CHEMICAL REVIEWS

Review

Advances in Structurally Characterized Lanthanide Alkoxide, Aryloxide, and Silyloxide Compounds

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Advances in Structurally Characterized Lanthanide Alkoxide, Aryloxide, and Siloxide Compounds

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1. Introduction

1.1. Need for this Review

Often referred to as the "rare earths", the lanthanide (Ln) elements have gained increased attention over the past few decades. This has been due to the development of better separation techniques, reduced prices for pure compounds, and the addition of exciting new fundamental chemistries concerning these cations.[1–8] The monotonic decrease in the ionic radius, resulting from the sequential filling of the inner f orbitals (the lanthanide contraction), has permitted a systematic probing of the chemistry of these cations. From the rapidly developing families of metalorganic and organometallic complexes, $Ln^{+2/+3}$ alkoxide $(Ln(OR)_x)$ complexes have come to the forefront as a unique series of compounds for the production of advanced materials as well as molecules that effect useful organic transformations. This has not only led to a more detailed understanding of structure/property relationships in complexes containing the 4f elements but has also underscored the potential utility of these species in several practical applications.

The purpose of this review is to present a brief account of recent developments in the structural elucidation of "simple" $Ln(OR)_x$ (Ln = Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu) including the group 3 (Sc, Y, and La) cations.[9] Surprisingly, even though the rapid growth of these species continues to expand, up to the beginning of 2008 only three books concerning the *general* subject of metal alkoxide[10–12] chemistry were available and none of these books delve into the details of the structural properties of the Lns. Furthermore, journal reviews addressing the general topic of metal alkoxides do not cover the expanding lanthanide members of this class of compounds in any great depth.[13–17] The few reviews that do, are over a decade[17–19] old; meanwhile numerous advances have been made in the development of structural properties of $Ln(OR)_x$ compounds. For this review, material that was included in the previous reviews and books will be limited to brief referencing or tabular descriptions.

1.2. Past Reviews

As mentioned before, there are relatively few collective works detailing the structural characteristics of $Ln(OR)_x$.[17–19] A 1991 review by Mehrotra et al. describes the syntheses, chemical properties, and spectroscopic characteristics of this general class of compound, coupled with some structural information gleaned via single crystal X-ray characterization.[17] Four years later, a short review by Hubert-Pfalzgraf described the implications of lanthanide complexes as

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molecular precursors in materials science.[18] In addition, in 1996 Anwander reported some of the structural aspects of Ln(OR)$_x$ and functionalized ligands emphasizing the design and synthesis of ligand environments to create tailored precursors.[19] In the decade following these reviews, numerous advances have been realized in the syntheses, characterization, and structural elucidation of various examples of molecules containing Ln-OR fragments, but a detailed review of these compounds has not been proffered.[1,9–18] As can be discerned, there is a significant void in the compilation of Ln(OR)$_x$ compounds.

1.3. Range of Review

For this review, we have elected to limit the scope of our presentation to Ln(OR)$_x$ compounds that have been *definitively* characterized via X-ray crystallographic studies.[9] In

Scheme 1. Schematic of Some of the Standard Alkoxide Ligands Commonly Employed for Ln(OR)$_x$ Structures: (a) Methoxide (OMe), (b) Ethoxide (OEt), (c) *n*-Propoxide (OPr^n), (d) *iso*-Propoxide (OPr^i), (e) *tert*-Butoxide (OBu^t), (f) *neo*-Pentoxide (ONep), (g) 2,3-Dimethyl-2-butoxide (DMB), (h) Di-*tert*-butyl Methoxide (DBM), (i) Tri-*tert*-butyl Methoxide (TBM), (j) Methoxy Ethoxide (OEtOMe), (k) Dimethyl Methoxy Ethoxide (MMPO), and (l) Dimethyl Methoxy Propoxide (MMBO)
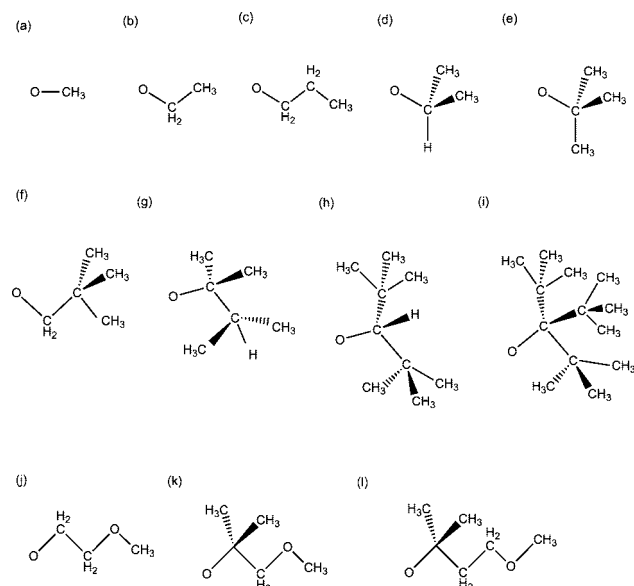

addition, we have chosen to avoid a comprehensive discussion of heteroleptic derivatives in an effort to focus on the most commonly found classes of Ln(OR)$_x$ (some of the standard OR ligands and common central cores of Ln(OR)$_x$ are shown in Schemes 1–4). In this regard, we have omitted discussion of several of the ligand sets that are widely used but are typically detrimental for advanced materials applications and limits their practical utility in these systems. Although this foregoes the inclusion of additional compounds that are intrinsically chemically and structurally interesting and otherwise deserving of discussion (especially the oxo species), the volume of *all* structurally characterized Ln containing examples is simply too vast to be adequately addressed here. Therefore, all salt (metalate) derivatives, heterometallic species, halide, chalcogenide, and select pnictide containing derivatives have been excluded from our discussion. Whenever possible, references to earlier reports are cited and should be sought out for a more complete description of both the syntheses and structural aspects of the compounds reported.

2. Synthesis of Lanthanide Alkoxide Complexes

In this section, we will briefly describe the variety of synthetic routes that are employed in the preparation of metal alkoxides, (in particular, those that may result in highly pure complexes for use as materials precursors). Although detailed descriptions of synthetic methodologies are available in the literature,[1,9–18] the various problems and limitations associated with these strategies are addressed below. The general chemistry of the lanthanide elements is dominated by the trivalent oxidation state (Ln^{+3}) which holds true for the majority of homoleptic alkoxide supported compounds. Other oxidation states have also been accessed for certain members of the series. In molecular complexes, the divalent oxidation state (Ln^{+2}) has been observed.[20–46] In the case of cerium, several tetravalent complexes (Ce^{+4}) have also been

Scheme 2. Schematic of the Central Cores Commonly Found for Ln(OR)$_x$ Compounds: (I) Monomers: (a) Trigonal Planar (tp), (b) Tetrahedral (Td), and (c) Trigonal Biplanar (tbp); (II) Dinuclear: (d) Td, (e) tbp, and (f) Octahedral (Oh); (III) Trinuclear: (g) Cyclic-Oh and (h) Linear-tbp; (IV) tetranuclear (μ-OR and -OR Not Shown): (i) Cubic-Td, (j) Td-Td, (k) Butterfly, (l) M$_4$O$_{12}$
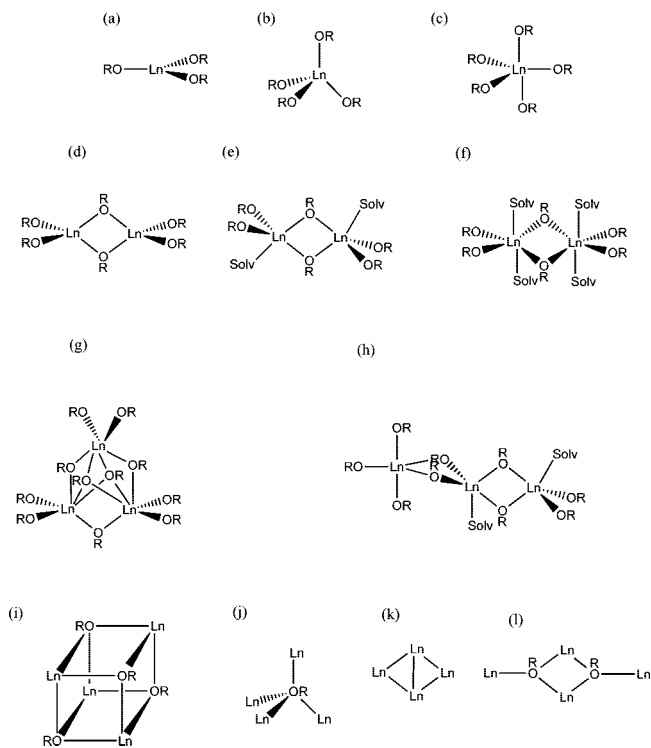
Scheme 3. Schematic drawings of common phenoxides: (a) phenoxide (OPh), (b) 2,6-dimethyl phenoxide (DMP), (c) 2,6 di-*iso*-propyl phenoxide (DIP), (d) 2,6-di-*tert*-butyl phenoxide (DBP), (e) 2,6-diphenyl phenoxide (DPP), and (f) naphthanoxide (ONap)
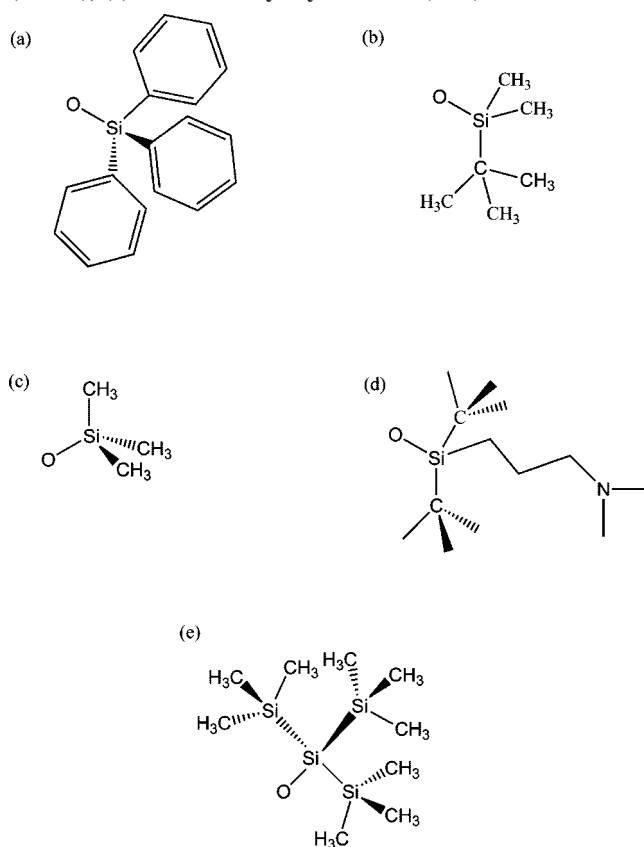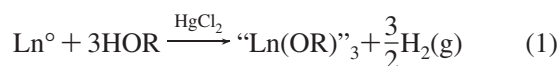

Scheme 4. Schematic Representation of Common Siloxide Ligands: (a) Triphenyl Siloxide (TPS), (b) Dimethyl-*t*-butoxide Siloxide (DMBS), (c) Trimethyl Siloxide (TMS), (d) (1-Bis(*t*-butyl))(3-(dimethylamino)butyl Siloxide (OSPA), (e) Tris-trimethylsilyl Siloxide (SST)

adducts). The majority of these pathways involve the reaction of various anionic ligands (i.e., alkoxide, halide, amide) with alcohols; however, several other viable pathways are also available.

2.1.1. Metal Alcoholysis

The effectiveness of the reaction between Ln metal (Ln°) and excess alcohol (HOR) is limited by the general nonreactivity of both precursors. The surface layer that readily forms on the bulk metal significantly reduces the utility of this pathway. Several routes have been reported to activate Ln°, with HgCl$_2$[2,4,49,50] or Hg(C$_6$F$_5$)$_2$ [25,27,30,36] being the most widely used catalyst to clean the metal surface and initiate the reaction (eq 1).[2,4,49,50] Once the metal is activated, the alkoxide complex is formed via introduction of an alcohol to the metal. In the diverse array of readily available alcohols, *iso*-propanol (HOCHMe$_2$) is the most commonly employed. Using the above methodology (eq 1), ligand decomposition or adventitious water due to the difficulties in drying alcohols often leads to alkoxo oxo clusters, as evidenced by the numerous structurally characterized examples of Ln$_5$(μ_5-O)(OCHMe$_2$)$_{13}$ (Ln= Eu, Nd, Gd, Er, and Yb).[51−62]

characterized.[47,48] The main +3 and +2 synthesis routes are discussed below.

2.1. Trivalent Lanthanide Alkoxides

A number of synthetic pathways are available to prepare the +3 homoleptic lanthanide alkoxides (and their Lewis base

$$Ln° + 3HOR \xrightarrow{\text{HgCl}_2} \text{``Ln(OR)''}_3 + \frac{3}{2}H_2(g) \qquad (1)$$

In addition, it should be noted that solventless or inert fluxes involving phenols have also been found to react with Ln° to yield the lanthanide aryloxides (Ln(OAr)$_x$). Alternatively, redox transmetalation/ligand metatheses involving Hg(R)$_2$ R

= C_6H_5 or C_6F_5 or Tl(OAr) are now established routes for the synthesis of La(OAr)$_3$ derivatives.[25,27,28,30,36,63]

2.1.2. Alcoholysis

The alcoholysis methodology involves a protonolysis reaction (exchange) of one or more coordinated alkoxide ligands (eq 2) with another alcohol of interest. This is a convenient methodology when the initial Ln(OR)$_x$ precursor is commercially available; however, the solubility of these Ln species can be very low which limits the utility of this route. The extent of ligand substitution is ultimately dependent upon several conditions and can vary from system to system. A slight excess of alcohol and heating of the reactions are typically used to induce complete ligand exchange, although this is not always successful.
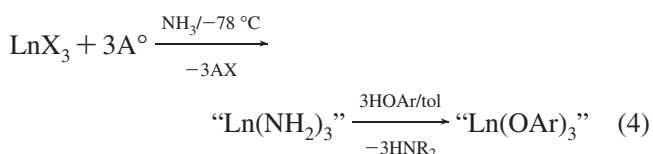
$$\text{“Ln(OR')}_3\text{”} + 3\text{H}-\text{OR} \rightarrow \text{“Ln(OR)}_3\text{”} + 3\text{H}-\text{OR'} \quad (2)$$
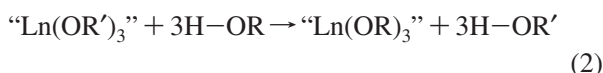
2.1.3. Halide Metathesis

Another approach to generating alkoxides relies on the halide metathesis route. This method utilizes lanthanide halides LnX$_3$ complexes (X = Cl, Br, I) most of which are commercially available or as the Lewis base (e.g., THF) adducts;[1–6,9,17–19] however, aqueous adducts must be avoided or dried prior to attempting the synthesis due to the potential side reactions. The general metathesis reaction (eq 3) can be hampered by the reduced solubility of the base free LnX$_3$ compounds (*note*: the iodides have been shown to be more soluble than the other halides[64]) and oxo-group formation, for example Ln$_3$(μ-O)(μ-X)(OR)$_6$(solv).[65,66] In addition, elimination of the metathetical salt product (typically an alkali metal or thallium analog) can be incomplete, resulting in the formation of heterometallic complexes.

$$\text{LnX}_3 + 3\text{M'(OR)} \rightarrow \text{“Ln(OR)}_3\text{”} + 3\text{M'X} \quad (3)$$
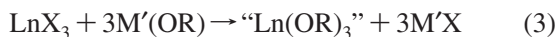
One methodology that is often employed to circumvent the insolubility issue of non-Lewis base adducts is to employ an ammoniacal synthesis.[67] In this system, ammonia gas is condensed onto the LnX$_3$ precursor, resulting in dissolution. The appropriate alkali metal (A°) is then added, followed by the addition of the desired HOR. This mechanism presumably proceeds via a short-lived tris-amide intermediate.[67]

$$\text{LnX}_3 + 3\text{A°} \xrightarrow[-3\text{AX}]{\text{NH}_3/-78\ ^\circ\text{C}}$$

$$\text{“Ln(NH}_2)_3\text{”} \xrightarrow[-3\text{HNR}_2]{3\text{HOAr/tol}} \text{“Ln(OAr)}_3\text{”} \quad (4)$$
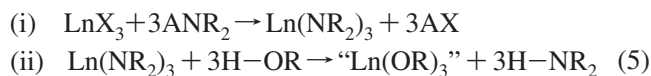
It is important to note that some reports indicate that this route is only viable for *aryl*-oxide derivatives, since the use of simple alkyl substituted groups can lead to the incorporation of the alkali metal.[68]

2.1.4. Amide Alcoholysis

The amide alcoholysis route (eq 5) has proven to be the most effective and versatile route for the production of Ln(OR)$_x$ compounds, if the tris-amido “Ln(NR$_2$)$_3$” complex produced in step (i) of eq 5 is free of alkali metal salt contamination. The purification of the resultant product is critical to its utility and often involves multiple crystalliza-

tions and/or sublimation of the Ln(NR$_2$)$_3$.[10–12,34,35,69–76] In general, sterically encumbered alkali metal amides (ANR$_2$ where R = SiMe$_3$) are employed to maintain the monomeric nature of the Ln amide precursor (i.e., Ln(NR$_2$)$_3$). The Ln(NR$_2$)$_3$ have been crystallographically characterized as monomeric species supported via a distorted trigonal planar arrangement of amide ligands.[34,35,69,71–76] The exchange with alcohols (step ii) usually proceeds rapidly in a variety of solvents and is often performed at low temperature.

(i) $\text{LnX}_3 + 3\text{ANR}_2 \rightarrow \text{Ln(NR}_2)_3 + 3\text{AX}$

(ii) $\text{Ln(NR}_2)_3 + 3\text{H}-\text{OR} \rightarrow \text{“Ln(OR)}_3\text{”} + 3\text{H}-\text{NR}_2 \quad (5)$

2.2. Divalent Lanthanide Alkoxides

The next most abundant oxidation state known for the Ln(OR)$_x$ family is divalent (+2). The Ln(OR)$_2$ that have been crystallographically characterized include Sm, Eu, and Yb. Ce and Nd have some evidence of the +2 oxidation state but structural verification has not been reported.[23] In general, routes in sections 2.1.1–2.1.4 are used for synthesis of +2 species with two specific routes being favored for production of Ln(OR)$_2$ species: (i) metal alcoholysis or (ii) divalent precursors.

2.2.1. Metal Alcoholysis

If the alcohol is reactive enough, simple dissolution of the metal in the H$-$OR[34–36] at glovebox pressure or with a few drops of Hg[28,40] followed by high pressure synthesis sometimes results in the isolation of the +2 species (eq 6). Alternatively, the use of liquid ammonia favors dissolution of the metal followed by reaction with the appropriate alcohol and in some instances yielded Ln(OR)$_2$ species.[21,31,32,38] The favoring of the +2 over the +3 oxidation state has not yet been explained.[22,23] Other routes to divalent Ln(OR)$_2$ that use the bulk metal include redox transmetalation/ligand exchange reactions that employ either Hg(C$_6$F$_5$)$_2$[25,27,30] or thallium(I) phenolates[25] reagents.

$$\text{Ln°} + \text{(xs)H}-\text{OR} \rightarrow \text{“Ln(OR)}_2\text{”} + \text{H}_2\text{(g)} \quad (6)$$
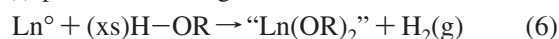
2.2.2. Divalent Precursor Metathesis

Another approach is to start with a divalent precursor such as YbI$_2$ which undergoes direct metathesis with alkaline earth alkoxides[39] (eq 7) to yield the divalent species. In addition, as noted for the +3 species, an amide intermediate can be synthesized which will easily exchange with a variety of alcohols (eq 8) while retaining its +2 charge.[20,22–24,41,42,44] Finally rare cases of stable lanthanide aryls will readily react with phenol without oxidizing to the +3 state[25] (eq 9).

$$\text{LnX}_2 + 2\text{AOR} \rightarrow \text{Ln(OR)}_2 + 2\text{AX} \quad (7)$$

$$\text{Ln(NR}_2)_2 + 2\text{H}-\text{OR} \rightarrow \text{Ln(OR)}_2 + 2\text{H}-\text{NR}_2\text{(g)} \quad (8)$$

$$\text{LnR}_2 + 2\text{H}-\text{OR} \rightarrow \text{Ln(OR)}_2 + 2\text{H}-\text{R(g)} \quad (9)$$

As can be discerned from the discussion above, synthetic routes to Ln(OR)$_2$ species are available; however, additional research is necessary to develop rational methods that yield Ln(OR)$_2$.

3. Homoleptic Alkoxide Structures

Due to their large ionic radii, Ln ions exhibit a propensity to maximize their coordination number unless large, very

sterically encumbered ligands are employed. Therefore, examples of coordination numbers greater than six in the general chemistry of the 4f series elements are quite common.[9] Within the context of alkoxide chemistry this typically occurs via bridging ligand (μ-OR) interactions that satisfy the steric/electronic requirements at each metal center forming dimers, trimers, tetramers, and larger oligomers. Complexes represented as "Ln(OR)$_x$" are therefore more accurately represented as [Ln(OR)$_x$]$_n$ (n = 1, 2, 3, 4, etc.).

It is worth pointing out that the degree of oligomerization observed in the solid state structures of these molecules can differ from that observed in solution. Unfortunately the study of solution structure is often complicated by the paramagnetic nature of most of these ions or the complex dynamic behavior that metal alkoxides often demonstrate as a result of rapid ligand exchange. Combined, these traits hinder achieving a detailed understanding of Ln(OR)$_x$ structure/nuclearity in the solution phase. We therefore often have to rely on the determination of a solid state structure to predict what may occur in terms of solution chemistry of these molecules. This review focuses only on examples *definitively* characterized by X-ray diffraction. Figure 1 shows the color key used for each of the lanthanide cations and ligand atoms throughout this paper. It is of interest that for the radioactive β-emitter Pm metal there are no alkoxide species reported.[9]

3.1. General "Ln(OR)$_3$" Constructs

An intrinsic feature of the coordination chemistry of [Ln(OR)$_x$]$_n$ is the tendency toward maximizing their coordination number. Coordination numbers of 3−6 are typically noted for the *d*-block elements, but higher formal coordination numbers are often observed in "Ln(OR)$_3$" complexes. Lewis basic solvents can be employed to "break up" higher nuclearity species and engender products containing fewer metals. The general bonding modes, central cores observed, and metrical data are discussed below. Metrical data are listed in Table 1 and crystallographically characterized species with ligand abbreviations are listed in Table 2.

3.1.1. Bonding Motifs

The lone pairs of electrons of the oxygen atoms of the OR$^-$ ligands provide for the stabilization of a wide variety of binding modes. This is observed to some extent in transition metal coordination chemistry, but is even more pronounced in the descriptive chemistry of the f elements. Binding modes span terminal [(OR)-Ln], bridging [(μ-OR)-Ln$_2$], triply bridging [(μ_3-OR)-Ln$_3$], and more rarely quadruply bridging [(μ_4-OR)-Ln$_4$] interactions which reflect the degree of steric and electronic saturation required at each metal center. More complicated motifs are found with oxo containing species or when bidentate ligands are employed. Also observed is the presence of aryl groups which may yield unexpected π interactions facilitated by the presence of the aromatic rings. The bond distances and angles noted for the Ln compounds reviewed here were obtained from the Cambridge Structural Data Base and are only reported as averaged values in order to illustrate general trends.[9]

3.1.2. Central Core Constructs

The nuclearity of the various homoleptic "Ln(OR)$_3$" complexes typically range from mono- through decanuclear cores (see Table 2). The geometries around these metals have

been found to encompass simple trigonal planar (tp), tetrahedral (Td), trigonal bipyramidal (tbp), square base pyramidal (sbp), octahedral (Oh), and higher order coordination numbers and geometries. The geometries identified, the ligands, and abbreviations used throughout this paper are shown in Schemes 1, 3, and 4 with the various structure types observed listed in Scheme 2. Further aspects of these structure types are discussed below.

3.1.2.1. Mononuclear. Mononuclear species are stabilized by a variety of bulky alkoxides, both in the presence and absence of Lewis bases. These most commonly exhibit coordination tp, Td, to tbp, and Oh ligand arrangements around the metals. tp geometries are most often observed for aryloxide ligated species, especially for the DBP derivatives.[9] The presence of Lewis basic solvents (e.g., NH$_3$, THF, and py) ultimately play a large role in dictating both the nuclearity and coordination environment within these molecules.

3.1.2.2. Dinuclear. Within the dinuclear [Ln(OR)$_3$]$_2$ complexes, the "(OR)Ln(μ-OR)$_2$Ln(OR)" moiety is a standard building block, wherein the metals often exhibit typical (pseudo) Td or Oh configurations. This standard arrangement is illustrated by the [La(μ-TPM)(TPM)$_2$]$_2$ (TPM = OC(C$_6$H$_5$)$_3$) (Figure 2) compound.[72] Within the series of dinuclear homoleptic complexes, an average Ln−Ln distance of 3.86 Å was noted.

3.1.2.3. Trinuclear. Two geometrical constructs have been identified in the case of trinuclear complexes specifically cyclic or linear. The former is observed for the majority of species often supporting a central μ_3-OR. Each of the three planar metal centers bridge two μ_3-OR groups and are further linked to each other by μ-OR ligands. This cyclic structure is exhibited by a number of species such as Ce$_3$(μ_3-OBu^t)$_2$(OBu^t)$_3$(OBu^t)$_4$(HOBu^t)$_2$ (OBu^t = OC(CH$_3$)$_3$) (Figure 3).[47]

Linear arrangements have also been noted, however these are less abundant most likely due to the potential to form insoluble polymers if no driving force (e.g., solvent coordination) is available to limit oligomerization, as seen in Dy[(μ-DMP)$_2$Dy(DMP)(NH$_3$)]$_2$[68] (DMP = OC$_6$H$_3$(CH$_3$)-2,6) compound. The Dy−Dy distances noted for this compound were on average 3.72 Å.

3.1.2.4. Tetranuclear. Several types of tetranuclear constructs have been reported. These include butterfly, cyclic, linear, standard M$_4$O$_{12}$ [M$_4$(μ_3-O)$_2$(μ-O)$_4$], and cubic arrays. The only report of a butterfly motif was that of Eu$_4$(μ_4-OPr^i)(μ_3-OPr^i)$_2$(μ-OPr^i)$_2$(OPr^i)$_3$(H-OPr^i)$_2$·H-OPr^i[61] (OPr^i = OCH(CH$_3$)$_2$) (average Ln−Ln distances of 3.64 Å (3.63−3.65 Å, see section 3.2.1). The cyclic tetranuclear ONep [OCH$_2$C(CH$_3$)$_3$] derivatives were found to form a central rhombohedral tetranuclear Ln core with average M−M distances that systematically ranged from 3.28 (Sc) to 3.85 (La) Å ([Lu(μ-ONep)$_2$(ONep)]$_4$ shown in Figure 4a).[77] The size of the central core void varied from 4.64 (Sc) to 5.43 (La) Å^3.[77] The linear construct noted for [(THF)$_3$(ONap)Eu(μ-ONap)$_2$Eu(THF)$_2$(μ-ONap)]$_2$,[31] (ONap = naphthyloxo see section 3.3.2.5) exhibits a Ln−Ln separation of 3.98 Å. For the M$_4$O$_{12}$ geometry observed in the mixed ligand Sm complex, Sm$_4$(μ_3-OPr^i)$_3$(μ-OPr^i)$_4$(DIP)$_3$(THF)[78] (section 4.0b), the metals are 3.68 Å apart. Within the cubic complexes, [Eu(μ_3-OEtOMe)(OEtOMe)(OAr)]$_4$·tol(OEtOMe=OCH$_2$CH$_2$-OCH$_3$) (OAr = DIP (OC$_6$H$_3$(CH(CH$_3$)$_2$)-2,6) and DMP (OC$_6$H$_3$(CH$_3$)$_2$-2,6) (see Figure 4b)) the Ln−Ln distances average 3.92 and 3.99 Å, respectively.[34] Collectively the

Table 1. Metrical Data for Ln(OR)

Ln	Ln-μ_4-OR Å (ligand)[a]	ref	Ln-μ_3-OR Å (ligand)	ref	Ln-μ-OR Å (ligand)[a]	ref	Ln-OR Å (ligand)	ref
Sc					2.10 (ONep)	77	1.96−1.89 (OAr) 1.89 (ONep)	77
Y			2.41 (OBu^t)	74	2.25 (ONep)	77	1.97−2.28 (OAr)	
			2.43 (IPE)	74	2.30 (OBu^t/HOBu^t)	79	2.04 (ONep)	77
La			2.57 (HOBu^t)	93	2.40 (ONep)	77	2.46−2.23 (OAr)	
					2.44 (OBu^t)	93	2.16 (ONep)	77
					2.48(DBP-3,5/THF)	81	2.29 (OBu^t)	93
					2.42(DMP/THF)	73		
					2.48(DBzp)	40		
					2.44(TPM)	72		
Ce			2.55 (DBP-3,5)	81	2.38 (ONep)	77	2.25−2.18 (OAr)	47
			2.47 (OBu^t)	47	2.31(OBu^t)	47	2.12 (OBu^t)	47
					2.39(DBM)	83	2.14 (ONep)	77
					2.32 (OPr^i/HOPr^i)	84		
					2.33 (OPr^i/HOPr^i)	85		
					2.43 (OBu^t:TBM)	89		
Pr					2.37 (ONep)	77	2.135−2.280 (OAr) 2.12 (ONep)	77
Nd			2.52 (OBu^t/THF)	80	2.34 (ONep)	77	2.18−2.11 (OAr)	
			2.61(TMS)	135	2.43 (OBu^t/THF)	80	2.16 (OBu^t/THF)	80
			2.54 (DBP-3,5, THF)	81	2.42(OMes/py)	86	2.14 (ONep)	77
			2.55 (DBP-3,5, THF-HDBP)	81	2.42 (DMP/THF)	70		
					2.37(DBM/CNMe)	87		
					2.36 (2OPr^i:B4MP)	90		
Sm			2.46 (OPr^i)/DIP	78	2.32 (ONep)	77	2.17−2.09 (OAr, III)	
					2.38 (ONap/DBP-Me-4)	91	2.35−2.29 (OAr, II)	
					2.35 (OPr^i/DIP)	78	2.09 (ONep)	77
Eu	2.65(OPr^i)	61	2.53 (OEtOMe/DMP)	34	2.30 (ONep)	77	2.36−2.32 (OAr, II)	
			2.54 (OEtOMe/DIP)	34	2.49 (ONap/THF)	31	2.08 (ONep)	77
			2.60 (OPr^i)	61	2.50 (DMP/THF)	139		
					2.38(OPr^i)	61		
Gd					2.32 (ONep)	77	2.09−2.15 (DIP) 2.10 (ONep)	104 77
Tb					2.28 (ONep)	77	2.06 (ONep)	77
Dy			2.42 (ONep/py)	68	2.26 (ONep)	77	2.03−2.26 (OAr)	
			2.42 (OBu^t)	68	2.28 (DMP)	,68	2.04 (ONep)	77
					2.31 (OBu^t/HOBu^t)	68		
						68		
Ho					2.25 (ONep)	77	2.25−2.04 (OAr) 2.03 (ONep)	77
							2.03−2.32 (OAr, III)	
							2.12−2.32 (OAr, II)	
Yb					2.24(DBP-3,5/THF)	81		
					2.26 (DBz)	40		
					2.23(ONap/NCCH$_3$)	31		
					2.24 (OPr^i:B4MP)	90		
Er			2.40 (HOBu^t)	95	2.25 (ONep)	77	2.00−2.24 (OAr)	
					2.27 (DBP-3,5/THF)	81	2.03 (ONep)	77
					2.39 (Quin)	120		

[a] Ligand abbreviations shown are listed at the end of Table 2.

average distances in which a single oxygen atom separates the metal centers is 3.78 Å were found for the IPE derivatives.

3.1.2.5. Octanuclear. $Y_8(\mu_3\text{-IPE})_6(\mu\text{-IPE})_{10}(\text{IPE})_8$[74] (IPE = $O(CH_2)_2OCH(CH_3)_2$, shown in Figure 5, is the only homoleptic octanuclear cluster reported and can be thought of as two M_4O_{12} units bound together. The M_4O_{12} geometry has been observed within early metal alkoxides (i.e., $Ti(OEt)_4$ or $Ti(OMe)_4$) and involves two μ_3-OR ligands that bridge two similar and two distinct metals further bridged by μ-OR groups, $M_4(\mu_3\text{-OR})_2(\mu\text{-OR})_4(\text{OR})_6$. The Ln−Ln separation of 3.65 Å.

3.1.2.6. Decanuclear. The two species possessing decanuclear cores are cyclic oligomers, $[\text{Ln}(\mu\text{-OEtOMe})_2(\text{OEtOMe})]_{10}$ where Ln = Y[75] or Dy[76] (Figure 6). Within the smaller building dinuclear species, the Ln−Ln distances are on average 2.30 Å. The central core hole created by these species was found to be on average 11.7 Å in diameter.

3.1.3. Bond Distances

Table 1 shows some of the ranges and average values for the observed bond distances noted for these compounds.

Table 2. Crystallographically characterized Ln(OR)$_x$ per metal

Ln	ligand (molecule/solv)	nucl.	additional characterization	coord. geometry	ref
Sc(III)	ONep	4	EA, IR	sbp	77
	DMP (dimethylpyrazolymethane)	1	EA, NMR	Oh	100, 101
	DBP-Me-4	1		tri	108
	DPP	1	EA, IR, MS, NMR	tri	30
	DPP-3,5-Bu^t (THF, $x = 1$)	1	EA, IR, Mp, NMR	Td	30
Y(III)	OBu^t (HOBu^t)	3		6	79
	ONep	4	EA, IR	sbp	77
	OEtOMe	10	NMR	pbp	75
	IPE	8	EA, IR,NMR	6/7/8	74
	DMP (THF, $x = 2$)	2	EA, IR,NMR	sbp	73
	DMP (THF, $x = 3$)	1	EA, IR,NMR	Oh	73
	DIP (η^6)	2	EA, IR,NMR	3LPS	102
	DIP (THF, $x = 2$)	1	EA, IR,NMR	tbp	102
	DPP (η^6)	1	EA, MS	tp	115
	TPS	2	NMR	4	133
	TPS (THF, $x = 3$)	1	EA, IR,NMR	Oh	130, 131, 140
	DMBS (HDMBS, $x = 1$)	2	EA, IR,NMR	Td/tbp	130
	OSPA	1	EA, MP, NMR	tbp	33
La(III)	OBu^t (HOBu^t, $x = 2$)	3	EA, IR, MS, NMR	Oh	93
	ONep	4	EA, IR	sbp	77, 94
	TPM	2	EA, IR,NMR	Td	72
	DMP (pentahexoapentadecane $x = 1$,OEt $x = 2$)	1	EA, NMR	8	99
	DIP (η^6)	2	EA, IR,NMR	3LPS	103
	DIP (NH$_3$, $x = 4$)	1	EA, IR,NMR	Oh	103
	DIP (THF, $x = 2$)	1	EA, IR,NMR	tbp	103
	DBP-3,5(H$_2$O)	4	EA, IR,NMR	Oh	81
	DBP-3,5 (THF, $x = 6$)	2	EA, IR, NMR	pbp	81
	DPP (η^6, η^3)	1	EA, MS	tp	115
	DPP (THF, $x = 2$)	1	EA, IR,NMR	tbp	116, 118
	DBzP (η^3)	2	EA, IR, MP	sbp	40
	TPS (THF, $x = 3$)	1	EA, IR,NMR	Oh	130
Ce(III)	OPr^i (HOPr^i, $x = 2$)	2	EA, IR,NMR	Oh	84, 85
	ONep	4	EA, IR	sbp	47, 77
	OBu^t (HOBu^t, $x = 2$)	3	EA, IR	Oh	47
	DBM	2	NMR	Td	83
	TBM (CNBut, $x = 2$)	2			96
	oBP (THF, $x = 3$)	1	EA, IR	Oh	47
	DMP (THF, $x = 4$; py, $x = 4$)	2	EA, IR	Oh	47
	DIP (THF, $x = 3$)	1	EA, IR	Oh	47
	DBP	1	EA, IR,NMR	tp	109
	DBP (CNBu^t, $x = 2$)	1	EA, IR,NMR	tbp	109
	DPP (η^6)	1	EA, MS	tp	115
	DPP (THF, $x = 2$)	1	EA, IR	5	47
	TPS	2	EA, IR,NMR	sbp	72
	TPS (THF, $x = 3$)	1	EA, IR, NMR	Oh	131
	TPS (DME, $x = 1$)	1	EA, IR,NMR	Oh	141
	SSQ (py, $x = 3$)	1	EA, NMR	pbp	138
Mixed	6TBM/1(O(C$_6$H$_4$)O)	2	EA	Td	89
	4TBM/2OBu^t	2	EA	Td	89
	3OPr^i/1MAEA	2	EA, IR, NMR	7	88
(IV)	OBu^t	4	EA, IR	Oh	47
	DMB	2	NMR	tp	48
	DMB (DMAP, $x = 2$)	1	EA, NMR	Oh	48
Pr	ONep	4	EA, IR	sbp	77
	DIP (THF, $x = 2$)	1	EA, IR,NMR	tbp	104
	DBP	1	IR, Ram, UV	tri	110
	DPP (η^6)	1	EA, MS, UV/IR	TPy	115
	TPS (THF, $x = 3$)	1	EA, IR,NMR	Oh	131
Nd(III)	ONep	4	EA, IR	sbp	77, 94
	OBu^t (THF, $x = 2$)	3	EA, NMR	Oh	80, 82
	DBM (NCMe, $x = 1$)	2	EA, IR	5	87
	DPM (THF, $x = 2$; py, $x = 2$; DME, $x = 1$)	2	EA, IR, NMR	tbp	67
	TBM (NCMe, $x = 2$)	1	EA, IR	tbp	97
	TBM (THF, $x = 1$)	1	EA, IR, NMR	Td	98
	MMBO	2	EA, NMR	Oh	82
	DMP (THF, $x = 4$)	2	EA, IR	Oh	70
	DIP (η^6)	2	EA, IR,NMR	3LPS	104
	DBP	1		tri	110

Table 2. Continued

Ln	ligand (molecule/solv)	nucl.	additional characterization	coord. geometry	ref
	DBP-3,5 (THF, $x = 4$)	3	EA, IR, NMR	Oh/pbp	81
	DBP-3,5 (THF, $x = 1$/HDBP-3,5, $x = 2$)	3	EA, IR, NMR	Oh/pbp	81
	OMes (py, $x = 4$)	2	EA, IR,NMR	Oh	86
	DBP-Me-4 (THF, $x = 1$)	1	EA, IR	Td	63
	DBP-OMe (THF, $x = 1$)	1	EA, IR, NMR	Td	27
	DPP (η^6)	1	EA, IR, MS, UV	tbp	116, 117
	DPP (THF,$x = 1$) (η^3)	1	EA, IR, MS,UV	tbp	116, 117
	DPP (THF, $x = 2$)	1	EA, IR, MS,UV	tbp	116, 118
	DPP (DME, $x = 1$)	1	EA, IR, UV	tbp	29
	TMS	4	EA, IR	Oh	135
	BHS	2	EA, IR	Td	134
mixed	2OPr^i/(B4MP)(THF, $x = 4$)	2	EA, IR, MP	Oh	90
Sm(III)	ONep	4	EA, IR	sbp	77
	DIP (η^6)	2	EA, IR,NMR	3LPS	104
	DIP (THF, $x = 2$)	1	EA, IR,NMR	tbp	106
	DIP (THF, $x = 3$)	1	EA, IR,NMR	Oh	105
	OMes (THF, $x = 3$)	1	EA, IR,NMR	Oh	86
	DBP-Me-4 (NCCH3, $x = 2$)	1		5	113
	DBP-Me-4 (THF, $x = 1$)	1	MS	Td	112
	DBP-OMe (DME, $x = 1$)	1	EA, IR,NMR	sbp	27
	OBPy	1	EA, IR,NMR	sbp	71
	TPS (THF, $x = 3$)	1	EA, IR,NMR	Oh	105
	TBOS	2	EA, NMR	5	137
mixed	8 OPr^i/3 DIP	4	EA, IR,NMR	tbp/Oh	78
	4 DBP(Me-4)/2 quinolinolato	2		5	91
	2 DBP(Me-4)/1 fluorenone (THF, $x = 2$)	1	ESR, NMR, UV	tbp	42, 122
	4 DBP(Me-4)/1 bifluorenonyl (OEt$_2$, $x = 2$)	2	ESR, NMR, UV	Td	42, 122
(II)	DBP-Me-4 (THF, $x = 3$)	1	EA, IR,NMR	tbp	41−45
	DBP-OMe (THF, $x = 3$)	1	EA, IR,NMR	sbp	27
	TBP (THF, $x = 3$)	1		5	46
	TBP (DME, $x = 2$)	1		6	46
Eu(III)	ONep	4	EA, IR	sbp	77
	(III,II)OPr^i (H-OPr^i, $x = 3$)	4	IR, UV−vis	6	61
	(III,II)4 CARB/3 DIP	3		6,8	123
(II)	OEtOMe (HDMP, $x = 4$; HDIP, $x = 4$)	4	EA, IR, mag	Td	34
	DMP (THF, $x = 6$)	3	EA, IR, mag	tap/tpz	35
	DMP (MeIm, $x = 5$)	2	EA, mag	Oh	36
	DMP (DME, $x = 3$)	2	EA, IR,mag	6/7	37
	DIP (NCCH$_3$, $x = 5$)	2	EA, mag	Oh	36
	DBP (NCCH$_3$, $x = 4$)	1	EA, IR, Mag, NMR, UV	Oh	38
	DBP (THF, $x = 3$)	1	EA, IR	tbp	21
	DBP(Me-4) (THF, $x = 3$)	1	EA,IR	tbp	21, 39
	DPP (η^2,σ^3)	2	EA, IR, MS	Td	28
	DBzP (η^1, η^2, η^3)	2	EA, IR, MP	sbp	40
	ONap (THF, $x = 10$)	4	EA, IR	Oh	31
Gd(III)	ONep	4	EA, IR	sbp	77
	DIP (THF, $x = 2$)	1	EA, IR, NMR	tbp	104
	SST (THF, $x = 2$)	1	EA, IR	tbp	136
	SST (diasabicyclo, $x = 2$)	1	EA, IR	tbp	136
Tb(III)	ONep	4	EA, IR	sbp	77
Dy(III)	OBu^t (HOBu^t, THF, py: $x = 2$)	3	EA, IR	Oh	68
	ONep	4	EA, IR	sbp	68
	ONep (py, $x = 2$)	3	EA, IR	Oh	68
	DBM (NCMe, $x = 2$)	1	EA, IR, MS	tbp	87
	OEtOMe	10	IR,UV	7	76
	DIP (η^6)	2	EA, IR	3LPS	68
	DMP (NH$_3$, $x = 2$)	3	EA, IR	tbp	68
	DMP (py, $x = 3$)	1	EA, IR	Oh	68
	DIP (THF, $x = 2$)	1	EA, IR	tbp	68
	DIP (py, NH$_3$, $x = 3$)	1	EA, IR	Oh	68
	DBP	1	EA, IR	tri	68
	DBP (NH$_3$, THF, $x = 1$; py, $x = 2$)	1	EA, IR	Td, Td, tbp	68
	TPS	2	EA, IR	Td	68
	TPS (THF, py, $x = 3$)	1	EA, IR	Oh	68
Ho(III)	ONep	4	EA, IR	sbp	77
	DIP (THF, $x = 2$)	1	EA, IR	tbp	107
	DBP-OMe (THF)	1	EA, IR,NMR	Td	27
	Quin	3	EA, IR	sap	119

Table 2. Continued

Ln	ligand (molecule/solv)	nucl.	additional characterization	coord.geometry	ref
Er(III)	OBu^t (HOBu^t, $x = 2$)	3	EA, IR	Oh	95
	ONep	4	EA, IR	sbp	77, 95
	DMP (THF, $x = 3$;py, $x = 3$)	1	EA, IR	Oh	95
	DIP (η^6)	2	EA, IR	3LPS	95
	DIP (THF $x = 2$)	1	EA, IR	tbp	95, 104
	DBP (py, $x = 2$)	1	EA, IR	tbp	95
	DBP-3,5 (THF, $x = 4$)	2	EA, IR	Oh	81
	DBP-4Me (THF, $x = 1$)	1	EA, IR	Td	111
	TPS	2	EA, IR	Td	95
	TPS (THF, $x = 3$; py, $x = 3$)	1	EA, IR	Oh	95
	Quin	3	IR, MS, UV	ap	120
Tm(III)	ONep	4	EA, IR	sbp	77
mixed	TBM (NH$_2$Si(CH$_3$)$_2$CH$_2$Si(CH$_3$)$_2$NH$_2$)	2	EA, IR	Td	124
Yb(III)	ONep	4	EA, IR	sbp	77
	DBP-3,5 (THF, $x = 4$)	2	EA, IR, NMR	Oh	81
	TBP (THF, $x = 1$)	1	EA, IR, NMR	sbp	114
	DPP (η^6)	1	EA, IR, MS	tp	117
	DPP (THF, $x = 2$)	1	EA	sbp	114, 117
	DPP (DME, $x = 1$)	1	EA, IR	sbp	29
	DPP-3,5-Me (THF, $x = 1$)	1	EA, IR, MP, MS, NMR	tp	30
	DPP-3,5 Bu^t (THF, $x = 1$)	1	EA, IR, MP, MS, NMR	tp	30
	DPP-3,5 Ph (DME, $x = 1$)	1	EA, IR, MS, NMR	sbp	30
	DBzP(η^1, η^2, η^3)	2	EA, IR, MP	sbp	40
(III,II)	[Yb(DPP)$_2$][Yb(DPP)$_4$] (η^1, η^2, η^6)	2	NMR	Oh/Td	28
mixed	(III) 1(B4MP)/2 OPr^i (THF, $x = 4$)	2	EA, IR, MP	Oh	90
	(III) 2 DBP-Me-4/1 O-fluoreneone (THF, $x = 2$)	1	EA, UV	tbp	122
(II)	TBM (THF, $x = 2$)	1	NMR	Td	20
	DBP (NCMe, $x = 4$)	1	EA, IR, NMR	Oh	21
	DBP-Me-4	2	EA, NMR	tri	22, 23
	DBP-Me-4 (OEt$_2$, $x = 2$)	1	EA, NMR	Td	23, 24
	DBP-Me-4 (THF, $x = 2$)	1	EA, NMR	Td	24
	DBP-Me-4 (THF, $x = 3$)	1	EA, NMR	sbp	24
	TBP (THF, $x = 3$)	1	EA, IR, MS, NMR, UV	sbp	25, 26
	DBP-OMe (THF, $x = 3$)	1	EA, IR, NMR	sbp	27
	DPP (η^1, η^2, η^4, η^6)	2	EA, IR, MS, NMR	pyd	28
	DPP (THF, $x = 3$)	1	EA, IR, MS, UV	tbp	29
	DPP (DME, $x = 2$)	1	EA, IR	tpz	29
	DPP-3,5-Me (THF, $x = 3$)	1	EA, IR, MS, NMR	tbp	30
	ONap (NCMe, $x = 2$; THF, $x = 2$)	2	EA, IR	Oh	31
	DMBS (DME, $x = 2$)	2	NMR	tbp/sbp	32
	OSi(Bu^t)$_2$[(CH$_2$)$_3$NMe$_2$](H-OSi(Bu^t)$_2$[(CH$_2$)$_3$NMe$_2$], $x = 1$)	1	EA, MS, NMR	Td	33
Lu(III)	ONep	4	EA, IR	sbp	77
	MMPO	2	EA, IR, NMR	7	69
	DIP (THF $x = 2$)	1	EA, IR, NMR	tbp	104
	DPP (η^6)	1	EA, MS	tp	115

abbreviations		
coordination abbv.		analytical methods

3LPS = 3 legged piano stool	tp = trigonal pyramidal	EA = elemental analysis
sbp = square base pyramidal;	tpl = trigonal planar	IR = infrared spectroscopy
tbp = trigonal bipyramidal;	tpz = trigonal prismatic	Mag = magnetic moment
Oh = octahedral	tap = trigonal antiprismatic	MP = melting point
tri = trigonal	ap = antiprismatic	MS = mass spectroscopy
Td = tetrahedral	pyd = pyramidal	NMR = multication
pbp = pentagonal bipyramidal		Ram = raman spectroscopy
a number indicates no geometry presented just coordination number		UV = ultraviolet−visible spectrosopy

ligand abbreviations					
type	abbv.	formula	type	abbv.	formula
alkyl	OPr^i	OCH(CH$_3$)$_2$	silanols	TMS	OSi(CH$_3$)$_3$
	ONep	OCH$_2$C(CH$_3$)$_3$		TPS	OSi(C$_6$H$_5$)$_3$
	OBu^t	OC(CH$_3$)$_3$		DMBS	OSi(CH$_3$)$_2$C(CH$_3$)$_3$
	DMB	OC(CH$_3$)$_2$CH(CH$_3$)$_2$		BHS	OSiH(C(CH$_3$)$_3$)$_2$
	DBM	OCH(C(CH$_3$)$_3$)$_2$		TBOS	OSi(OC(CH$_3$)$_3$)$_3$
	DPM	OCH(CH(CH$_3$)$_2$)$_2$		SST	OSi(Si(CH$_3$)$_3$)$_3$
	TBM	OC(C(CH$_3$)$_3$)$_3$		OSPA	OSi(C(CH$_3$)$_3$)$_2$(CH$_2$)$_3$N(CH$_3$)$_2$
	TPM	OC(C$_6$H$_5$)$_3$		SSQ	silsesquioxane
	MeOEtO	OEtOMe			
	CARB	OEt(CH$_2$)$_2$O(CH$_2$)$_2$O			
	IPE	O(CH$_2$)$_2$OCH(CH$_3$)$_2$			

Table 2. Continued

type	abbv.	formula	type	abbv.	formula
	MMPO	OC(CH₃)₂(CH₂)OCH₃			
	MMBO	OC(CH₃)₂(CH₂)₂OCH₃			
aryl	oBP	OC₆H₄(C(CH₃)₃)-2	solvents	NH₃	ammonia
	DMP	OC₆H₃(CH₃)₂-2,6		OEt₂	diethylether
	DIP	OC₆H₃(CH(CH₃)₂)-2,6		CNMe	acetonitrile
	DBP	OC₆H₃(C(CH₃)₃)₂-2,6		CNBuᵗ	t-butyl cyanide
	DBP-3,5	OC₆H₃(C(CH₃)₃)-3,5		THF	tetrahydrofuran
	OMes	OC₆H₂(CH₃)₃-2,4,6		MeIm	1-methyl-imidazole
	DBP-Me-4	OC₆H₃(C(CH₃)₃)₂-2,6,(CH₃)-4		DME	dimethoxyethane
	TBP	OC₆H₂(C(CH₃)₃)₃-2,4,6		py	pyridine
	DBP-OMe	OC₆H₂(C(CH₃)₃)₂-2,6,(OCH₃)-4		DMAP	dimethyl amino pyridine
	DPP	OC₆H₃(C₆H₅)₂-2,6		MAEA	2(2-dimethylaminoethylmethylamino)ethoxo-N,N′
	DPP-3,5-Me	OC₆H(C₆H₅)₂-2,6 (CH₃)₂-3,5		B4MP	2,2′-methylene-bis(6-t-butyl-4-methylphenolato)-O,O′
	DPP-3,5-Buᵗ	OC₆H(C₆H₅)₂-2,6 (C(CH₃)₃)₂-3,5			
	DPP-3,5 Ph	OC₆H(C₆H₅)₄-2,3,5,6			
	DBzP	OC₆H₃(CH₂C₆H₅)₂-2,6			
	TAP	OC₆H₂(CH₂N(CH₃)₂)₃-2,4,6			
	ONap	naphthyloxo			
	Quin	quinalato			
	OBPy	OC(C(CH₃)₃)(CH₂PyCH₃-2)₂			

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

C O N Si
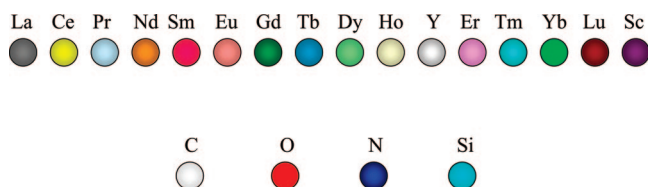
Figure 1. Color key for the Ln cations used throughout this review.
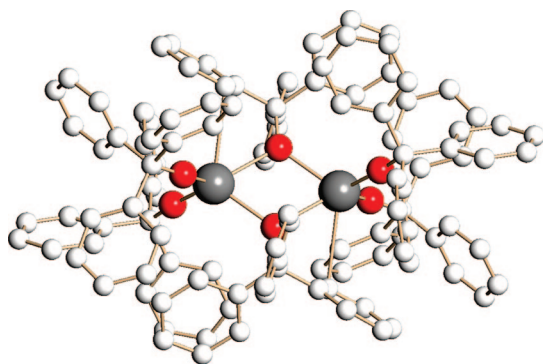
Figure 2. Structure plot of [La(μ-TPM)(TPM)₂]₂.

Again, these are averaged distances and limited to 3 significant figures.

3.1.3.1. Terminal. Terminal Ln−O bond distances vary significantly from complex to complex and are sensitive to the nature of the co-ligands. Within the aryloxide derivatives described herein (excluding any Sc species) terminal Ln−OAr distances span the range 2.02−2.46 Å (with divalent Ln-O distances being longer than the corresponding Ln−OAr distances.) In the case of the trivalent alkyl analogs, the only ligand that has been structurally characterized for the entire series of metals is the *neo*-pentoxide (i.e., [Ln(ONep)₃]₄).[77] This series exhibits a systematic decrease in bond distances as the 4f series is traversed [these range from 2.16 Å (La) to 1.89 Å (Sc)]. Other complexes supported by alkoxides follow a similar trend.

3.1.3.2. Bridging. There are numerous examples of *tris*-alkoxy complexes containing bridging ligands. The nuclearities of these molecules range from dinuclear to decanuclear. Ln−(μ-OR) distances also span a wide range of values between 2.23 and 2.60 Å (omitting Sc) with an average of

2.35 Å for the compounds listed in Table 1. The majority of these species are bimetallic compounds which heavily weights this toward the (μ-OR)-Ln₂ averaged value (the corresponding average in trinuclear species is 2.38 Å, and in tetranuclear species is 2.41 Å (av. 2.28 Å for the Ln(μ-ONep)₂(ONep)]₄ species),[77] hexanuclear 2.67 Å, and 2.31 Å for decanuclear species).

3.1.3.3. Triply Bridging. Within the context of the Ln complexes of interest to this review, only a handful of compounds have been characterized via X-ray diffraction in which μ₃-OR interactions are observed. Ln-(μ₃-OR) distances were found to vary from 2.32 to 2.81 Å.[9] In general the average values were all very close, for example, 2.41, 2.42, and 2.52 Å for Y,[79] Dy,[68] and Nd[80] in Ln₃(μ₃-OBuᵗ)₂(μ-OBuᵗ)₃(OBuᵗ)₄(solv)₂, 2.43 Å for (Y₈(μ₃-IPE)₆(μ-IPE)₁₀-(IPE)₈,[74] 2.53 and 2.54 Å for HOAr = DIP in [Eu(μ₃-OEtOMe)(OEtOMe)(HOAr)]₄·(tol),[34] 2.54 and 2.55 Å for solv = THF and H-DBP3,5/THF in Nd₃(μ₃-DBP-3,5)₂(μ-DBP-3,5)₃(DBP-3,5)₄(solv)₄,[81] and 2.60 Å for Eu₄(μ₄-OPrⁱ)(μ₃-OPrⁱ)₂(μ-OPrⁱ)₂(OPrⁱ)₃(H-OPrⁱ)₂·(H-OPrⁱ).[61]

3.1.3.4. Quadruply Bridging. The μ₄-OR arrangement (excluding μ₄-OH) is relatively rare for *all* metal alkoxides.
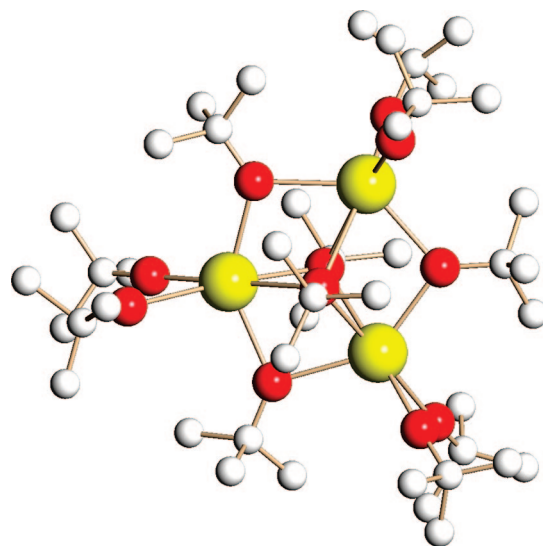
Figure 3. Structure plot of Ce₃(μ₃-OBuᵗ)₂(μ-OBuᵗ)₃(OBuᵗ)₄-(HOBuᵗ)₂.

a

b
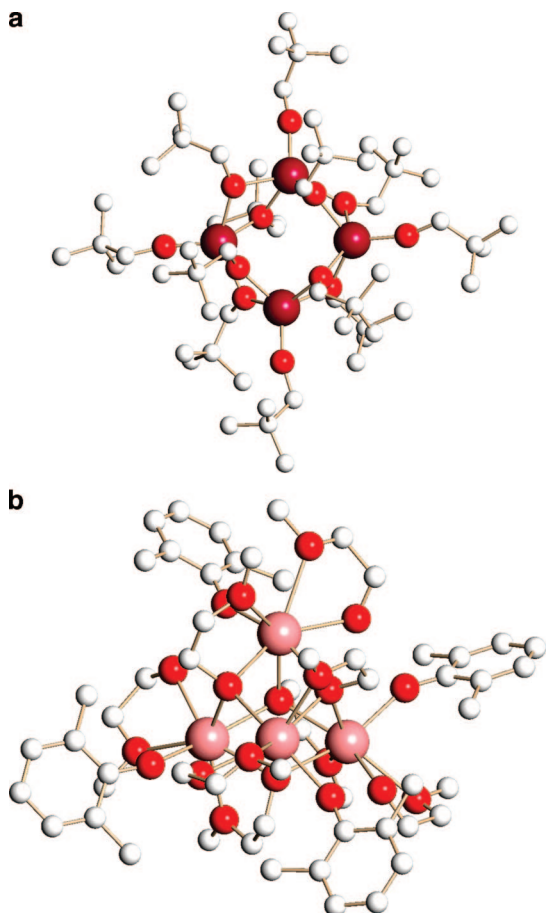
Figure 4. (a) Structure plot of [Lu(μ-ONep)$_2$(ONep)]$_2$. (b) Structure plot of [Eu(μ_3-MeOEtO)(MeOEtO)(DMP)]$_4$·toluene (toluene omitted for clarity).
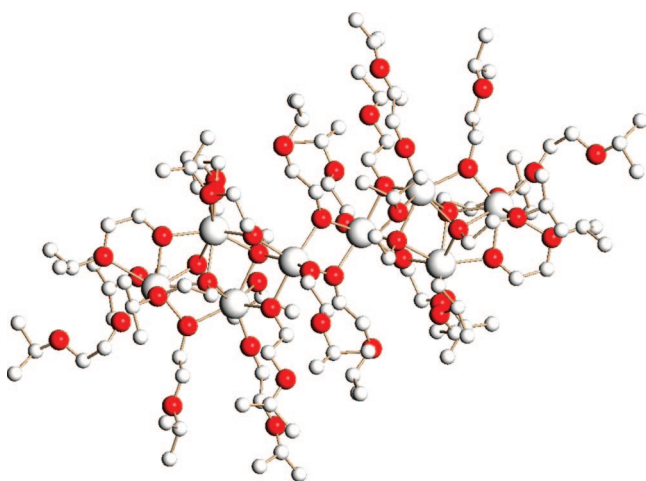
Figure 5. Structure plot of Y$_8$(μ_3-IPE)$_6$(μ-IPE)$_{10}$(IPE)$_8$.

In fact, only 42 X-ray structures reveal the presence of a μ_4-OR group with 40 of those involving an alkali metal. It is therefore not surprising that only Eu$_4$(μ_4-OPr^i)(μ_3-OPr^i)$_2$(μ-OPr^i)$_2$(OPr^i)$_3$(H-OPr^i)$_2$·(H-OPr^i) matches the criteria for this review and possesses the μ_4-OR-Ln$_4$ moiety with an average distance of 2.65 Å (2.49 to 2.81 Å).[61]

3.1.4. Bond Angles

For Ln(OR)$_x$, bond angles are typically distorted from ideal values due to the constraints imposed by bridging OR groups or by secondary π-interactions involving terminally bound
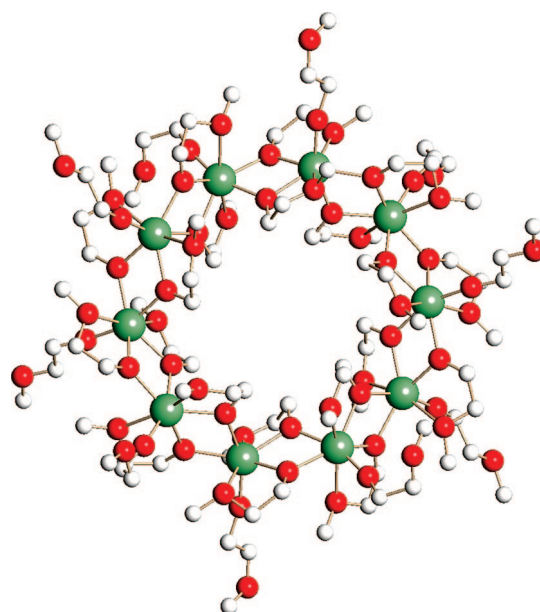
Figure 6. Structure plot of [Dy(μ-OEtOMe)$_2$(OEtOMe)]$_{10}$.

ligands. The M-O-M angles are a useful means to determine the strain imposed on a particular molecule. For example, Eu$_4$(μ_4-OPr^i)(μ_3-OPr^i)$_2$(μ-OPr^i)$_2$(OPr^i)$_3$(H-OPr^i)$_2$·(H-OPr^i)[61] shown in section 3.2.1 possess all three types of bridging ligands which allow for easy comparison within the same molecule. The angles found within the Eu−(μ_4-OR)−Eu fragment range from 85.9 to 169.4° whereas Eu-(μ_3-OR)-Eu angles range from 92.55 to 96.59 ° (av 94.3°) while Eu−(μ-OR)−Eu angles span the range from 99.44 to 100.85° (av 99.9°).

For Ln$_3$−(μ_3-OR) fragments, the M−O−M angles were found to vary from 85.9 to 108.2°.[36,61,68,74,78,79,81] For trinuclear species that have both Ln−(μ-OR)−Ln and Ln−(μ_3-OR)−Ln, the former angles were found to range from 92.0 to 108.2°.[34,61,68,74,78,79,81] In comparison, the simple bimetallic species the Ln−(μ-OR)−Ln span the range from 88.3 to 113.5°.[31,37,40,48,67,69,70,72,73,81–91]

3.1.5. Summary of Metrical Data

Some general trends can be discerned from metrical data listed in Table 1. As the cation size decreases across the series, the Ln−O distance decreases in a linear fashion. As would be predicted, Ln−O bond distances fall in the following order: OR < μ-OR < μ_3-OR < μ_4-OR. It is important to note that the nature of the co-ligands(s) can significantly affect the variability of each class of Ln−O bonding interaction. As discussed above, the ligands influence the final structure to a significant degree, therefore, the following discussions follow the different ligands available to Ln(OR)$_x$. Table 2 lists the crystallographically characterized Ln(OR)$_x$ separated by metal.

3.2. Aliphatic Alkoxides

Only a few examples of alkyl alkoxide ligand have been crystallographically characterized as the homoleptic Ln(OR)$_3$ complexes.[9] Most often these are comprised of ligands that have fewer than six carbon atom chains and are often branched, since larger straight chained species do not appear to crystallize as efficiently. The discussion of the structural types below follows the trend of general increase in steric bulk of the ligands, spanning methoxide (OCH$_3$, OMe),
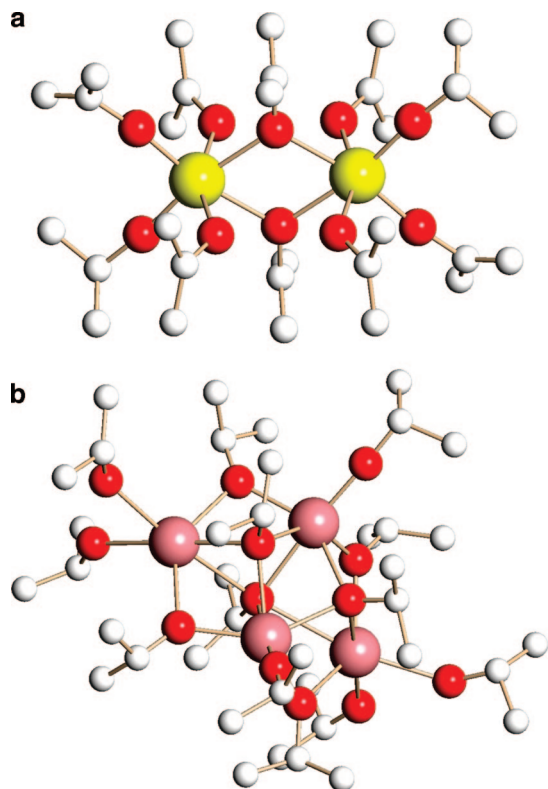
Figure 7. (a) Structure plot of $[Ce(\mu\text{-}OPr^i)(OPr^i)_3(HOPr^i)]_2$. (b) Structure plot of $Eu_4(\mu_4\text{-}OPr^i)(\mu_3\text{-}OPr^i)_2(\mu\text{-}OPr^i)_4(OPr^i)_3(H\text{-}OPr^i)_2\cdot H\text{-}OPr^i$.

ethoxide (OCH_2CH_3, OEt), *n*-propoxide ($O(CH_2)_2CH_3$, OPr^n), *n*-butoxide ($O(CH_2)_3CH_3$, OBu^n), *iso*-propoxide ($OCH(CH_3)_2$, OPr^i) *neo*-pentoxide ($OCH_2C(CH_3)_3$, ONep), and *tert*-butyl derivatives ($OC(CH_3)_3$, OBu^t). Schematics of these ligands are shown in Scheme 1.

For transition metals, it is widely observed that any significant increase in steric bulk around the metal center generally leads to a reduction in nuclearity. Not surprisingly, larger ligands block open coordination sites on these small metal centers. Whether or not the same occurs for the Ln cations is of interest due to their much larger radii in comparison.[92] Also, the ability of alkoxide ligands to supplement the metal−ligand σ-bonding with π-bonding via donor atom lone pairs may be different for the highly Lewis acidic Ln ions versus a number of their transition metal counterparts. Scheme 2 illustrates the central core constructs of various common isolated "Ln(OR)$_3$" species deduced from the crystallographically identified species discussed below.

3.2.1. Methoxide/Ethoxide/Propoxide Derivatives

There are no reports of Ln cations supported solely by OMe, OEt, or OPr^n ligands; however, reports of several species containing these ligands and oxo groups are available.[11,48,65,67,68,79,80,82,83,93] The lack of homoleptic examples of these alkoxides is most likely due to the tendency toward oligomerization and the low solubility that would likely result in the cases of the clusters presumably produced. There are two reports of crystallographically characterized homoleptic lanthanide *iso*-propoxide compounds: $[Ce(\mu\text{-}OPr^i)(OPr^i)_3(HOPr^i)]_2$[84,85] and $Eu_4(\mu_4\text{-}OPr^i)(\mu_3\text{-}OPr^i)_2(\mu\text{-}OPr^i)_2(OPr^i)_3(HOPr^i)_2\cdot(HOPr^i)$.[61] The Ce(IV) compound's structure is illustrated in Figure 7a and consists of a simple edge-shared bioctahedral geometry in which OPr^i ligands occupy two of the axial positions within the octa-
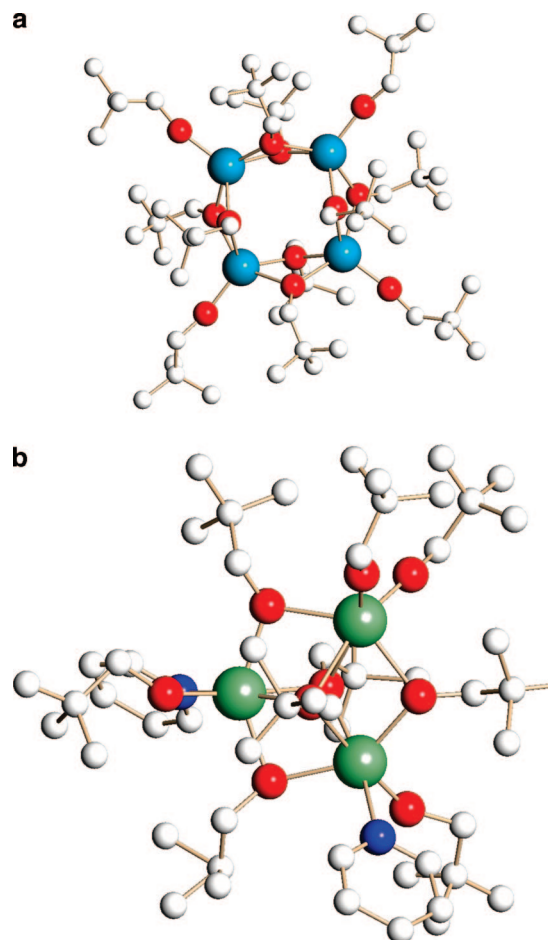
Figure 8. (a) Structure plot of $[Tb(\mu\text{-}ONep)_2(ONep)]_4$. (b) Structure plot of $Dy_3(\mu_3\text{-}ONep)_2(\mu\text{-}ONep)_3(ONep)_4(py)_2$.

hedrally (Oh) coordinated Ce centers. The coordination of two equivalents of *iso*-propanol allows for both electronic and steric saturation of the Ce metal centers in this case. For the Eu(II, III) compound, Figure 7, a butterfly arrangement within the metal core was observed wherein the OPr^i groups coordinates in a variety of binding modes supporting the complex involving a rare μ_4-OR, two μ_3-OR, four μ-OR, and three terminal OR ligands. Furthermore, two coordinated alcohol ligands complete the coordination sphere while a further molecule of crystallization of $HOPr^i$ is also observed by X-ray crystallography.

3.2.2. neo-Pentoxide Derivatives

Single crystal X-ray structure complexes have been obtained for every member of the Ln series yielding $[Ln(\mu\text{-}OR)_2(OR)]_4$ where OR = $OCH_2C(CH_3)_3$, alternatively referred to as OCH_2Bu^t or ONep. These ONep derivatives demonstrate the only structural case where each of the trivalent series Ln cations are coordinated by the same alkoxide ligand. All of these family members were found to adopt an identical tetrameric structure in the solid state, $[Ln(\mu\text{-}ONep)_2(ONep)]_4$[77] where Ln = Sc, Y, La,[94] Ce,[47] Pr, Nd,[94] Sm, Eu, Gd, Tb, Dy,[68] Ho, Er,[95] Tm, Yb, and Lu. In all cases, each metal exhibits a five coordinate trigonal bipyramidal (tbp) geometry.[77] Figure 8a shows the structure of $[Tb(\mu\text{-}ONep)_2(ONep)]_4$[77] as an example of the general constructs identified for this series and is the first structurally characterized example of a homoleptic Tb alkoxide complex. The *neo*-pentoxide ligand also led to isolation of the first
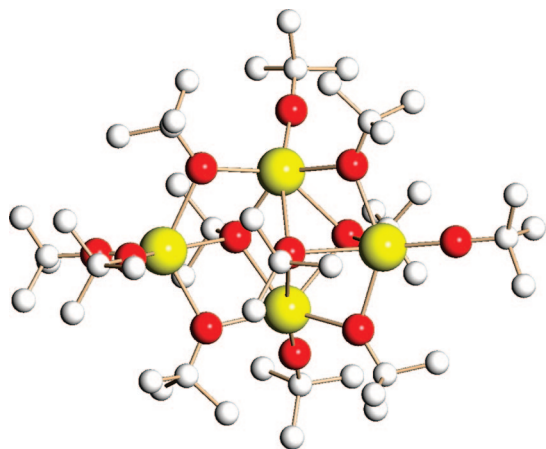
Figure 9. Structure plot of $[Ce_2(\mu_3\text{-OBu}^t)(\mu\text{-OBu}^t)_2(OBu^t)_3]_2$.

crystallographically characterized alkoxides reported for (Sc, Pr, Gd, Ho, Er,[95] Tm, and Lu).[77] It is surprising that the more than 0.3 Å range in cationic radius that occurs between La and Sc still allows for the *iso*-structural series observed here. In the presence of a Lewis base, these oligomers convert to trinuclear species as evidenced by reports of $Dy_3(\mu_3\text{-ONep})_2(\mu\text{-ONep})_3(ONep)_4(py)_2$[68] (shown in Figure 8b). Lower nuclearity species have not been observed with this ligand.

3.2.3. tert-Butoxide Derivatives

Similar to the often observed chemistry of the d-block elements, further increase in the steric bulk of the coordinated ligand results in a reduction of the nuclearity of the resulting complex. Therefore, in moving from OPr^i or ONep ligands to the significantly more sterically demanding OBu^t group, it might have been expected that parallel behavior would be observed. Base free structures supported by this ligand set are not common but have been observed in constructs similar to the ONep solvated derivatives (e.g., $[Ce_2(\mu_3\text{-OBu}^t)(\mu\text{-OBu}^t)_2(OBu^t)_3]_2$, Figure 9).[47] In this particular class, the large size of the Ln^{3+} ion still facilitates tetramer formation in the absence of Lewis bases.[47] However, the majority of structurally characterized species isolated containing this ligand are the solvated trinuclear clusters, $Ln_3(\mu_3\text{-OBu}^t)_2(\mu\text{-OBu}^t)_3(OBu^t)_4(solv)_x$ where $Ln(solv)_x = Y(HOBu^t)$,[79] $La(HOBu^t)_2$,[93] $Ce(HOBu^t)_2$,[47] $Nd(THF)_2$,[80,82] $Dy(HOBu^t)_2$,[68] $Dy(py)_2$,[68] and $Er(HOBu^t)_2$.[95] These are similar in constructs to the halide alkoxy species such as the $Ln_3(\mu\text{-O})(\mu\text{-X})(OR)_6(solv)_x$ derivatives that are ubiquitous in the literature.[65,66] The structural differences exhibited by the Ln elements (as compared to their d-block counterparts) again serves to illustrate the dramatic effect that the large ionic radii can have on their fundamental coordination chemistry.

3.2.4. Sterically Bulky Methoxide Derivatives

Formal derivatization of the OMe ligand with other alkyl groups permits even more sterically hindered ligands to be prepared. These act to reduce the nuclearity to more "standard" di- and mononuclear species. The di-*iso*-propyl-methoxide ($OCH(CHMe_2)_2$ or DPM) ligand has been found to produce dinuclear solvated species $[Nd(\mu\text{-DPM})(DPM)_2(solv)]_2$ where solv = THF or py.[67] In contrast, in the presence of dimethoxyethane (DME) the polymeric species, $[Nd_2(DPM)_6(\mu\text{-DME})]_\infty$[67] was isolated. In adding more steric bulk to the methoxide fragment such as in the 2,3-dimethyl
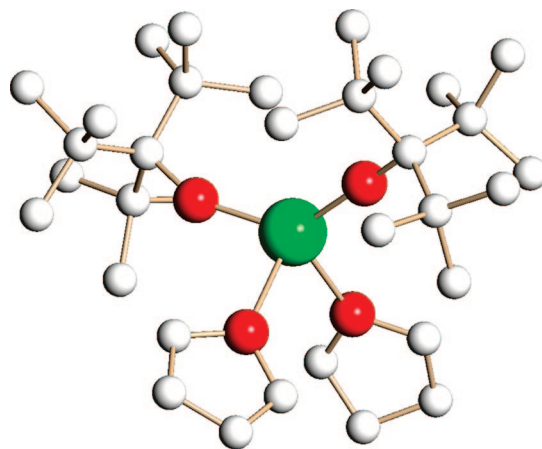
Figure 10. Structure plot of $Yb(TBM)_2(THF)_2$.

2-butoxide (DMB) ligand, the dinuclear species $[Ce(\mu\text{-OBu}^t)(DMB)_3]_2$ was observed. When solvated with 4-dimethylamino pyridine (DMAP), a mononuclear species was isolated as $(DMAP)_2Ce(DMB)_4$.[48]

Other bulky examples include the di-*tert*-butylmethanol ($HOCH(C(CH_3)_3)_2$ = DBM-H) ligand which also provides a dinuclear complex, $[Ce(\mu\text{-DBM})(DBM)_2]_2$ when no donor solvent is present.[83] However, in the presence of acetonitrile (CH_3CN) both dinuclear and mononuclear species were produced as $(CH_3CN)(DBM)_2Nd(\mu\text{-DBM})_2Nd(DBM)_2$[87] and $Dy(DBM)_3(CH_3CN)_2$.[87] The reduced nuclearity of these compounds is directly attributable to the sterically encumbered nature of the ligand. Further increasing the number of Bu^t groups to form tris-(*tert*-butyl)methanol (H-OC-$(C(CH_3)_3)_3$) = TBM-H) provides a series of monomeric complexes: $Ln(TBM)_3(solv)_x$ where $Ln(solv)_x = Ce(N-CCH_3)_2$,[96] $Nd(NCCH_3)_2$,[97] and $Nd(THF)$.[98] The tetrahedrally coordinated divalent species $Yb(TBM)_2(THF)_2$[20] (Figure 10) was also reported. Additional steric bulk of the triphenyl-methoxide ($OC(C_6H_5)_3$ = TPM) ligand yielded a dinuclear species $[La(\mu\text{-TPM})(TPM)_2]_2$.[72] One additional (*tert*-butyl)-methanol derivative was isolated as $Sm(OBpy)_3$ where OBpy $= OC(CH_3)_3(CH_2NC_5H_5\text{-CH}_3\text{-2})_2$.[71]

3.2.5. Bidentate Ligands

In addition to the use of monodentate alkoxide, multidentate ligands have also found utility in altering the properties of transition $M(OR)_x$. These ligands are especially useful for controlling the oligomerization of molecules via steric hindrance and saturation of available coordination sites. Typically with bidentate systems, both the alkoxide oxygen and the second oxygen donor atom (i.e., an OMe group) can coordinate, as noted in the case of (methoxy)ethoxide (OEtOMe) and (methoxy)propoxide (OPrOMe=OC(Me)_2-$CH_2(OMe)$) ligands. Within the Ln series, only two species, with identical cores were reported for the bidentate OEtOMe ligand, $[Ln(\mu\text{-OEtOMe})_2(OEtOMe)]_{10}$ where Ln = Y[75] (Figure 11a), Dy.[76] These molecules are composed of symmetric decanuclear rings cojoined by chelating bridging OEtOMe groups, with one terminally bound ligand per metal center. The introduction of Lewis basic solvents in the form of (aryl)alcohols reduces the nuclearity, and results in the tetranuclear examples, $Eu_4(\mu\text{-OEtOMe})_4(OEtOMe)_4(H\text{-OAr})_4$ (OAr = DMP[34] and DIP[34] (shown in Figure 11b)). In addition, another derivative with a longer alkyl group (IPE = 2-(*iso*-propoxy)ethanolato) led to larger oligomers $Y_8(\mu_3\text{-IPE})_6(\mu\text{-IPE})_{10}(IPE)_8$.[74]

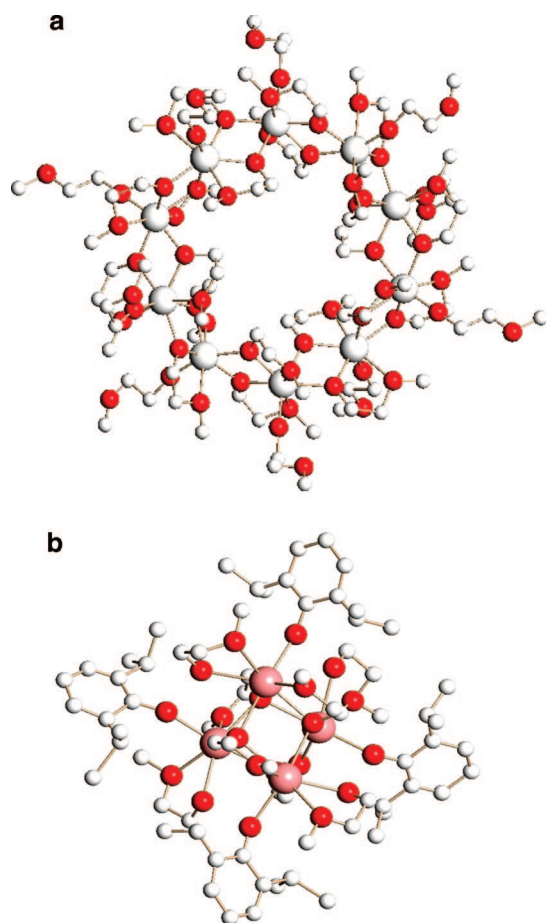**Figure 11.** (a) Structure plot of $[Y(\mu\text{-OEtOMe})_2(\text{OEtOMe})]_{10}$. (b) Structure plot of $Eu_4(\mu\text{-OEtOMe})_4(\text{OEtOMe})_4(\text{H-DIP})_4$.

The introduction of more steric bulk in the form of additional methyl groups also reduces the metals' ability to oligomerize. Examples include $(\text{MMPO})\text{Lu}(\mu\text{-MMPO})_3\text{Lu-}$ $(\text{MMPO})_2$[69] $(\text{MMPO}=\text{OC}(\text{Me})_2\text{CH}_2(\text{OMe}))$ and $[(\text{MMBO})_2\text{Nd}(\mu\text{-MMBO})]_2$ MMBO $= \text{OC}(\text{Me})_2\text{CH}_2\text{CH}_2(\text{OMe})$.[82] However, even in these cases, dinuclear species are still isolated.

3.3. Aryloxides

Aryloxides or phenoxides are widely employed as ligands, in part due to the ease with which the substituents on the aromatic ring can be manipulated. This permits a wide range of steric control with respect to the resulting metal coordination chemistry. In particular, ortho substituted aryloxides are frequently used, as this ring position has the largest effect on the steric "cone" around each metal ion. A large variety of aryl group substitution patterns are available, including the widely used 2,6-disubstituted aryloxides, dimethylphenoxide (DMP), di-*iso*-propylphenoxide (DIP), di-*tert*-butylphenoxide (DBP), diphenylphenoxide (DPP), and 1-napthanoxide (ONap) derivatives. A schematic representation of these aryloxide ligands are presented in Scheme 3.

3.3.1. Monosubstituted Phenoxides

Currently, there are no structural reports of *homoleptic* analogs supported by ligands containing unsubstituted phenyl (OPh) groups. For the monoalkyl substituted phenoxide ligands, there were no descriptions of structurally characterized examples until the recent report of $Ce(o\text{BP})_3(\text{THF})_3$[47]

where $o\text{BP} = \text{OC}_6\text{H}_3(\text{C}(\text{CH}_3)_3)_2\text{-2}$; however, it is of note that several other aryloxides with different substituents (i.e., NO_2, Cl, etc.)[9] are available. Again, the presence of these moieties leads to undesirable contamination issues in resulting materials processing; therefore, these derivatives have been excluded from further discussion.

3.3.2. Disubstituted Phenoxides

Symmetric substitution of the ortho positions or "2, 6-disubstitution" of the aryl group has been extensively examined to probe the effect of steric influence on the resulting molecular structure. The examples shown in Scheme 3 are the standard ligands that have been studied and complexes supported by these arylyoxides are discussed below in order of increasing steric bulk. Based on the nature of the ortho substituents, a variety of bonding modes have been found, including H-bonded interactions, π-bonding (via the aromatic cloud of the aryl substituent), as well as other interesting modes resulting from the steric/electronic unsaturation of the large Ln ions.

3.3.2.1. Di(methyl)phenoxide Derivatives. Several structural motifs have been observed in complexes supported by the 2,6-dimethyl phenoxide (DMP) ligand. The nature of these compounds largely being dependent on the reaction conditions employed. In all isolated "Ln(DMP)$_3$" species, coordinated solvent is retained. The structure of these compounds ranges from trinuclear $Eu[(\mu\text{-DMP})_3Eu(\text{THF})_3]_2$[35] (Figure 12a) or $(\text{DMP})\text{Dy}[(\mu\text{-DMP})\text{Dy}(\text{DMP})_2(\text{NH}_3)]_2$[68] to dinuclear species such as $[\text{Ln}(\mu\text{-DMP})(\text{DMP})_2(\text{THF})_2]_2$ (Ln = Y[73] and Nd[70]) (Figure 12b) to mononuclear adducts such as $\text{Ln}(\text{DMP})_3(\text{solv})_x$, where $\text{Ln}(\text{solv})_x = \text{Er}(\text{THF})_3$[95] (Figure 12c), $\text{Er}(\text{py})_3$,[95] $Y(\text{THF})_3$,[73] $\text{Ce}(\text{THF})_4$,[47] $\text{Ce}(\text{py})_4$,[47] and $\text{Dy}(\text{py})_3$.[68] As may be expected, substitution in the para position has no structural consequence as evidenced in $\text{Sm}(\text{OMes})_3(\text{THF})_3$[86] and $\text{Nd}(\text{OMes})_3(\text{py})_4$[86] $(\text{OMes}=\text{OC}_6\text{H}_2(\text{CH}_3)_3\text{-}2,4,6)$. The degree of solvation change, and the radius of the cation both play an important role in determining the ultimate solid state structure. Two different solvents can confer the same structure as in the cases of $Eu_2(\mu\text{-DMP})_3(\text{DMP})(\text{MeIm})_5$[36] and $Eu_2(\mu\text{-DMP})_3(\text{DMP})(\text{DME})_3$.[37] Multidentate donor solvents can also contribute to the formation of monomeric complexes such as $\text{La}(\text{DMP})_3(\text{pentaoxapentadecane})(\text{OEt}_2)$[99] or $\text{Sc}(\text{DMP})_3\text{-}$ (dimethylpyrazolylmethane).[100,101]

3.3.2.2. Di-*iso*-propylphenoxide Derivatives. Increasing the steric bulk of the ortho substituents to ethyl groups (i.e., 2,6-diethylphenoxide) has not yielded any structurally characterized "Ln(OAr)$_3$" species. However the 2,6-di-*iso*-propylphenoxide (DIP) fragment is one of the most thoroughly utilized aryloxide ligands in $\text{Ln}(\text{OR})_x$ chemistry. In the presence of a Lewis base, monomeric species such as $\text{Ln}(\text{DIP})_3(\text{THF})_x$ are observed where $\text{Ln}(\text{solv})_x = Y(\text{THF})_2$,[102] $\text{La}(\text{THF})_2$,[103] $\text{Ce}(\text{THF})_3$,[47] $\text{Pr}(\text{THF})_2$,[104] $\text{Sm}(\text{THF})_3$,[105] $\text{Sm}(\text{THF})_2$,[106] $\text{Gd}(\text{THF})_2$,[104] $\text{Dy}(\text{THF})_2$,[68] $\text{Ho}(\text{THF})_2$ (Figure 13),[107] $\text{Er}(\text{THF})_2$,[95,104] and $\text{Lu}(\text{THF})_2$.[104] Other less sterically demanding donors can also stabilize monometallic systems, including mononuclear compounds $\text{Ln}(\text{DIP})_3(\text{solv})_x$ where $\text{Ln}(\text{solv})_x = \text{La}(\text{NH}_3)_4$,[103] $\text{Dy}(\text{NH}_3)_3$,[68] and $\text{Dy}(\text{py})_3$,[68] and dinuclear compounds such as $(\mu\text{-NCCH}_3)[(\mu\text{-DIP})\text{Eu}(\text{DIP})\text{-}$ $(\text{NCCH}_3)_2]_2$.[36]

When donor solvents are rigorously excluded from the synthetic route employed, the bimetallic complexes $[\text{Ln}(\eta^6\text{-}$ $\text{DIP})(\text{DIP})_2]_2$ where Ln = Y,[102] La,[103] Nd,[104] Sm (Figure 14),[104] Dy,[68] and Er[95] are obtained. The two *tris*-phenoxide

a

b

c

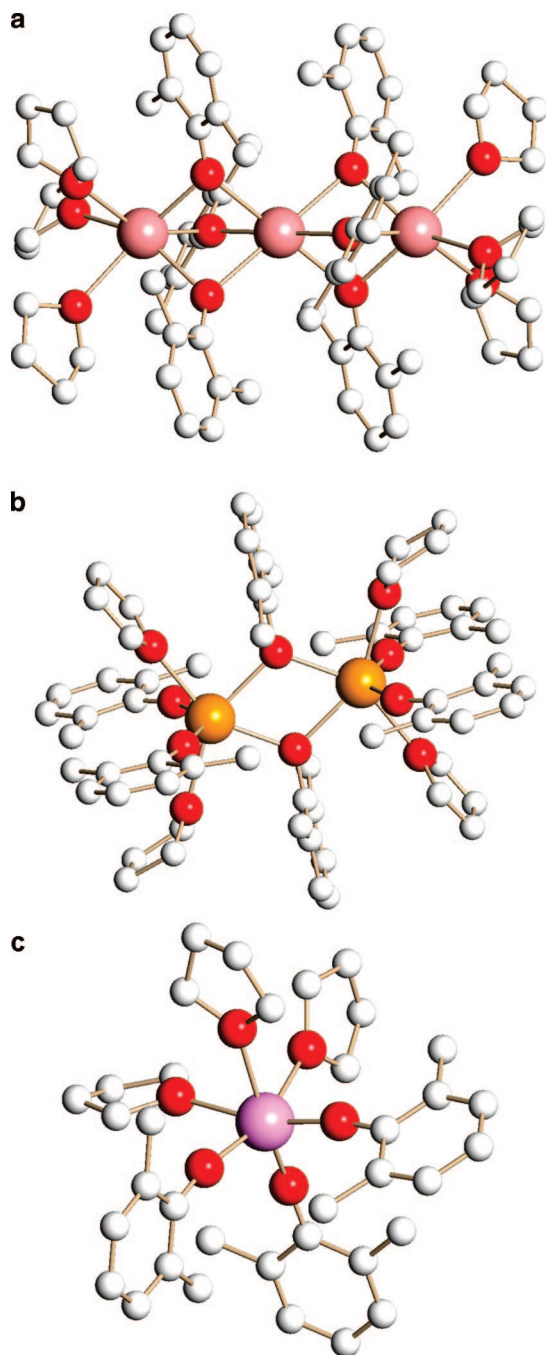**Figure 12.** (a) Structure plot of $Eu[(\mu\text{-}DMP)_3Eu(THF)_3]_2$. (b) Structure plot of $[Nd(\mu\text{-}DMP)(DMP)_2(THF)_2]_2$. (c) Structure plot of $Er(DMP)_3(THF)_3$.

"halves" of this molecule are held together via the agency of π-arene interactions. NMR spectroscopy has shown that the dimeric structure is maintained in solution as well as in the solid state (in the absence of a suitable donor).

This general structure has been shown to be relatively easily disrupted however, irreversibly forming mononuclear compounds in the presence of Lewis bases such as THF (as noted above Figure 13).

3.3.2.3. Di-*tert*-butylphenoxide Derivatives. A variety of species have been isolated using the 2,6-di-*tert*-butyl-phenoxide (DBP) ligand (as well as derivatives of the ligand substituted in the para position, DBP-R-4). This variant is among the most sterically demanding of the available aryloxide ligands, and not surprisingly, the DBP-R-4 ligand
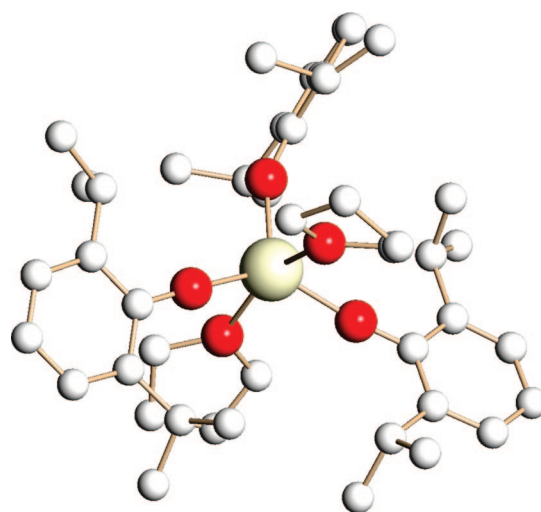
Figure 13. Structure plot of $Ho(DIP)_3(THF)_2$.
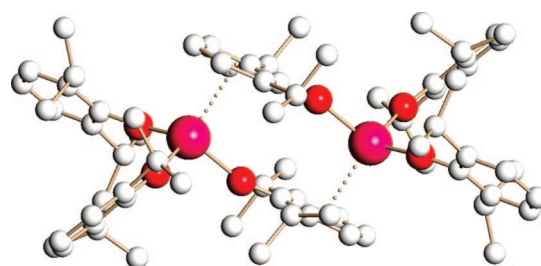
Figure 14. Structure plot of $[Sm(\eta^6\text{-}DIP)(DIP)_2]_2$.

allows for the isolation of the monomeric base-free complexes $Ln(DBP\text{-}R\text{-}4)_3$ where Ln = Sc(R = Me),[108] Ce (R = H),[109] Pr (R = H) (Figure 15a),[110] Nd,[110] and Dy.[68] Solvated monomeric adducts have also been reported: $Ln(DBP)_3(solv)_x$ where $Ln(solv)_x$=Ce(NCBu^t)$_2$,[109] Eu(NCCH$_3$)$_4$,[38] Dy(NH$_3$),[68] Dy(THF),[68] Dy(py)$_2$,[68] Eu-(THF)$_3$,[21] Er(py)$_2$,[95] and Yb(NCMe)$_4$.[21] Monometallic examples are isolated independent of both the size of the cation and the nature of the donor solvent employed (or even the charge of the molecule).

One unusual example includes meta di-*tert*-phenoxide ($OC_6H_3(CMe_3)_2$-3,5 or DBP-3,5), which has its steric bulk, removed from the ortho ring position. This permits the isolation of dinuclear complexes $[Ln(\mu\text{-}DBP\text{-}3,5)(DBP\text{-}3,5)_2(solv)_x]_2$ where $Ln(solv)_x$ = La(THF)$_3$,[81] Er(THF)$_2$,[81] and Yb(THF)$_2$.[81] Trinuclear complexes were also isolated in the case of $Nd_3(\mu\text{-}DBP\text{-}3,5)_5(DBP\text{-}3,5)_4(THF)_4$[81] and $Nd_3(\mu\text{-}DBP\text{-}3,5)_5(DBP\text{-}3,5)_4(H\text{-}DBP\text{-}3,5)_2(THF)$.[81] In addition, a reported aqua complex was isolated as $[La(\mu\text{-}DBP\text{-}3,5)_2(DBP\text{-}3,5)]_4(H_2O)$.[81]

The nature of para position substitution has little effect on the solid state structure as evidenced by the examples of $Ln(DBP\text{-}Me\text{-}4)_3(solv)_x$ where Ln^{3+} $(solv)_x$ = Nd(THF) (Figure 15b),[63] Eu(THF)$_3$,[21,39] Er(THF),[111] and in the corresponding Ln^{2+} species: Sm (THF),[112] Sm (NCCH$_3$)$_2$,[113] Sm(THF)$_3$,[24] Yb(THF)$_2$,[24] Yb(OEt$_2$)$_2$,[24] and Yb(THF)$_3$.[25,26] Furthermore the 2,4,6-tri-*tert*-butyl derivatives were also observed to be monomeric as in the case of Yb(TBP)$_3$(THF)[114] or in Ln^{2+} (TBP)$_2$(solv)$_x$ where Ln^{2+} $(solv)_x$ = Sm(THF)$_3$,[46] Sm(DME)$_2$,[46] and Yb(THF)$_3$.[25,26] One notable exception here is the dinuclear base free complex, $[Yb(\mu\text{-}DBP\text{-}Me\text{-}4)(DBP\text{-}Me\text{-}4)]_2$ (Figure 15c).[20,22] Also,
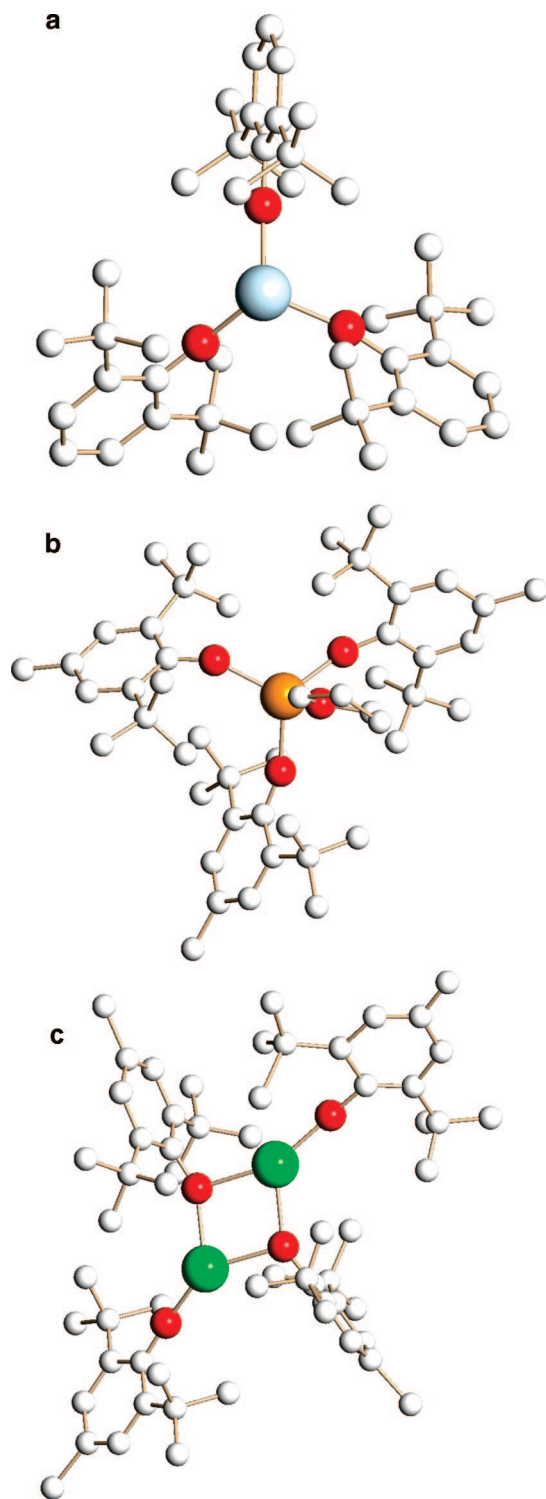
Figure 15. (a) Structure plot of Pr(DBP)$_3$. (b) Structure plot of Nd(DBP-Me-4)$_3$(THF). (c) Structure plot of [Yb(μ-DBP-Me-4)(DBP-Me-4)]$_2$.

methoxy derivatives (OC$_6$H$_2$(Bu^t)$_2$-2,6,(OMe)-4 or DBP-OMe have been reported for Ln(DBP-OMe)$_3$(solv)$_x$ where Ln(solv)$_x$ = Nd(THF),[27] Ho(THF),[27] and Ln^{2+} (DBP-OMe)$_2$(solv)$_x$ where Ln(solv)$_x$ = Sm(THF)$_3$,[27] Sm(DME),[27] and Yb(THF)$_3$.[27] No π-arene bridged inter- or intramolecular interactions were observed in any of the characterized DBP derivatives, most likely as a reflection of the increased steric influence of the *tert*-butyl versus *iso*-propyl groups.

3.3.2.4. Di(phenyl)phenoxide Derivatives. The addition of the ortho phenyl groups to diphenylphenoxide (DPP = OC$_6$H$_3$(C$_6$H$_5$)$_2$-2,6) allows for not only a steric variation but also a η interaction for the π-ring of the arene. In the case of scandium, only the solvent free monomeric complex, Sc(DPP)$_3$,[30,115] was observed. In the cases of Ln = Y,[115] La,[115] Ce,[115] Pr,[115] Eu,[28] Nd,[116] Yb,[117] and Lu (Figure 16a),[115] a secondary η^6-arene interaction involving the *ortho* phenyl rings of a DPP ligand was reported for Ln(DPP-(η^6-Ph-2)(DPP)$_2$)). A divalent Yb^{2+} DPP adduct was also isolated exhibiting numerous π-interactions.[28] The π-interaction are easily disrupted upon the introduction of suitable donor solvents noted in the cases of Ln(DPP)$_3$(solv)$_x$ where Ln(solv)$_x$ = La(THF)$_2$,[116,118] Ce(THF)$_2$,[47] Nd(THF),[116,118] Nd(THF)$_2$,[116,118] Nd(DME),[29] Yb(DME),[29] and system Yb(THF)$_2$.[114,117] Solvated adducts of some lanthanide DPP analogs (or their 3,5-substituted derivatives, DPP-R$_2$-3,5) are also described, including Ln(DPP-R$_2$-3,5)$_3$(solv)$_x$ where R = H: La(THF)$_2$ (Figure 16b),[116,118] Yb(THF);[30] R= Bu^t: Sc(THF)[30] (Figure 16c) and Yb(THF);[30] R = Ph: Yb-(DME).[30] In addition an unusual charge separated species was observed in the case of [Yb$_2$(μ-η^6-DPP)$_3$][Yb(DPP)$_4$][28] (Figure 16d) and divalent complexes were isolated as Ln(DPP)$_2$(solv)$_x$ where Ln(solv)$_x$ = Yb(DME)$_2$,[29] Yb-(THF)$_3$.[29]

A similar compound has recently been reported as [Ln(D-BzP)(DBzP)$_2$]$_2$ where DBzP = OC$_6$H$_3$(CH$_2$(C$_6$H$_5$)$_2$)$_2$-2,6 Ln = La, Eu, and Yb in which an η^6-bonding interaction between the metal and one benzyl group of each bridging ligand occurs.[40]

3.3.3. Complex Aryloxide Derivatives

Using 1-naphthanol (H-ONap), two polynuclear species were isolated as [(μ-ONap)(THF)$_2$Eu(μ-ONap)$_2$Eu(ONap)-(THF)$_3$]$_2$ (Figure 17)[31] [Yb(μ-ONap)(ONap)$_2$(THF)-(NCCH$_3$)]$_2$.[31] The ONap ligand can act as bridging or terminal ligand with little steric hindrance brought about by the second ring.

Additionally, the potentially bidentate quinalolato (Quin) derivatives were isolated as trinuclear species. The quinalato acts as a bridge and terminal ligand forming (Quin)Ln[(μ-Quin)$_3$Ln(Quin)]$_2$ where Ln = Ho[119] or Er.[120] In addition, the first ever structurally characterized Pr alkoxide was reported as the water stable Pr(TAP)$_3$(H$_2$O) where TAP = OC$_6$H$_2$(CH$_2$CH$_2$NMe$_2$)$_3$-2,4,6.[121]

4. Mixed Alkoxide Derivatives

The number of structural reports on complexes supported by mixed (heteroleptic) alkoxide systems is limited. This may be as a result of solution disproportionation reactions that yield the corresponding homoleptic species. The previously mentioned Eu$_4$(μ-OEtOMe)$_4$(OEtOMe)$_4$(H-OAr)$_4$ where OAr = DMP[34] and DIP[34] (Figure 11b) compounds are considered solvated derivatives but could be included in the mixed ligated species. The Ce dimer [Ce(μ-OBu^t)(TBM)$_2$]$_2$[89] (Figure 18a) and the tetrameric example Sm$_4$(μ_3-OPr^i)$_3$(μ-OPr^i)$_4$(OPr^i)$_2$(DIP)$_3$(THF)[78] (shown in Figure 18b) represent mixed alkoxides.

When polydentate ligands are employed, several additional mixed alkoxide species are produced. A series of bridging alkoxide ligands led to the isolation and structural characterization of Ce$_2$[(μ-(O(C$_6$H$_4$)O)](TBM)$_6$,[89] [Sm(DBP-4-Me)$_2$(μ-O-bi-fluorenone)(OEt$_2$)]$_2$,[42,122] [Sm(μ-Quin)(DBP-4-Me)$_2$]$_2$,[91] and
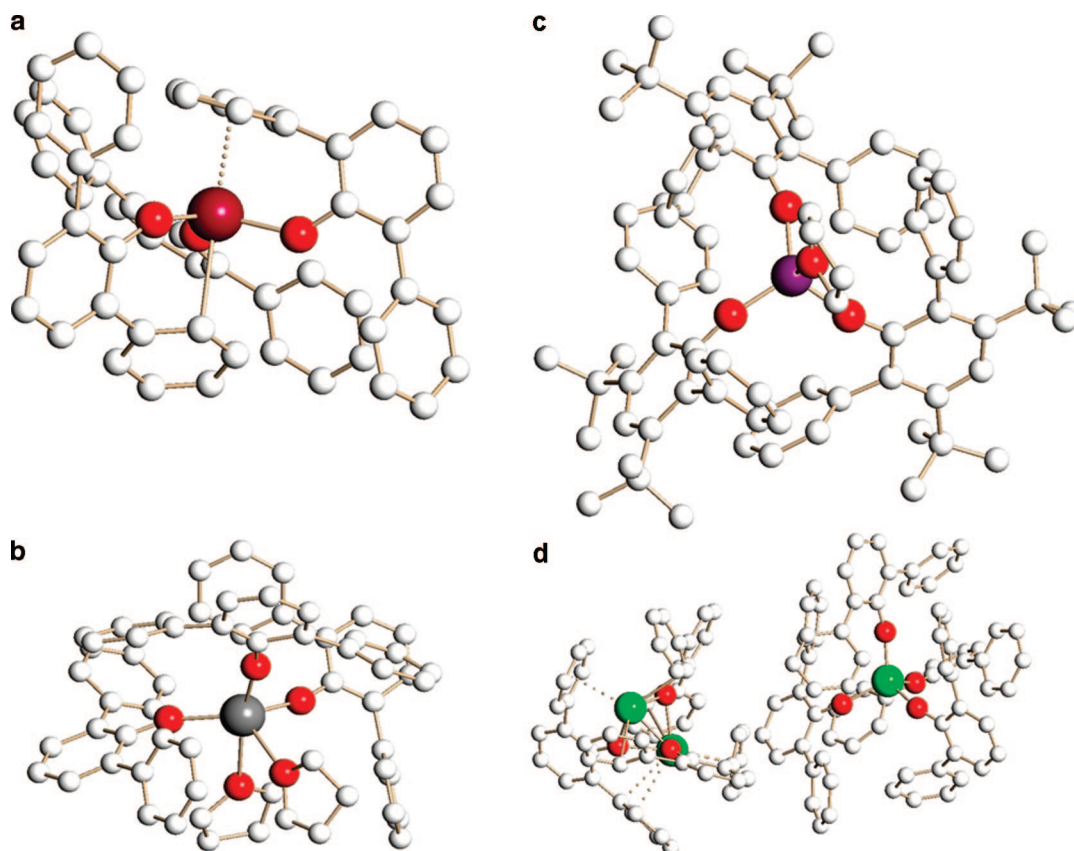
Figure 16. Structure plot of Lu(DPP-η^6-Ph-2)(η^2,σ^3 DPP)$_2$). (b) Structure plot of La(DPP)$_3$(THF)$_2$. (c) Structure plot of Sc(DPP(Bu^t)$_2$-3,5)$_3$(THF). (d) Structure plot of [Yb$_2$(μ-η^6-DPP)$_3$][Yb(DPP)$_4$].
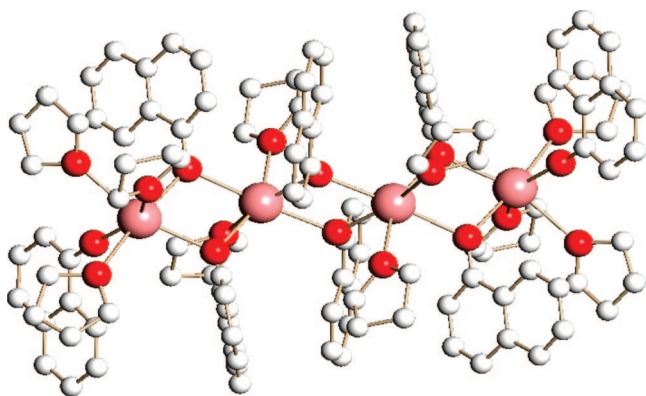
Figure 17. Structure plot of [(μ-ONap)(THF)$_2$Eu(μ-ONap)$_2$Eu(ONap)(THF)$_3$]$_2$.

[Ce(OPr^i)$_3$(μ-MAEA)]$_2$[88] where MAEA = dimethylamino-ethylmethylaminoethoxy N,N′,O,O), Eu$_3$(DIP)$_3$(CARB)$_4$[123] where CARB = carbitoxide, [Ln(μ-OPr^i)(B4MP)(THF)$_2$]$_2$[90] where Ln = Nd,[90] Yb[90] and B4MP = 2,2′-methylene-bis(6-t-butyl-4methylphenolato-O,O′). A silylamine based ligand system bridges metal centers in (TBM)$_3$Tm(μ-NH$_2$Si(CH$_3$)$_2$(CH$_2$)$_2$Si(CH$_3$)$_2$NH$_2$)Tm(TBM)$_3$ (Figure 19),[124] and Ln(DBP-4-Me)$_2$(O-fluorenone)(THF)$_2$ Ln = Sm,[42,122] Yb,[122] and (μ-bifluorenonyl)(Sm(DBP-4-Me)$_2$)$_2$.[42,122]

5. Siloxides Derivatives

Another group of ligands of interest are the silicon based alcohol derivatives, coined siloxides (OSiR$_3$). These ligands are of practical interest due to the potential incorporation of Si into a target solid state material; however, this has been

of limited utility due to the preferential production of oxides versus silicates.[125,126]

5.1. Homoleptic Siloxide Derivatives

Below, the homoleptic siloxide derivatives that are available in the literature are discussed. It is of note that there have been no mixed siloxide alkoxide complexes reported.[9]

5.1.1. (Triphenyl)siloxide Derivatives

The majority of Ln(OSiR$_3$)$_x$ species characterized utilize the sterically encumbered (triphenyl)siloxide (TPS) ligand. Most complexes containing this ligand require the use of a strong Lewis base to solubilize the resultant complex. This provides derivatives that include Ln(TPS)$_3$(solv)$_x$ where Ln(solv)$_x$ = Y(THF)$_3$,[127–129] La(THF)$_3$,[130] Ce(THF)$_3$,[131] Pr(THF)$_3$,[131] Sm(THF)$_3$,[105] Dy(THF)$_3$,[68] Dy(py)$_3$,[68] Er(THF)$_3$ (Figure 20a),[95] and Er(py)$_3$.[95] With THF, these species all adopt a standard pseudo-octahedral geometry as shown in Figure 20b. Bidentate solvents can also serve to reduce the coordination number as illustrated by Ce(TPS)$_3$(DME).[132] In the absence of a base, a dinuclear species was isolated in the case of [Ln(μ-TPS)(TPS)$_2$]$_2$ where Ln = Y (Figure 20b),[133] Er,[95] Ce,[72] and Dy.[68]

5.1.2. tert-Butyl Substituted Siloxide Derivatives

In the absence of potential donor solvents, the use of dimethyl *tert*-butyl siloxide (DMBS), a less sterically demanding ligand than the TPS ligand, yields the dimeric species, [Y(μ-DMBS)(DMBS)$_2$]$_2$ (Figure 21).[130] In addition,
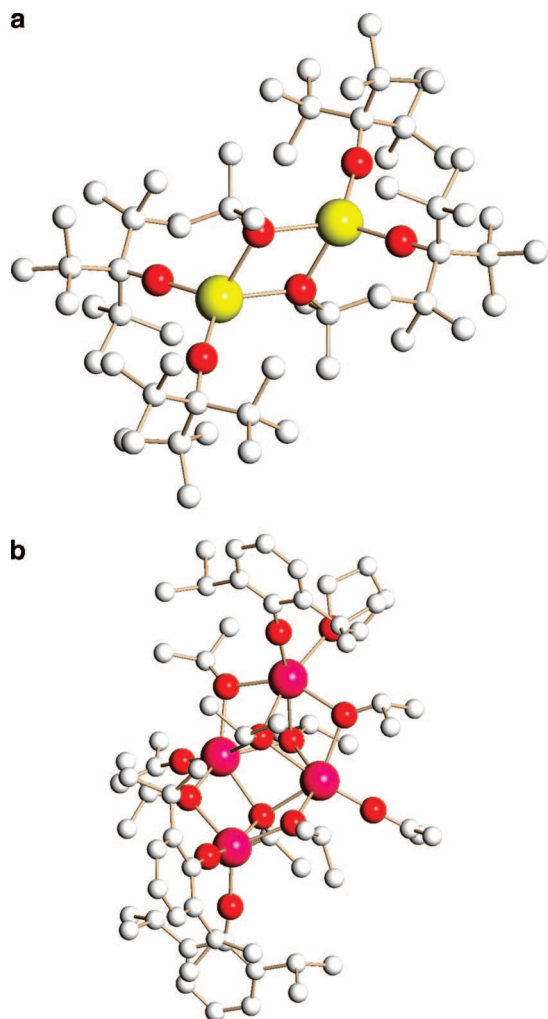
a

b

Figure 18. (a) Structure plot of [Ce (μ-OBu^t) (TBM)$_2$]$_2$. (b) Structure plot of Sm$_4$(μ_3-OPr^i)$_3$(μ-OPr^i)$_4$(OPr^i)$_2$(DIP)$_3$(THF).
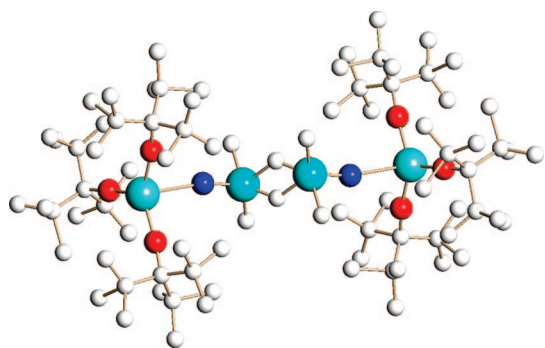
Figure 19. Structure plot of (TBM)$_3$Tm(μ-NH$_2$Si(CH$_3$)$_2$-(CH$_2$)$_2$Si(CH$_3$)$_2$NH$_2$)Tm(TBM)$_3$.

a

b

Figure 20. (a) Structure plot of Er(TPS)$_3$(THF)$_3$. (b) Structure plot of [Y(μ-TPS)(TPS)$_2$]$_2$.
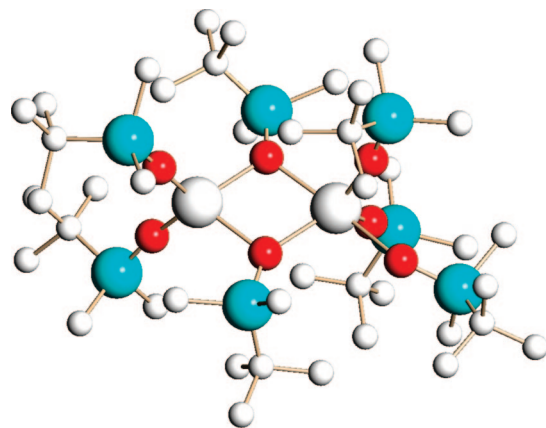
Figure 21. Structure plot of [Y(μ-DMBS)(DMBS)$_2$]$_2$.

a solvent free structure was reported for the di-*tert*-butyl siloxide [Nd(μ-OSi(H)(Bu^t)$_2$)(OSi(H)(Bu^t)$_2$)$_2$]$_2$.[134] Both compounds contain a dinuclear edge-shared tetrahedral coordination environment. The dinuclear arrangement is maintained even if the charge is reduced, as in [Yb(DMBS)$_2$(DME)]$_2$.[32]

5.1.3. (Trimethyl)siloxide Derivatives

Surprisingly only one trimethylsiloxide (TMS) derivative has been reported, Nd$_4$(μ_3-TMS)$_3$(μ-TMS)$_4$(TMS)$_5$.[135] This compound adopts an arrangement of Nd cation as shown in Figure 22 with both Oh and TBP coordination spheres.
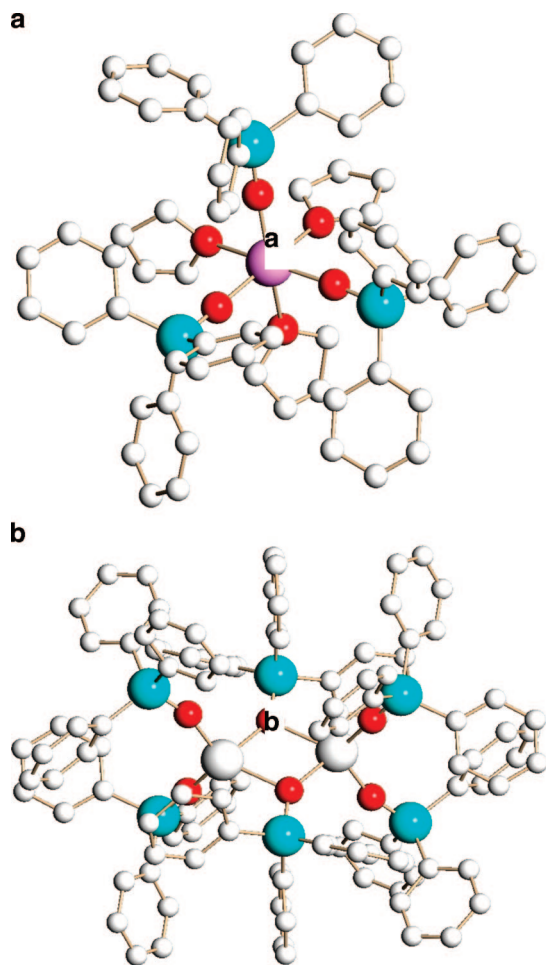
5.1.4. Alternative Siloxide Derivatives

Other silyl derivatives have been reported as two (solvated) species supported by the trimethylsilylsiloxide (SST) ligand structurally characterized as monomers: Gd(SST)$_3$(solv)$_2$ where solv = diazabicyclooctane[136] or THF[136] shown in Figure 23.

Other polyfunctional ligands with increasing steric bulk for example di-*tert*-butylpropylamylsiloxide ligand have been employed. These polyfunctional silyl ligands provide the monomeric complexes Y(OSPA)$_3$[33] and Yb(OSPA)$_3$(H-OSPA) where OSPA = OSiC(Bu$^t_2$)(CH$_2$)$_3$NMe$_2$[33] respec-

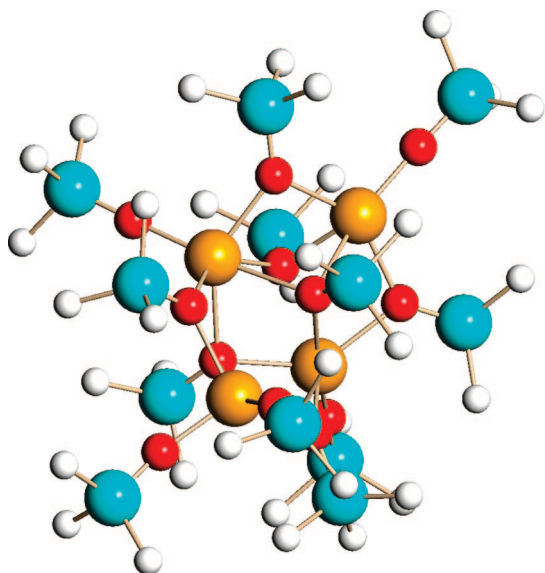**Figure 22.** Structure plot of $Nd_4(\mu_3\text{-}TMS)_3(\text{-}\mu TMS)_4(TMS)_5$ (tol not shown).
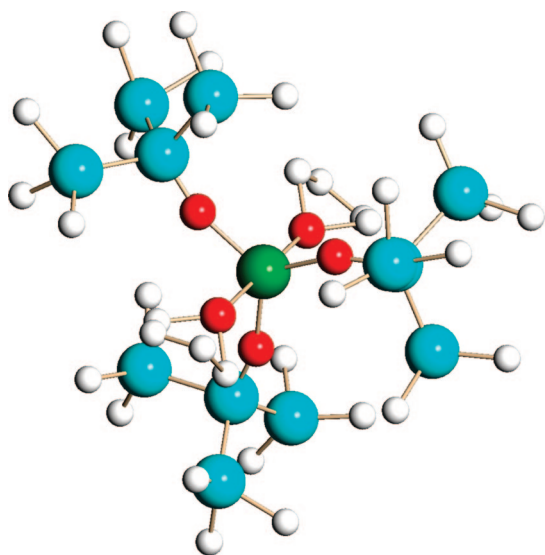
Figure 23. Structure plot of $Gd(SST)_3(THF)_2$.

a

b

Figure 24. (a) Structure plot of $Y(OSPA)_3$. (b) Structure plot of $Yb(OSPA)_3(H\text{-}OSPA)$.
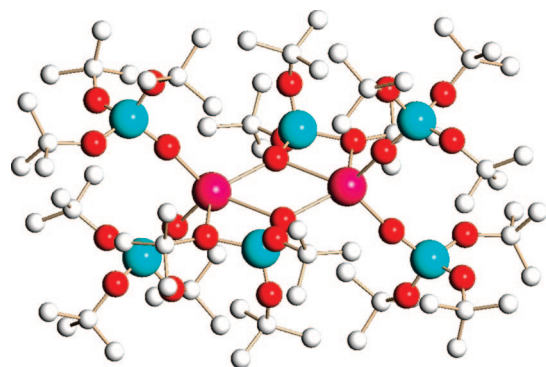
Figure 25. Structure plot of $[Sm(\mu\text{-}TBOS) (TBOS)_2]_2$.

tively shown in Figure 24, a and b. Depending on metal−ligand combination, either monodentate or bidentate binding modes have been noted.

More complex siloxide systems are accessible such as the *tert*-butoxide siloxide ligand $(OSi(OBu^t)_3 = TBOS)$ which yields the dimeric species $[Sm(\mu\text{-}TBOS)(TBOS)_2]_2$[137] (Figure 25). Other complex silicon based ligands such as the silsesquioxanes can further reduce the nuclearity to a monomeric species as was noted for $Ce(SSQ)_3(py)_3 \cdot 2H_2O$.[138]

6. Summary and Outlook

This review presented an overview of the progress made in structurally characterized lanthanide alkoxides $(Ln(OR)_x$ where $x = 2$ or 3) over the past couple of decades. (i) The large cation size combined with the electronic influence of the d and f orbitals and (ii) the steric bulk of the uninegative alkoxide ligands lead to problems in rationalizing structures a priori. This often tends toward incorrect formulations as noted for some commercially available $Ln(OR)_x$. Therefore, this review focused only on the structurally characterized
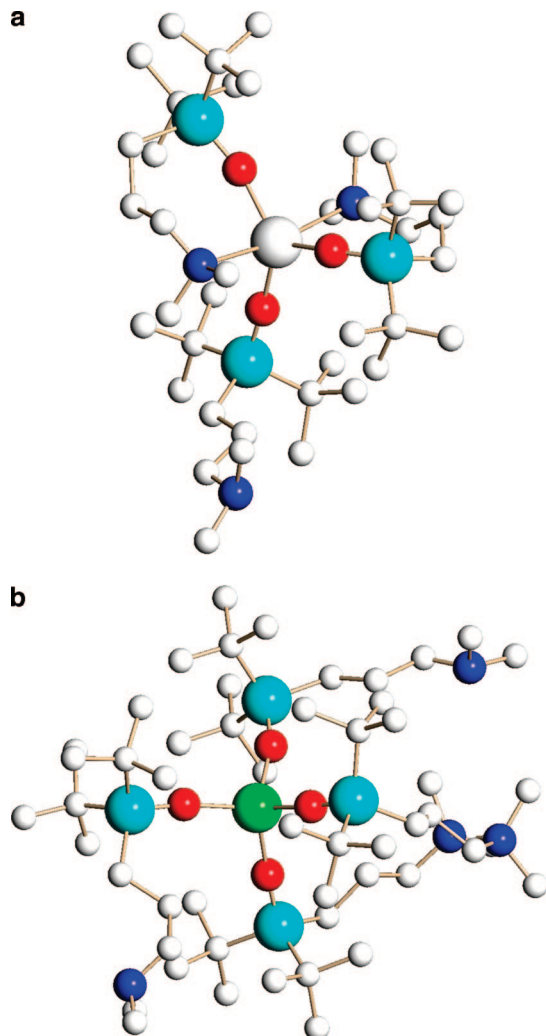
$Ln(OR)_x$ available in the literature and organized them in terms of ligand steric bulk in the text and by metal in Table 2. Due to the narrow focus of this review, we have had to omit a number of important series of heteroleptic species that require the same type of tabulation. However, it is obvious from the discussions presented here, that a large number of homoleptic alkoxide compounds have been structurally characterized and are readily available for exploitation in a variety of systems.

From crystallographic data, there are a number of trends that can be observed. As noted for transition metals, increased

steric bulk favors smaller nuclearities; however, unlike transition metals, these Ln(OR)$_x$ tend to favor a wider range of coordination numbers ranging from 6−9 and higher. Nuclearities also vary from monomer to decamers based on the steric bulk and denticity the ligand or the presence of Lewis basic solvents. The metrical data of these compounds is controlled by the ligand characteristics, solvents bound to the metal, and the size and charge of the cation.

The rational synthesis of Ln(OR)$_x$ continues to develop for a wide range of alkoxide ligands, which will allow for tailored precursors to be developed. This coupled with the controlled change in the size of the cations means fine-tuning of these the precursors will be achievable at a level that is far beyond that of the transition metal alkoxide. As more and more structurally identified species are synthesized, it is expected that Ln(OR)$_x$ will grow in utility, forming the vital components of the synthetic chemist's arsenal. However, as exists for transition metal alkoxides, understanding how to routinely synthesize controlled heterometallic lanthanide species, as well as understanding oxo, halide, and other anion inclusion compounds are a critical need for this field of study. The variability of the properties (i.e., solubility, volatility, and decomposition temperatures) of these compounds allow for a wide range of processing conditions (i.e., sol−gel, metalorganic vapor deposition, nanoparticle synthesis) for a large number of applications (i.e., materials, catalysis, bioimaging, etc).

In view of the tremendous progress made in the past couple of years in characterizing these unique molecules, the production of controlled, complex Ln(OR)$_x$ is expected, along with their introduction into mainstream applications. However, for this to occur, an understanding of how these compounds behave under different processing conditions is necessary. With this knowledge, tailor-made Ln(OR)$_x$ precursors will allow for amazing control over the systems where they are employed.

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