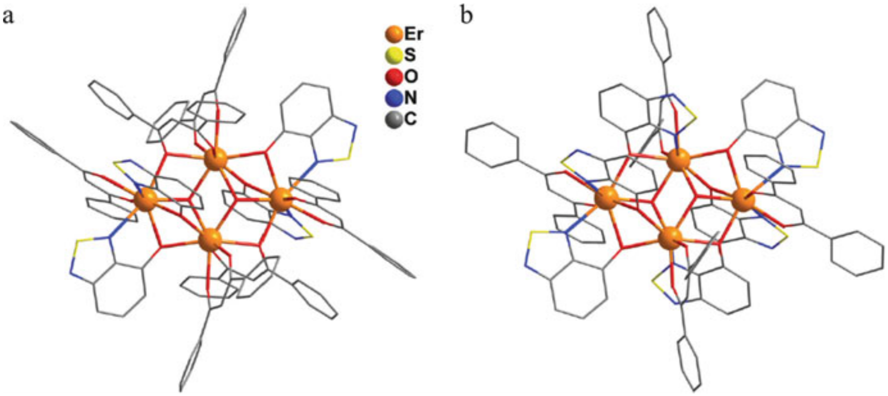


Fig. 24 Structure of: (**a**) $[Er_4(dbm)_6(O\text{-}btd)_4(OH)_2]$ and (**b**) $[Er_4(dbm)_4(O\text{-}btd)_6(OH)_2]$. Reprinted with the permission from [49] Copyright 2015 Royal Society of Chemistry

common formula $[Ln_4(\mu_3\text{-}OH)_2(L_6)_2(acac)_6]\cdot xH_2L_6\cdot yCH_3CN\cdot zH_2O\cdot(Ln = Sm, Gd, Tb, and Dy)$ [50]. The synthesis was carried out by slowly adding a methanolic solution of a lanthanide acetylacetonate hydrate to an acetonitrile solution of H_2L_6, followed by reflux of the resulting solution mixture. Two opposite edges of the rhomboid cluster core are each bridged by one L_6phenol O, while the other two edges are each bridged by one L_6phenol O as well as one O atom of the chelating–bridging acac ligand. Each of the lanthanide ions is further coordinated by one chelating-only acac ligand (Fig. 25).

Lastly, Urbatsch et al. reported two tetranuclear complexes formulated as $[Ln_4(\mu_3\text{-}OH)_2\{(\mu\text{-}O)\text{-}k^2\text{-}htp\}_2\{(\mu\text{-}O)_2\text{-}k^2\text{-}htp\}_2(k^2\text{-}htp)_6]$ (Ln = Nd, Eu) by using (*Z*)-3-hydroxy-3-phenyl-1-(thiophen-2-yl)prop-2-en-1-one (Hhtp; Fig. 26a) – a thiophene-containing *β*-diketone – as supporting ligand [51]. The rhomboid cluster core is coordinated with the diketonate ligands in three different modes: Two

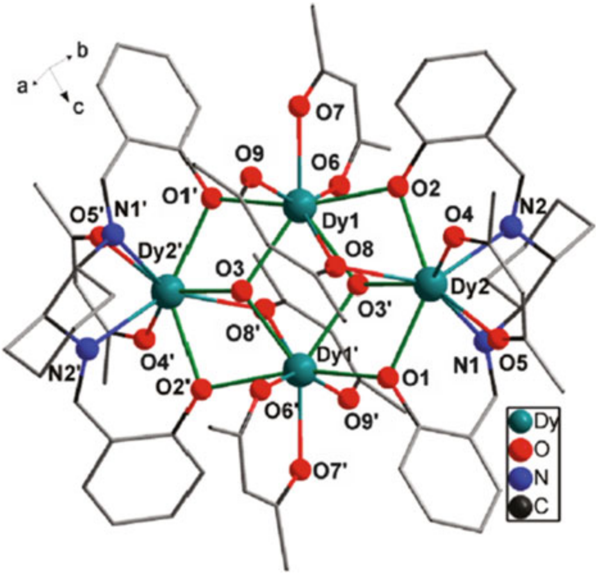


Fig. 25 Structure of $[\mathrm{Dy_4}(\mu_3\text{-OH})_2(\mathrm{L_6})_2(\mathrm{acac})_6]$. Reprinted with the permission from [50] Copyright 2011 American Chemical Society

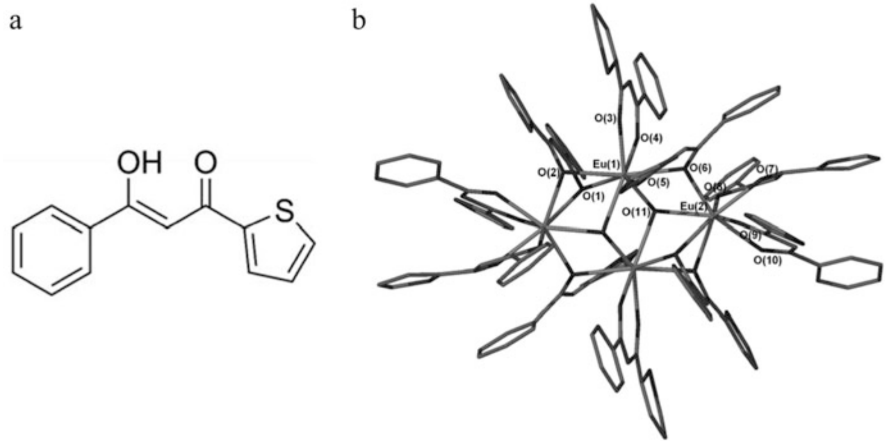


Fig. 26 (**a**) Schematic illustration of the Hhtp ligand and (**b**) structure of $[\mathrm{Eu_4}(\mu_3\text{-OH})_2\{(\mu\text{-O})\text{-k}^2\text{-htp}\}_2\{(\mu\text{-O})_2\text{-k}^2\text{-htp}\}_2(\text{k}^2\text{-htp})_6]$. Reprinted with the permission from [51] Copyright 2012 Wiley-VCH Verlag GmbH & Co

opposite edges are each uniquely bridged by the two O atoms from the same htp ligand, while the other two are each bridged by one htpO atom; these latter two htp ligands each chelate one lanthanide ion. The remaining 6 htp ligands are of the chelating-only type to complete the octacoordinate sphere for each lanthanide ion (Fig. 26b).

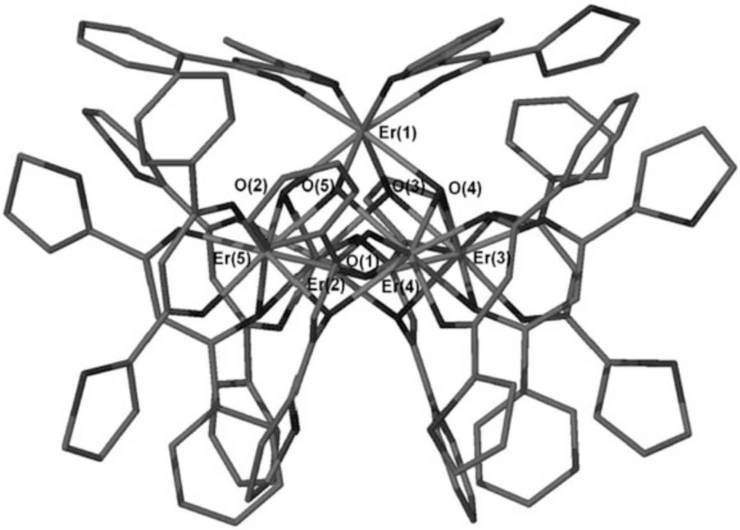


Fig. 27 Structure of [$Er_5(\mu_3\text{-}OH)_4(\mu_4\text{-}OH)(\mu\text{-}\eta^2\text{-}htp\}_4(\eta^2\text{-}htp)_6$). Reprinted with the permission from [51] Copyright 2012 Wiley-VCH Verlag GmbH & Co

Together with the above tetranuclear complexes, a pentanuclear complex $Er_5(\mu_3\text{-}OH)_4(\mu_4\text{-}OH)(\mu\text{-}\eta^2\text{-}htp\}_4(\eta^2\text{-}htp)_6$ was also isolated [51]. Though not entirely clear, the formation of a larger cluster under otherwise identical reaction conditions may be due to the difference in the lanthanide ion size (Er^{3+} versus Nd^{3+}/Eu^{3+}). The five Er^{3+} ions are organized into a square pyramid with a μ_4-OH group situated at the center of its basal plane and coordinating all four basal Er^{3+} ions. Each of the four triangular faces of the square pyramid is capped by a μ_3-OH group. This $[Er_5(\mu_3\text{-}OH)_4(\mu_4\text{-}OH)]^{10+}$ core is encapsulated in the coordination sphere formed by 10 htp ligands, of which four are bridging–chelating that uses one of its two ketonate O atoms to bridge one basal Er...Er linkage while using the very same O atom together with the other ketonate O to chelate one of the Er^{3+} ions. Each basal Er^{3+} is also coordinated by a second chelating-only htp ligand. The Er^{3+} ion at the axial position is unique; it is coordinated by two chelating-only htp ligands (Fig. 27).

It appears that such coordinating modes are prevalent. Despite the different diketonate ligands used, the same coordination modes have been observed in the six isostructural pentanuclear complexes $Ln_5(dbm)_{10}(\mu_3\text{-}OH)_4(\mu_4\text{-}OH)\cdot n(solvent)$ (Ln = Nd, Eu, Gd, Tb, Er, Yb; solvent = acetonitrile or toluene) independently reported by Holiday, Luneau, and their respective coworkers [52, 53], as well as in $Ln_5(\mu_3\text{-}OH)_4(\mu_4\text{-}OH)(Iphacac)_{10}$ (Ln = Tb, Dy, Yb; bis(*para*-iododibenzoyl)-methanide = Iphacac) by Thielemann et al. [54], and in $Ln_5(\mu_3\text{-}OH)_4(\mu_4\text{-}OH)(L_7)_{10}$ (Ln = Eu, Ho; 1,3-bis(4-ethoxyphenyl)propane-1,3-dione = HL_7) by Silberstein and his coworkers [55].

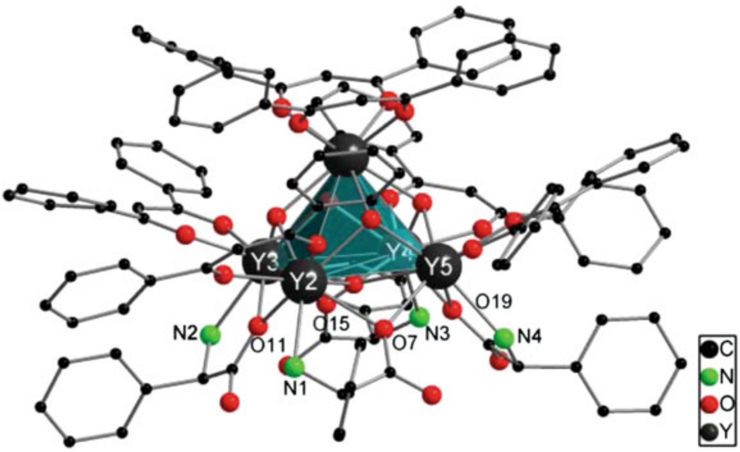


Fig. 28 Structure of [$Y_5(\mu_3\text{-OH})_4(\mu_4\text{-OH})(\text{D-PhGly})_4(\text{dbm})_6$]. Reprinted with the permission from [56] Copyright 2010 Royal Society of Chemistry

Interestingly, some of the diketonate ligands can be replaced by other types of ligands that are capable of both bridging and chelating metal ions. Roesky et al. reported four pentanuclear yttrium complexes of the general formula [$Y_5(\mu_3\text{-OH})_4(\mu_4\text{-OH})(\alpha\text{-AA})_4(\text{dbm})_6$] ($\alpha$-AA = D-phenyl glycine; L-proline; L-valine; and L-tryptophan) in which the amino acids can be viewed as a diketonate surrogate [56]. Each of the amino acid ligands uses one of its carboxylate O atom to bridge one basal Ln…Ln linkage while using this very same O atom together with the amino N atom to chelate one of the four basal lanthanide ions; the other carboxylate O remains uncoordinated (Fig. 28).

Using *o*-hydroxydibenzoylmethane (HO-Hdbm) as supporting ligand, Baskar et al. were able to obtain a hexanuclear complex [$Y_6(\text{O-dbm})_6(\text{HO-dbm})_4(\mu_3\text{-OH})_2(\text{MeOH})_4$] with a rare core motif (Fig. 29) [57]. The six Y^{3+} ions are nearly coplanar and can be viewed as being constructed by adding one Y^{3+} ion on each side of the planar tetranulcear motif. This is made possible by the coordination of the phenoxide O of 6 doubly negatively charged O-dbm ligands. The four Y^{3+} ions in the central rhomboid are bridged by two μ_3-OH groups with each of its edges being bridged by one O-dbm O atom. This very O atom, together with the phenoxide O of the same ligand, chelates one of the four Y^{3+} ions, while the same phenoxide O also bridges the added terminal Y^{3+} ion. Each of these two added Y^{3+} ions is additionally coordinated by two chelating HO-dbm whose phenol moiety remains neutral and uncoordinated (Fig. 29).

When in assessing the influence of ligand sterics on the structure of the resulting hydroxide clusters, Luneau et al. obtained two octanuclear complexes [$\text{Ln}_8(\text{thd})_{10}(\mu_4\text{-O})(\mu_3\text{-OH})_{12}$] (Ln = Eu, Y) with 2,2,6,6-tetramethylheptane-3,5-dione (Hthd), while pentanuclear clusters were isolated when dbm was the hydrolysis-limiting ligand under otherwise identical conditions [52]. The eight Ln^{3+} ions in the cluster

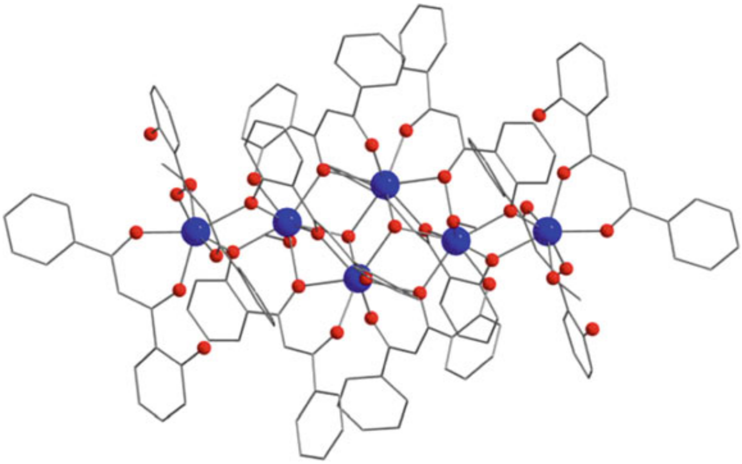


Fig. 29 Structure of $[Y_6(O\text{-dbm})_6(HO\text{-dbm})_4(\mu_3\text{-OH})_2(MeOH)_4]$. Reprinted with the permission from [57] Copyright 2009 Elsevier

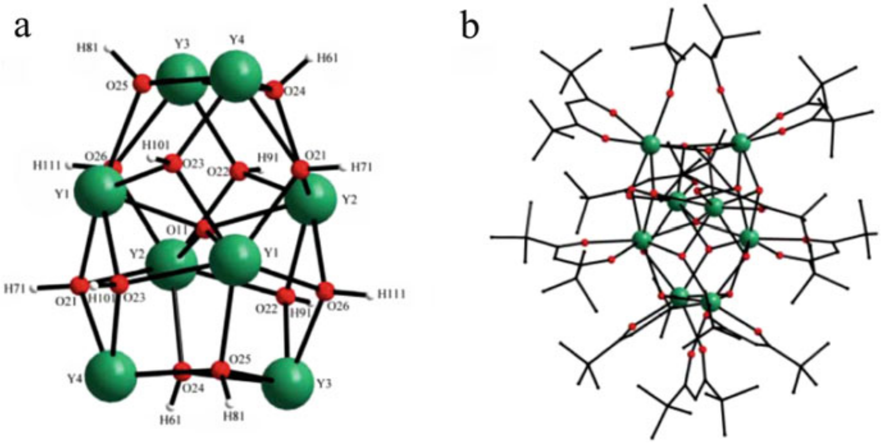


Fig. 30 Structure of: (**a**) the octanuclear cluster core with bridging oxo/hydroxo groups displayed and (**b**) $[Y_8(thd)_{10}(\mu_4\text{-O})(\mu_3\text{-OH})_{12}]$. Reprinted with the permission from [52] Copyright 2009 Royal Society of Chemistry

core are bridged by one μ_4-O group and twelve μ_3-OH groups (Fig. 30a). The structure may be viewed as two distorted cubanes joined together by the μ_4-O group with the Ln. . .Ln linkages (Y1. . .Y2) at the juncture disposed orthogonally with each other. Each lanthanide ion is chelated by one thd ligand. There are two additional ligands, each bridging a pair of "external" lanthanide ions that are not associated with the μ_4-O group (Fig. 30b).

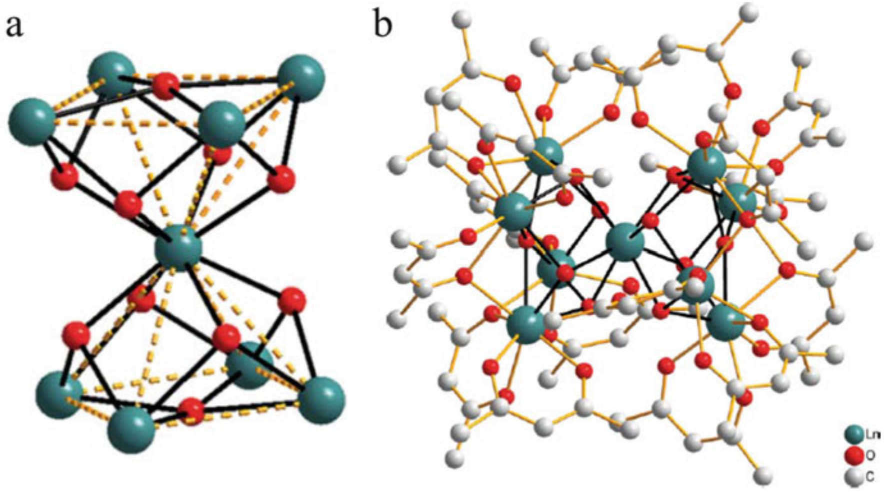


Fig. 31 Structure of: (**a**) the nonanuclear cluster core with bridging oxo/hydroxo groups displayed and (**b**) [$Ln_9(acac)_{16}(\mu_3\text{-}OH)_8(\mu_4\text{-}O)(\mu_4\text{-}OH)$]. Reprinted with the permission from [47] Copyright 2011 Royal Society of Chemistry

2.2.2 Nonanuclear or Higher-Nuclearity Clusters

From the hydroxide complexes presented above, it becomes clear that higher-nuclearity cluster core motifs can be formally constructed by using smaller polyhedral units as SBUs. If two pentanuclear square pyramids are joined by sharing the non-basal vertex lanthanide ion, an hourglass-shaped nonanuclear motif is produced (Fig. 31a). Such a core motif is present in [$Ln_9(acac)_{16}(\mu_3\text{-}OH)_8(\mu_4\text{-}O)(\mu_4\text{-}OH)$]·$H_2O$ (Ln = Eu, Gd, Tb, Dy, Er, Yb, Y), prepared independently by Luneau, Zheng, and their respective coworkers [47, 52, 58]. The two recognizable pentanuclear units are disposed 90° with respect to each other. One of the basal planes is capped by a μ_4-O group, while the other one by a μ_4-OH group. Each of the triangular faces is capped by a μ_3-OH to give the core formula of [$Ln_9(\mu_3\text{-}OH)_8(\mu_4\text{-}O)(\mu_4\text{-}OH)$]$^{16+}$. The acac ligands provide the coordination sheath with 8 being chelating only for each of the basal lanthanide ions and the remaining 8 being both chelating and bridging (Fig. 31b). It should be noted that the ligand coordination mode for the basal lanthanide ions is the same as exhibited by ketonate ligands in the pentanuclear cluster complexes discussed above.

The vertex-sharing can occur between other types of SBUs that are of the same or different kinds. Shown in Fig. 32 is the structure of a tetradecanuclear complex [$Dy_{14}(\mu_4\text{-}OH)_2(\mu_3\text{-}OH)_{16}(\mu\text{-}\eta^2\text{-}acac)_8(\eta^2\text{-}acac)_{16}$] [59]. The cluster core can be formally built by sandwiching a hexanuclear octahedral hydroxide unit between two pentanuclear square pyramids via vertex-sharing. The two terminal square basal faces are each capped by a μ_4-OH group. The coordination modes of the acac ligands for the basal lanthanide ions are exactly the same as seen above in the

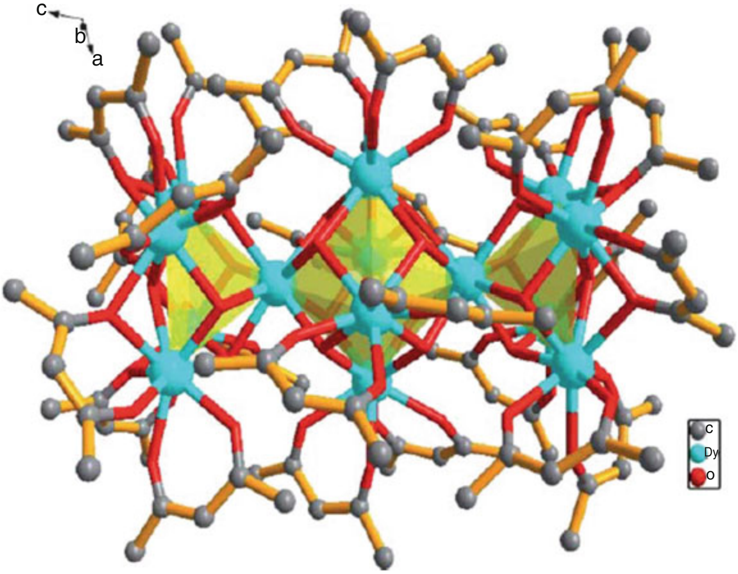


Fig. 32 Structure of $[Dy_{14}(\mu_4\text{-OH})_2(\mu_3\text{-OH})_{16}(\mu\text{-}\eta^2\text{-acac})_8(\eta^2\text{-acac})_{16}]$. Reprinted with the permission from [59] Copyright 2011 Royal Society of Chemistry

nonanuclear complex. The remaining eight acac ligands are chelating only, two on each of the four equatorial lanthanide ions of the central octahedral unit.

Pentadecanuclear hydroxide complexes with tyrosinate as supporting ligand are arguably one of the more notable high-nuclearity lanthanide clusters whose core motif features five cubane units joined together by sharing two vertex lanthanide ions with the assistance of a templating halide ion [11]. More recently, Roesky et al. reported a series of isostructural cluster complexes of the general formula $[Ln_{15}(\mu_3\text{-OH})_{20}(PepCO_2)_{10}(dbm)_{10}Cl]\cdot Cl_4\cdot$($PepCO_2 =$ 2-[{3-(((*tert*-butoxycarbonyl) amino)methyl)benzyl}-amino]acetate; Ln = Eu, Tb, Dy, Y) that contain the same pentadecanuclear core (Fig. 33) [60, 61]. The Eu^{3+} and Tb^{3+} complexes have been shown to luminesce in cellular structures and are therefore potentially useful for biological imaging and immunoassay.

2.3 *Phosphonates and Sulfonates*

Inspired by the great success of utilizing carboxylate and diketonate ligands as supporting ligands for the assembly of high-nuclearity lanthanide hydroxide clusters, chemists have also turned to other O-based ligands such as phosphonates and sulfonates with the hopes of creating cluster complexes with novel structures and properties. Such ligands can be used alone or in combination with other type(s) of ligands.

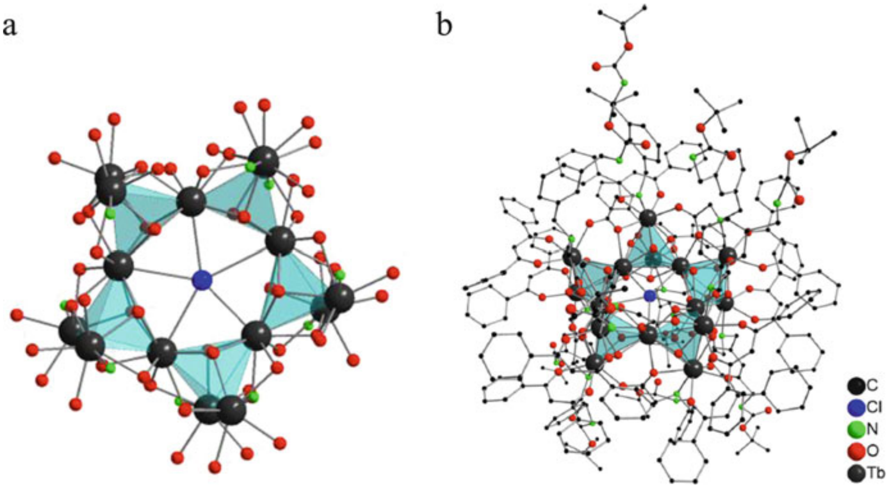


Fig. 33 Structure of: (**a**) the pentadecanuclear core with a templating chloride ion and (**b**) $[Tb_{15}(\mu_3\text{-}OH)_{20}(PepCO_2)_{10}(dbm)_{10}Cl]^{4+}$. Reprinted with the permission from [60] Copyright 2013 American Chemical Society

Treating lanthanide nitrate hydrates with pyridine in the presence of pivalic acid and *t*-butyl phosphonic acid in isobutanol under reflux led to the production of a series of tetranuclear lanthanide hydroxide complexes of the formula $[pyH]_4[Ln_4(\mu_3\text{-}OH)(O_3P^tBu)_3(HO_3P^tBu)(O_2C^tBu)_2(NO_3)_6]\cdot(Ln = Gd, Tb, Dy, Ho, Er)$ [62]. The representative structure of the Gd^{3+} complex is shown in Fig. 34. The tetranuclear core may be viewed as a μ_3-OH-bridged trinuclear cuboidal unit being connected to the fourth metal through the bridging of three $\mu_3\text{-}O_3P^tBu^{2-}$ ligands; each of the phosphate ligands uses one of its O atom to coordinate this fourth metal, the second to bridge two adjacent lanthanide ions within the cuboidal units, and the third, together with the second one, to chelate one of the three metals in the cuboidal unit. In addition, there are one $\mu_2\text{-}HO_3P^tBu^-$ and two $\mu_2\text{-}O_2C^tBu^-$ ligands along the edge of the cuboidal unit, each bridging a pair of adjacent lanthanide ions. Each lanthanide ion within the cuboidal unit is also chelated by an NO_3^- anion, whereas the coordination sphere of the fourth metal atom is completed with three chelating NO_3^- anions (Fig. 34).

With the same ligand set but using isopropylamine in place of pyridine to promote hydrolysis, Winpenny et al. were able to obtain three isostructural octanuclear complexes of the formula $[Ln_8(O_3P^tBu)_6(\mu_3\text{-}OH)_2(H_2O)_2(HO^iBu)(O_2C^tBu)_{12}](NH_3{}^iPr)_2\cdot(Ln = Gd, Dy, Tb; {}^iPrNH_2 = \text{isopropylamine}; HO^iBu = \text{isobutyl alcohol})$ [63]. The eight Ln^{3+} ions are arranged into a horseshoe-like structure (Fig. 35a) with the component lanthanide ions bridged together by six $O_3P^tBu^{2-}$ ligands, two $\mu_2\text{-}O_2C^tBu^-$, and four $\mu\text{-}\eta^2\text{-}O_2C^tBu^-$ ligands (Fig. 35b). The coordination spheres are completed by bidentate chelating $O_2C^tBu^-$ ligands, HO^iBu molecules, and aqua ligands. Alternatively, the cluster motif can be viewed as two μ_3-OH-containing cuboidal units joined together by two $O_3P^tBu^{2-}$ and one $\mu\text{-}\eta^2\text{-}O_2C^tBu^-$ ligands with an add-on lanthanide ion on each side of the double-cuboidal arrangement.

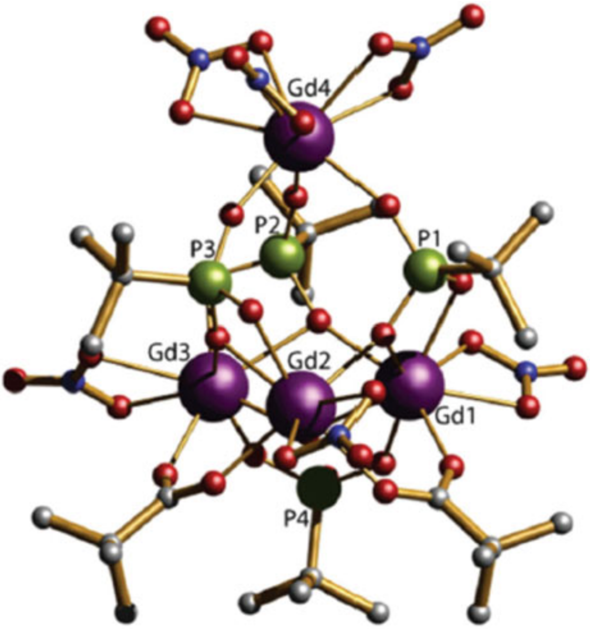


Fig. 34 Structure of the anionic cluster complex $[Gd_4(\mu_3\text{-}OH)(O_3P^tBu)_3(HO_3P^tBu)(O_2C^tBu)_2(NO_3)_6]^{4-}$. Reprinted with the permission from [62] Copyright 2014 Royal Society of Chemistry

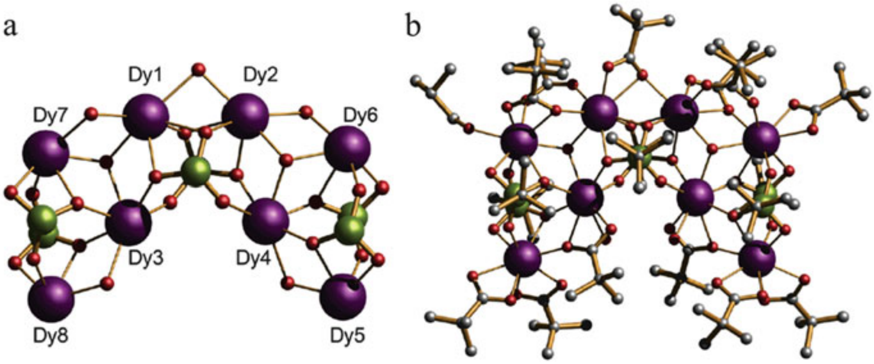


Fig. 35 Structure of: (**a**) the octanuclear core with bridging atoms displayed and (**b**) $[Ln_8(O_3P^tBu)_6(\mu_3\text{-}OH)_2(H_2O)_2(HO^iBu)(O_2C^tBu)_{12}](NH_3{}^iPr)_2$. Reprinted with the permission from [63] Copyright 2013 Royal Society of Chemistry

Cao et al. reported two isostructural nonanuclear complexes $[Ln_9(\mu_2\text{-}OH)(Hpmp)_{12}(ClO_4)(H_2O)_{26}](ClO_4)_{13}\cdot 18H_2O$ ($Ln = Nd$, Pr) by using *N*-piperidinomethane-1-phosphonic acid (H_2pmp) as supporting ligand [64]. The synthesis was carried out by adding NaOH into an aqueous solution containing $H_2pmp\cdot HCl$ and lanthanide perchlorate salt until pH reached about 6.2. The nine Ln^{3+} ions are

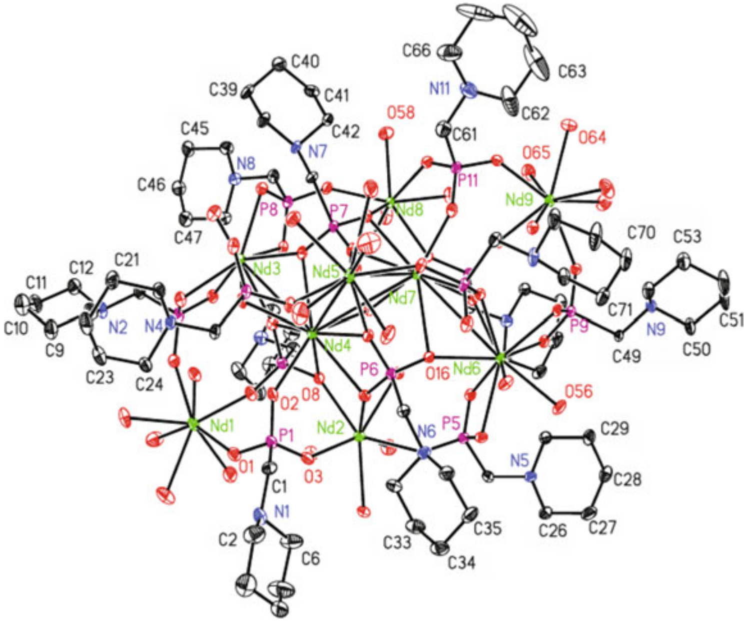


Fig. 36 Structure of cationic complex of $[Nd_9(\mu_2\text{-}OH)(Hpmp)_{12}(ClO_4)(H_2O)_{26}]^{13+}$. Reprinted with the permission from [64] Copyright 2009 Elsevier

organized into a unique lotus-leaf-shaped arrangement with one μ_2-OH group and 12 phosphonate bridging ligands. The coordination spheres are completed with ClO_4^- anion and aqua ligands (Fig. 36).

Phosphate can also be used as a second or ancillary ligand to support the assembly of polynuclear lanthanide hydroxide complexes. As an example, Hong et al. reported two isostructural decanuclear complexes $[Ln_{10}(TBC8A)_2(PhPO_3)_4(OH)_2(HCO_3)(HCOO)(DMF)_{14}]\cdot(H_6TBC8A)\cdot x DMF\cdot y CH_3OH\cdot$(Ln = Pr, Nd; H_8TBC8A = *p-tert*-butylcalix[8]arene; H_2PhPO_3 = phenylphosphonic acid) using a mixture of lanthanide nitrate hydrate, H_8TBC8A, and H_2PhPO_3 in DMF/methanol [65]. The ten Ln^{3+} ions are encapsulated by two $TBC8A^{8-}$ ligands that are in their cup-conformation with their lower-rim phenoxide O atoms coordinating the lanthanide ions (Fig. 37). Four $PhPO_3^{2-}$ ligands, two OH^- groups, one HCO_3^- anion, and one $HCOO^-$ ligand help further stabilize the multinuclear arrangement of the core. In the crystal lattice, the $[Ln_{10}(TBC8A)_2(PhPO_3)_4(OH)_2(HCO_3)(HCOO)(DMF)_{14}]^{2+}$ cations and $(H_6TBC8A)^{2-}$ anions are arranged alternatively to the stable crystalline bulk phase.

There is one report of lanthanide hydroxide cluster complex featuring a sulfonate supporting ligand. Zhang et al. isolated a hexanuclear complex $[Yb_6(\mu_6\text{-}O)(\mu_3\text{-}OH)_8(mds)_4(H_2O)_6]$ by reacting Yb_2O_3 with methylenedisulfonic acid (H_2mds) under hydrothermal conditions [66]. As shown in Fig. 38, the six Yb^{3+} ions are organized into a μ_6-O-centered regular octahedron with each of the triangular faces being capped by one μ_3-OH group. The complex unit is not a discrete one, however.

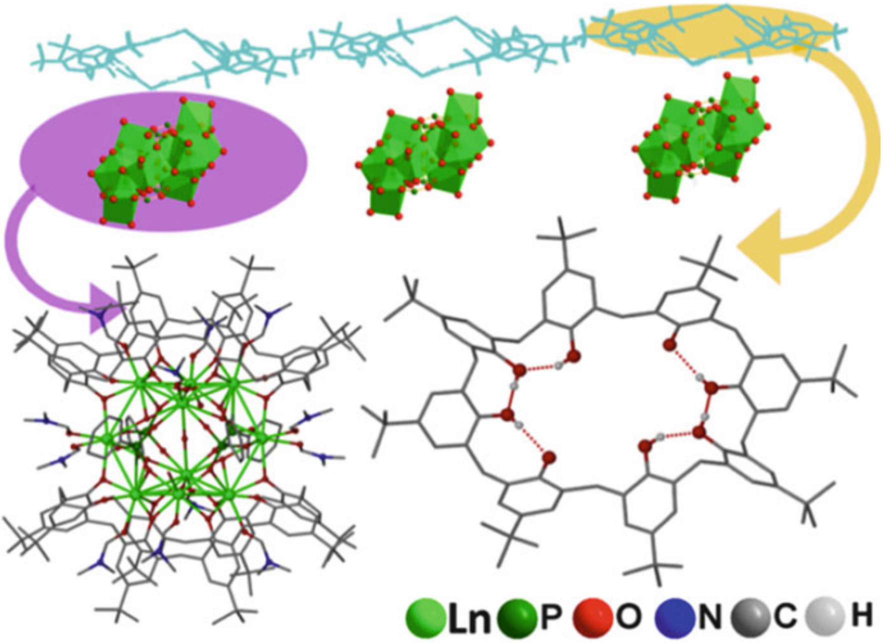


Fig. 37 Structure of [$Ln_{10}(TBC8A)_2(PhPO_3)_4(OH)_2(HCO_3)(HCOO)(DMF)_{14}](H_6TBC8A)$. Reprinted with the permission from [65] Copyright 2015 Elsevier

They are instead connected into a one-dimensional column structure via two opposite Yb^{3+} ions by way of mds coordination. Specifically, the disulfonate ligand is bridging with each of its two sulfonate groups contributing one O for the coordination of one Yb^{3+} from different cluster unit. This unit-connecting Yb^{3+} is also coordinated by two aqua ligands. The remaining four Yb^{3+} ions are of two different types in terms of their coordination spheres: Both are coordinated by one chelating mds ligand with one of them also coordinated by an aqua ligand but not the other.

2.4 Polyoxometalates

Another emerging class of ligands to support the assembly of lanthanide hydroxide complexes are POMs. POMs are known for their facile synthesis and tunable chemical composition [67–69], and have been found to be valuable for promoting many organic transformations [70, 71], catalyzing water-splitting process [72], and making novel memory devices [73, 74].

The increasing use of POMs in lanthanide coordination is due presumably to two reasons. First, POMs are anions with a large number of O atoms on the surface. The

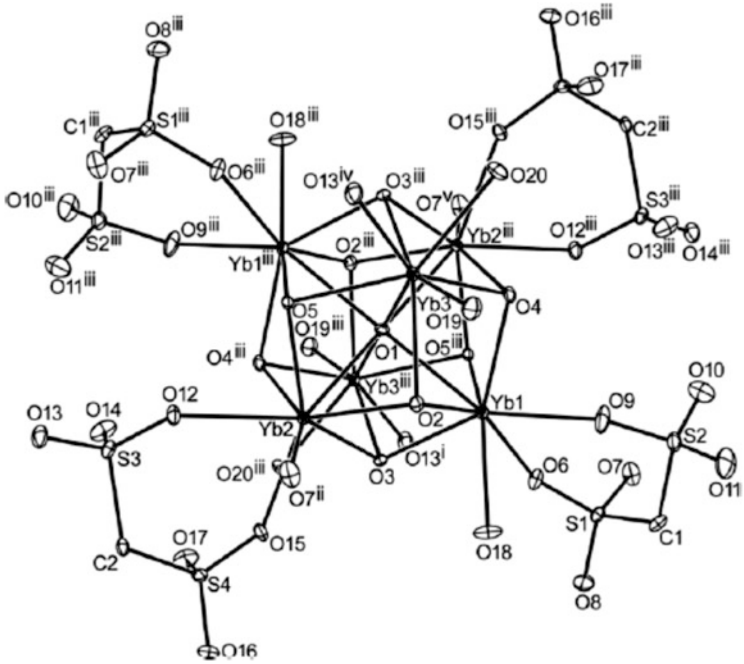


Fig. 38 Structure of $Yb_6(\mu_6\text{-}O)(\mu_3\text{-}OH)_8(mds)_4(H_2O)_6$. Reprinted with the permission from [66] Copyright 2008 IUCr Journals

electrostatic attractions between lanthanide ions and a POM, together with the desirable hard Lewis acid/base match, make POMs an attractive class of protecting ligands and/or templating anions for the assembly of lanthanide clusters. We must note that: (1) not all the examples shown below have the polyhedral Ln-O/OH motif to be qualified as “lanthanide oxide or hydroxide clusters”; the hydroxo groups in some cases are in fact associated with the metal ion in the POM ligands rather than a lanthanide ion and (2) many of the species actually contain lanthanide atoms that are separated by a distance beyond what is anticipated for a conventional cluster motif. Second, as POMs are generally weakly coordinating, the Lewis acidity of lanthanide ions is enhanced in an Ln-POM combination with respect to the complexes with more strongly coordinating ligands. This feature may help enhance the catalytic efficiency when Ln-POM complexes are used in Lewis acid-promoted reactions.

Zhang et al. reported three isostructural lanthanide tungstobismuthate complexes $Na_xH_{22\text{-}x}\{(BiW_9O_{33})_4(WO_3)[Bi_6(\mu_3\text{-}O)_4(\mu_2\text{-}OH)_3][Ln_3(H_2O)_6(CO_3)]\}\cdot nH_2O\cdot$ (Ln = Pr, Nd, La) from an aqueous reaction involving $Na_{12}[Bi_2W_{22}O_{74}(OH)_2]\cdot 44H_2O$, a lanthanide chloride hydrate, $Na_9[BiW_9O_{33}]\cdot 16H_2O$, and Na_2CO_3 [75]. As shown in Fig. 39, the three Ln^{3+} ions are organized into a trigonal planar arrangement around a $\mu_3\text{-}CO_3^{2-}$ that uses each of its O atoms to link two lanthanide ions along the edge of the triangle. Each Ln^{3+} ion is further coordinated with two aqua ligands. This $[Ln_3(H_2O)_6(CO_3)]^{7+}$ motif is then encapsulated by four

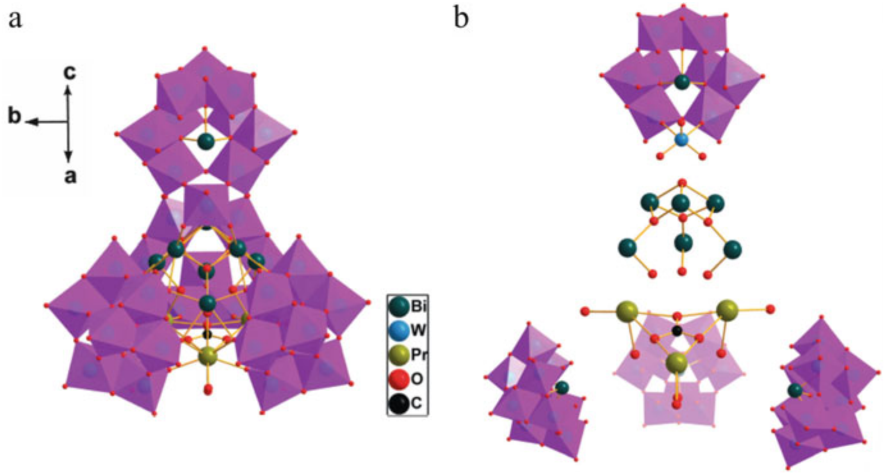


Fig. 39 (**a**) Structure of $\{(BiW_9O_{33})_4(WO_3)[Bi_6(\mu_3\text{-}O)_4(\mu_2\text{-}OH)_3][Pr_3(H_2O)_6(CO_3)]\}^{22-}$ and (**b**) building blocks for the cluster (H atoms and lattice solvent molecules were omitted for clarity). Reprinted with the permission from [75] Copyright 2012 Royal Society of Chemistry

$[BiW_9O_{33}]^{9-}$ anions, three of which being directly connected to the $[Ln_3(H_2O)_6(CO_3)]^{7+}$ core with the fourth one through one $[Bi_6(\mu_3\text{-}O)_4(\mu_2\text{-}OH)_3]^{7+}$ unit.

By reacting $Na_2WO_4{\cdot}2H_2O$, oxalic acid, and lanthanide chloride, without or with the presence KCl in an aqueous solution at pH 7.5, Chen et al. obtained $Na_{10}[Ln_2(C_2O_4)(H_2O)_4(\mu_2\text{-}OH)(W_4O_{16})]_2{\cdot}30H_2O$ and $K_4Na_{16}[Ln(C_2O_4)(W_5O_{18})]_4{\cdot}60H_2O{\cdot}(Ln = Eu, Ho, Er, Tb)$, respectively [76]. As shown in Fig. 40a, the core of the former consists of a rectangular arrangement of four lanthanide ions with its two longer sides each being bridged by a $C_2O_4^{\ 2-}$ ligand and the shorter side by a μ_2-OH group. In addition, there are two aqua ligands on each of the lanthanide ions. This core motif is then sandwiched along the direction of the longer side by two $W_4O_{16}^{\ 8-}$ units via O-Ln coordination to bridge the two lanthanide ions along the shorter side.

In the latter cluster complex, the four lanthanide ions are arranged into a square with each of its sides being bridged by a $C_2O_4^{\ 2-}$ ligand; there are no aqua ligands or hydroxo groups (Fig. 40b). Each of the lanthanide ions is then coordinated via O-coordination to one $W_5O_{18}^{\ 6-}$ capping ligand.

Another series of tetranuclear Ln-POM complexes, formulated as $[PMo^{V}_{8}Mo^{VI}_{4}O_{36}[Ln(H_2O)_4(OH)]_4]{\cdot}Cl_5{\cdot}xH_2O{\cdot}(Ln = La, Ce, Nd, Sm)$, were reported by Dolbecq and coworkers [77]. The $[PMo^{V}_{8}Mo^{VI}_{4}O_{36}]^{11-}$ anion in these compounds serves as a support or platform for the attachment of four $[Ln(H_2O)_4(OH)]^{2+}$ units into a tetrahedral arrangement (Fig. 41).

It is clear from the above examples, POM ligands can be used to protect lanthanide ions by encapsulation and to support the attachment of lanthanide ions onto their surface. In a rare example provided by Wang et al., these two coordination

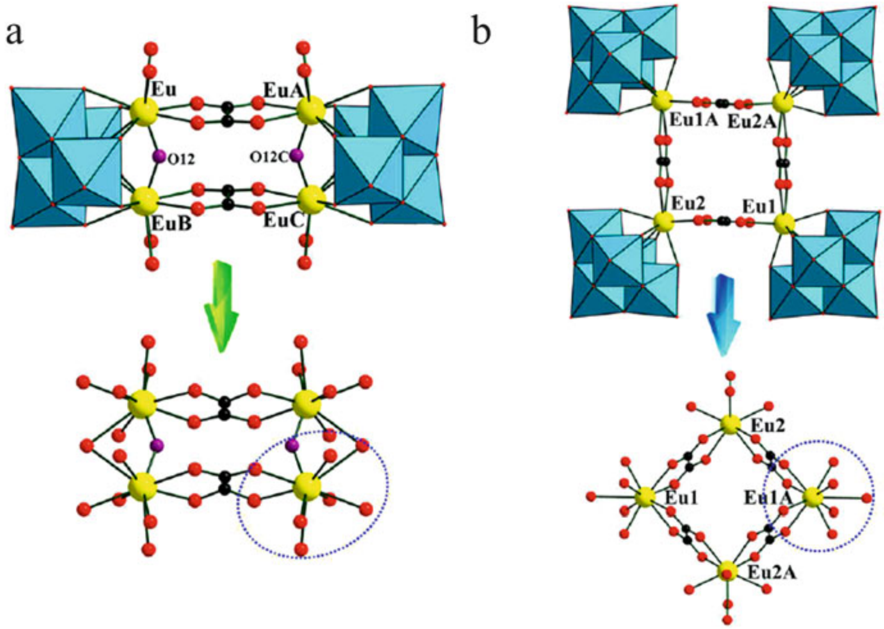


Fig. 40 Structure of: (**a**) $\{[Eu_2(C_2O_4)(H_2O)_4(\mu_2\text{-}OH)(W_4O_{16})]_2\}^{10-}$ (*top*) and cluster core (*bottom*) and (**b**) $\{[Eu(C_2O_4)(W_5O_{18})]_4\}^{20-}$ (*top*) and the cluster core (*bottom*). Reprinted with the permission from [76] Copyright 2014 American Chemical Society

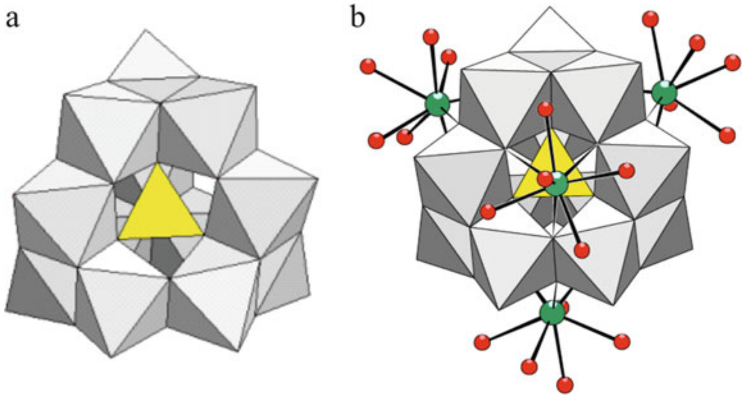


Fig. 41 (**a**) Structure of $[PMo^{V}{}_{8}Mo^{VI}{}_{4}O_{36}]^{11-}$ illustrating the triangular face used for the coordination of the $[Ln(H_2O)_4(OH)]^{2+}$ unit and (**b**) structure of $\{PMo^{V}{}_{8}Mo^{VI}{}_{4}O_{36}[Ln(H_2O)_4(OH)]_4\}^{5+}$. Reprinted with the permission from [77] Copyright 2011 Wiley-VCH Verlag GmbH & Co

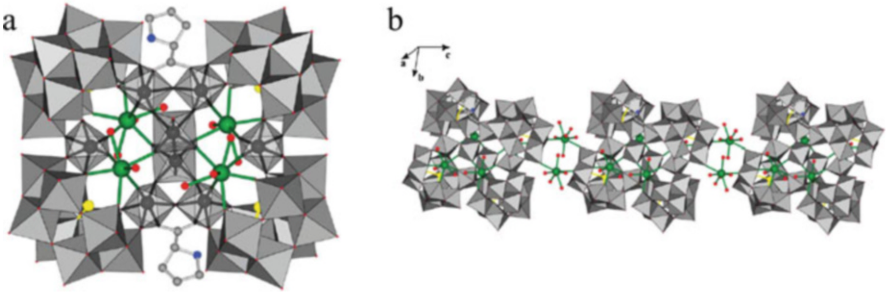


Fig. 42 Structure of: (**a**) the $[Ln_4(H_2O)_{16}\{As_4W_{44}(OH)_2(proline)_2O_{151}\}]^{16-}$ building block and (**b**) $[Ln_6(H_2O)_x\{As_4W_{44}(OH)_2(proline)_2O_{151}\}]^{10-}$. Reprinted with the permission from [78] Copyright 2013 Royal Society of Chemistry

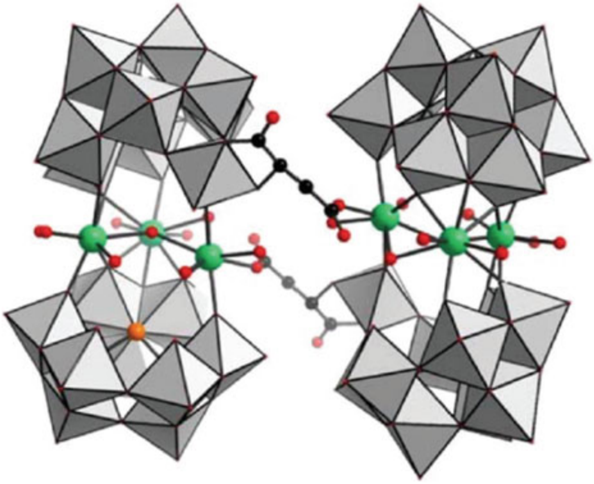


Fig. 43 Structure of $\{[Ln_3(\mu_3\text{-}OH)(H_2O)_8(AsW_9O_{33})(AsW_{10}O_{35})(mal)]_2\}^{22-}$. Reprinted with the permission from [79] Copyright 2015 Royal Society of Chemistry

modes of the POM ligands are demonstrated. Shown in Fig. 42 is the chain structure of the anionic complex in $Na_{10}[Ln_6(H_2O)_x\{As_4W_{44}(OH)_2(proline)_2O_{151}\}]\cdot nH_2O\cdot$ (Ln = Tb, Dy, Nd) linked through hydrated Ln^{3+} ions [78].

Linkages can also be provided by organic ligands that serve to coordinate metal ions from different Ln-POM SBUs. Shown in Fig. 43 is the structure of the anionic complex unit in $K_{20}Li_2[Ln_3(\mu_3\text{-}OH)(H_2O)_8(AsW_9O_{33})(AsW_{10}O_{35})(mal)]_2\cdot 17H_2O\cdot$ (Ln = Dy, Tb, Gd, Eu, Sm, mal = malate) [79]. It can be viewed as two μ_3-OH group-bridged cuboidal building blocks connected by two mal ligands. This complex motif is then sandwiched in between one $\{AsW_9O_{33}\}$ and one $\{AsW_{10}O_{35}\}$ unit with the latter being also coordinated by one mal ligand. The coordination sphere of the Ln^{3+} ion chelated by the mal ligand is completed by two aqua ligands while that of the other two Ln^{3+} ions is each completed by three aqua ligands.

Using an aqueous mixture of samarium chloride, Na_2CO_3, KCl, and $Na_{10}[A\text{-}\alpha\text{-}SiW_9O_{34}]\cdot xH_2O$, Davoodi et al. obtained $[(A\text{-}\alpha\text{-}SiW_9O_{34})_2(H_2OSm)_3CO_3]^{13-}$ which decomposed slowly in a concentrated solution to afford an anionic octanuclear complex $[(SiW_{10}Sm_2O_{38})_4(W_3O_8)(OH)_4(H_2O)_2)]^{26-}$ as the final product [80]. The complex unit can be viewed as eight Sm^{3+} ions wrapping around one $[W_3O_8(OH)_4(H_2O)_2]^{2-}$ template anion. This arrangement is then encapsulated by four $[SiW_{10}O_{38}]^{12-}$ ligands (Fig. 44).

Lastly, Patzke et al. reported a series of hexadecanuclear lanthanide polyoxotungstate complexes with the core formulated as $[Ln_{16}As_{16}W_{164}O_{576}(OH)_8(H_2O)_{42}]^{80-}\cdot(Ln = Eu, Gd, Tb, Dy, Ho)$ [81]. The product was obtained from an aqueous reaction of $K_{14}[As_2W_{19}O_{67}(H_2O)]$, lanthanide nitrate hydrate, NaCl, and CsCl. Each of the 16 Ln^{3+} ions is capped by one $\{AsW_9O_{33}\}$ unit, and the 16 $\{LnAsW_9O_{33}\}$ units are connected by 20 tungstate anions, eight OH^- groups, and four Cs^+ cations. The coordination spheres of Ln^{3+} ions are completed by aqua ligands (Fig. 45).

2.5 Miscellaneous Ligands

There are also some structurally interesting lanthanide hydroxide cluster complexes supported by ligands that do not belong to the types discussed above. For example, Alikberova et al. reported two hexanuclear complexes $[Ln_6(H_2O)_{23}(OH)_{10}]I_8\cdot 8H_2O\cdot(Ln = La, Nd)$ by directly reacting $La_2(CO_3)_3\cdot 6H_2O$ and Nd_2O_3 with an aqueous solution of HI [82]. We note that a very similar octahedral hexanuclear cluster complex with exclusively H_2O-based ligands was previously reported by direct hydrolysis of simple lanthanide salts [83]. The cluster core is essentially the same as in $Yb_6(\mu_6\text{-}O)(\mu_3\text{-}OH)_8(mds)_4(H_2O)_6$ discussed above [66] with six Ln^{3+} ions arranged into an octahedron centering around a μ_6-OH rather than a μ_6-O group. Each face of the octahedron was capped by one μ_3-OH group. The coordination spheres of five of the six Ln^{3+} ions are each completed by four aqua ligands, while that of the sixth one is fulfilled by three aqua ligands and one OH^- group (Fig. 46).

Complexes with similar hexanuclear core have also been reported with the use of a triazole ligand 4-amino-3,5-dimethyl-1,2,4-triazole (L_8) [84]. Cheng et al. reported a series of hexanuclear complexes of the common formula $[Ln_6(\mu_6\text{-}O)(\mu_3\text{-}OH)_8(L_8)_4(H_2O)_{14}]Cl_8\cdot 2\ L_8\cdot 6H_2O\cdot(Ln = Er, Ho, Dy)$. As shown in Fig. 47, ligand L_8 bridges four equatorial Ln...Ln edges of the octahedral core. The rest of the coordination sphere is fulfilled by either aqua ligands or an aqua/chloro ligand combination.

Batten et al. reported two tetradecanuclear lanthanide hydroxide complexes, $[Gd_{14}(CO_3)_{13}(ccnm)_9(OH)(H_2O)_6(phen)_{13}(NO_3)](CO_3)_{2.5}\cdot(phen)_{0.5}$ and $[Dy_{14}(CO_3)_{13}(ccnm)_{10}(OH)(H_2O)_6(phen)_{13}](CO_3)_{2.5}\cdot(phen)_{0.5}$ by using a combination of 1,10-phenanthroline (phen) and carbamoylcyanonitrosomethanide (ccnm) as the protecting ligands [85]. They share the same cluster core, differing only

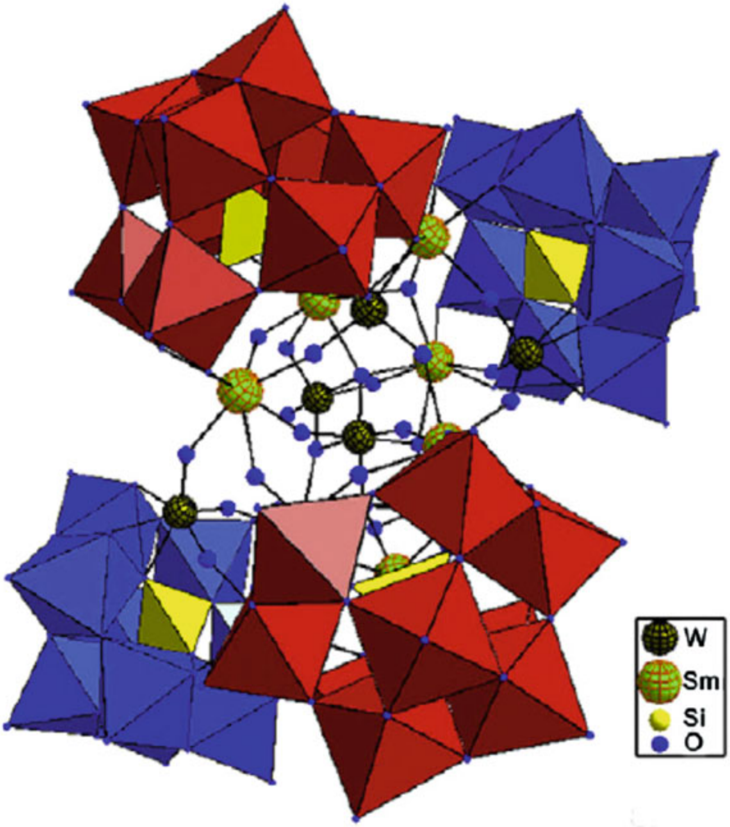


Fig. 44 Structure of the $[(SiW_{10}Sm_2O_{38})_4(W_3O_8)(OH)_4(H_2O)_2)]^{26-}$ cluster core. Reprinted with the permission from [80] Copyright 2012 Elsevier

slightly in the peripheral coordination ligands and anions. The structures of the core and the cationic Gd^{3+} complex are shown in Fig. 48. The 14 Gd^{3+} ions are bridged by one μ_3-OH group and 13 CO_3^{2-} anions (Fig. 48a). The coordination spheres of Gd^{3+} ions are completed by ccnm, phen, aqua, and chelating NO_3^- ligands (Fig. 48b).

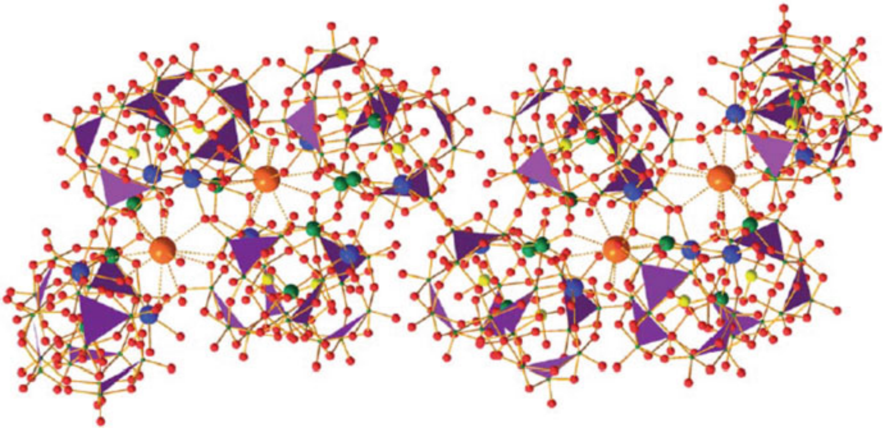


Fig. 45 Structure of the $[Ln_{16}As_{16}W_{164}O_{576}(OH)_8(H_2O)_{42}]^{80-}$ cluster core (color code: *blue*, Ln; *yellow*, As; *green*, W; *red*, O; *orange*, Cs; and *purple triangular planes*, W_3O_{13} triads of the $\{AsW_9O_{33}\}$ units). Reprinted with the permission from [81] Copyright 2011 Royal Society of Chemistry

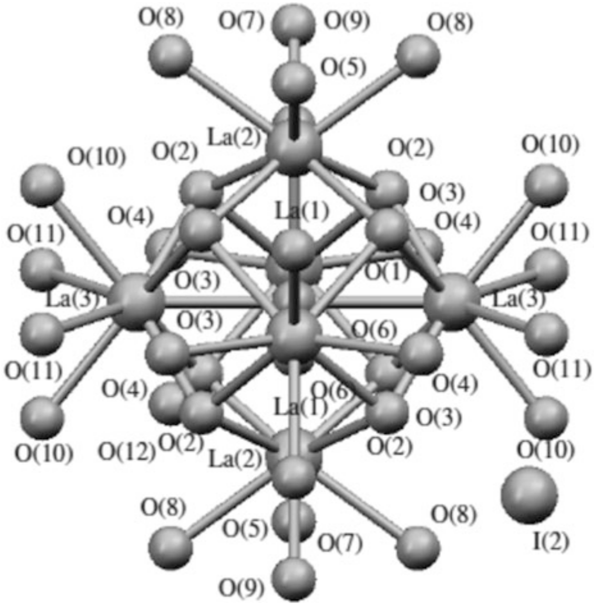


Fig. 46 Structure of $[La_6(H_2O)_{23}(OH)_{10}]^{8+}$. Reprinted with the permission from [82] Copyright 2009 Springer

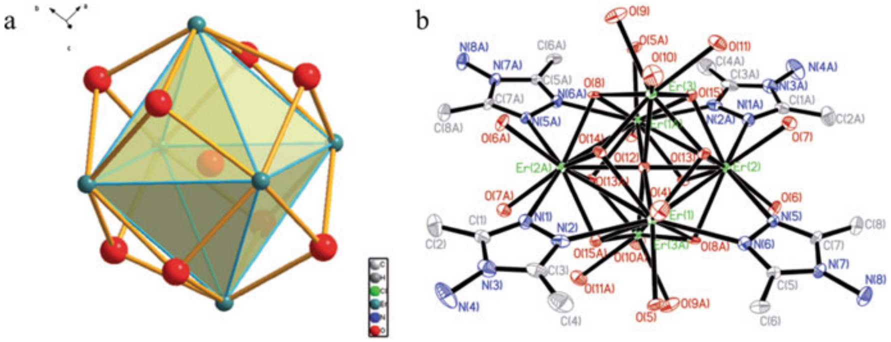


Fig. 47 Structure of: (**a**) the hexanuclear $[\mathrm{Ln_6(\mu_6\text{-}O)(\mu_3\text{-}OH)_8}]^{8+}$ cluster core and (**b**) $[\mathrm{Er_6(\mu_6\text{-}O)(\mu_3\text{-}OH)_8(L_8)_4(H_2O)_{14}}]^{8+}$. Reprinted with the permission from [84] Copyright 2009 Royal Society of Chemistry

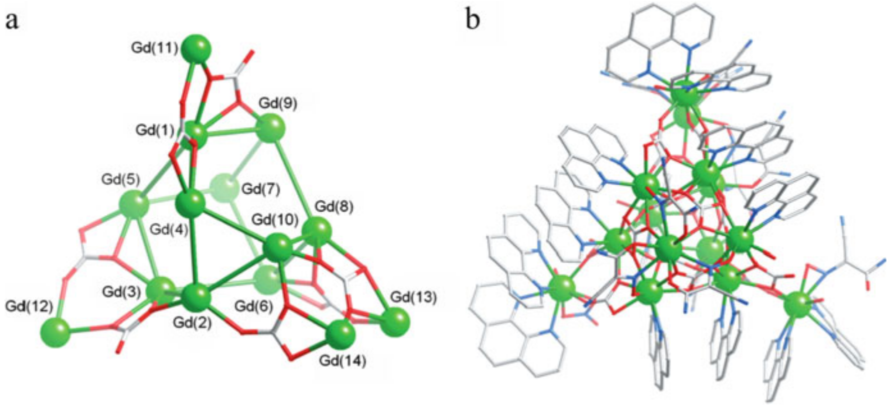


Fig. 48 Structure of: (**a**) the cluster core $[\mathrm{Gd_{14}(CO_3)_{13}(OH)(NO_3)}]^{14+}$ and (**b**) $[\mathrm{Gd_{14}(CO_3)_{13}(ccnm)_9(OH)(H_2O)_6(phen)_{13}(NO_3)}]^{5+}$. Reprinted with the permission from [85] Copyright 2012 Royal Society of Chemistry

3 Summary and Perspectives

In this chapter, we survey the lanthanide hydroxide cluster complexes that are supported by carboxylate, diketonate, phosphate, sulfonate, and POM ligands. The synthetic procedures leading to the production of the cluster species and the unique cluster core motifs are the focus of the discussion. The extensive scope in terms of the variety of ligands to control the lanthanide hydrolysis as well as the diverse structures of the cluster motifs indicates that this sub-area of lanthanide coordination chemistry is full of potential for further synthetic development and materials discovery. The following are the key conclusions drawn from the work summarized in this chapter and that prior to this review:

1. It is the high pH at which a reaction is conducted that makes the critical difference in the complex products when compared with lanthanide coordination with the same types of ligands at a lower pH. The assembly of the cluster species hinges upon the formation of the hydroxo intermediate produced upon deprotonation of aqua ligand(s).
2. Hydrolysis can occur in either aqueous or organic media, using hydrated lanthanide complexes or salts, or oxides, promoted by using an inorganic or organic base, and under ambient-pressure or hydro/solvothermal conditions.
3. The supporting ligands, most of which being organic with O-based functional groups, should support a reasonable degree of water solubility of their complexes if the hydrolysis is to be executed in an aqueous solution. This is exemplified by the results obtained by using amino acids as supporting ligands for lanthanide hydrolysis. In comparison, hydrated complexes with simple carboxylic acids are generally insoluble, and therefore precipitate out before any hydrolysis may occur.
4. Supporting ligands can be used alone or in combination with other ligands. The accompanying use of an O-based ligand, inorganic ones included, is generally required if the other supporting ligand does not carry any O-based functional groups. The nature (nuclearity and structure) of the lanthanide hydroxide clusters is critically dependent on the ancillary ligands used.
5. A number of factors other than the supporting ligand are also significant in determining the reaction outcome. These include the nature of the lanthanide ions (contrary to the common perception of lanthanide chemistry being similar among different lanthanide ions due to lanthanide contraction), the template effects of certain small anions, and the participation of transition metal ions (not discussed herein).
6. Highly sophisticated lanthanide-containing clusters can be formally constructed by using smaller and recognizable cluster units as formal secondary building units (SBUs).

One should not be surprised that the research activities of lanthanide hydroxide clusters will continue to grow with high possibility of finding interesting materials with useful applications that have not yet been realized or even contemplated. Rapid progress notwithstanding, questions such as the scope of the chemistry, the robustness of the synthetic approach, and effects of experimental conditions, and any structure–property relationship remain to be answered. Thus, the primary goal of any future efforts is to systematically assess the effects of factors such as the nature of supporting ligands and metal ions, and experimental conditions on the reaction outcome, with the hopes of developing a robust and generally applicable approach to these unique lanthanide-containing substances. The ultimate goal is to discover lanthanide-containing materials for catalysis, magnetic, optical, biomedical, and other advanced technological applications.

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