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Recent Advances in Alkoxo and Aryloxo Chemistry of Scandium, Yttrium, and Lanthanoids

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Contents

1. Introduction

The knowledge about chemical, structural,[1–26] and applied[27–37] aspects of alkoxo and aryloxo chemistry of lanthanoids, yttrium, and scandium (represented by the general symbol Ln) has progressed quickly during the last decade. An account of the earlier (up to 1977) developments of lanthanoid alkoxide chemistry has appeared in a review[2] dealing with Ln–O–C derivatives, and a reference to lanthanoid phenoxides was made in another article by Malhotra and Martin[3] in 1982, but a unified review dealing both alkoxo and aryloxo chemistry of lanthanoids is still unavailable, although a similar account[38] of derivatives of 5f elements has appeared recently. The purpose of this article is to present a brief account of the developments in the chemistry of alkoxides and aryl oxides of lanthanoids during the last decade or so up to 1990, limiting the work already included in earlier reviews[2,3] to the briefest reference possible for coherence.

2. The Alkoxo and Aryloxo Ligands

Although behaving generally as one-electron ligands ($^{\bullet}$OR)/two-electron donors (:OR$^-$) with notable flexibility, these can function sometimes in a "noninnocent" manner, showing more than one electronic and structural configuration (Figure 1) with a variable (terminal, μ_2- or μ_3-bridging) behavior as confirmed by X-ray crystallography, a technique which has to be pursued more vigorously for definitive information on these labile complexes.

In addition to π-bonding[43] in the complexes shown in Figure 1, the alternative explanation of a "soft energy surface" in the lanthanoid cation/alkoxide anion interaction could not be ruled out.

In view of their oxophilic nature, aryloxo ligands prefer to be O bonded (Figure 2a) with the lanthanoids,[7,8] resembling in this respect the actinoids,[38] although η^5-bonding with another phenyl ring intramolecularly in the case of ytterbium[44] and intermolecularly in uranium(III)[45] has been observed recently. There appear to be no examples of Ln with only η^5-bonded (Figure 2b) type of complexes observed in the case of transition metals.[46–51]

3. Homometallic Alkoxo and Aryloxo Derivatives

3.1. Preparative Methods

As described briefly below, almost all the synthetic routes used for alkoxides and aryl oxides for metals have been attempted for title compounds also.

a. Reactions of Metals with Alcohols and Phenols

In addition to earlier reports[1] based on chemical analyses and some spectroscopic properties on the synthesis of lanthanoid alkoxides by the route illustrated in eq 1, it has been recently utilized for the

$$\mathrm{Ln} + 3i\text{-PrOH} \xrightarrow[\text{heat}]{\mathrm{HgCl_2(catalyst)}} \underset{\mathrm{I}}{\text{“Ln(O-}i\text{-Pr)}_3\text{”}} + \tfrac{3}{2}\mathrm{H_2}\uparrow$$

$$\mathrm{Ln = Y,\ Dy,\ and\ Yb} \qquad (1)$$

following syntheses, out of which the product IIb has been characterized as a decamer by X-ray structural studies:

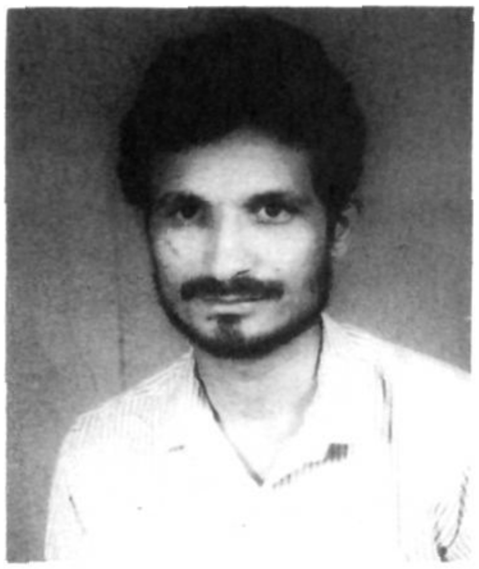
$$4\mathrm{Nd} + 16i\text{-PrOH} \rightarrow \underset{\mathrm{IIa}}{[\mathrm{Nd(O\text{-}}i\text{-Pr)}_3]_4\cdot 4i\text{-PrOH}} + 6\mathrm{H_2}\uparrow \qquad (2)^{52}$$

$$10\mathrm{Y} + 30\mathrm{HOCH_2CH_2OCH_3} \rightarrow \underset{\mathrm{IIb}}{[\mathrm{Y(OCH_2CH_2OCH_3)_3}]_{10}} + 15\mathrm{H_2}\uparrow \qquad (3)^{53}$$

By contrast, an interesting oxide isopropoxide, $Y_5O(O\text{-}i\text{-}Pr)_{13}$ (III), has been isolated and characterized crystallographically.[22] This is a rather intriguing report by highly reliable investigators, although the authors themselves report[33] that $Y\{Al(O\text{-}i\text{-}Pr)_4\}_3$ can be distilled out in 70% yield from the reaction mixture after addition of 3 mol of $Al(O\text{-}i\text{-}Pr)_3$, whereas III was found not to react with $Al(O\text{-}i\text{-}Pr)_3$. Synthesis (Ln = Sc, Y, and Yb) and crystallographic characterization (Ln = Yb) of a few other oxide alkoxides, $Ln_5O(O\text{-}i\text{-}Pr)_{13}$, have been more recently reported.[54]

R. C. Mehrotra (emeritus professor) D.Phil.(Alld.), Ph.D., D.Sc. (London), was born in Kanpur, U.P. (India) in 1922 and has been working in the field of alkoxide chemistry since 1950. He was awarded a Ph.D. degree from London University in 1952 for a thesis entitled "Alkoxides of Silicon, Titanium, Zirconium and Hafnium" in which he established for the first time the influence of steric factors in the chemistry of alkoxides. Among his other notable contributions are the "aging" phenomenon of aluminum alkoxides, the versatility of metal alkoxides as synthons for a variety of metal derivatives (e.g., aluminum tricarboxylates, and anhydrous lanthanoid β-diketonates, which cannot be synthesized, so far, by any other route), and the synthesis of a large number of heteropolymetal alkoxides. His contributions have been recognized by invitations to deliver special lectures on different aspects of alkoxide chemistry at the International Conferences on Coordination Chemistry at Sao Paulo (1977), Toulouse (1980), and Athens (1986), followed by International Conferences on "Sol-Gel Chemistry" at Kyoto (1987, 1990), Reno (1988), and Rio de Janerio (1989). He is a coauthor of three books on M–O–C derivatives (alkoxides, β-diketonates and Carboxylates) which currently are the only reference books available on these topics. His recent book on Organometallic Chemistry is coauthored with Dr. A. Singh.

Dr. Anirudh Singh is Associate Professor of Chemistry at the University of Rajasthan, Jaipur. He was born in Bahraich, U.P. (India) in 1938. He obtained a M.Sc. degree in inorganic chemistry from the University of Lucknow and his Ph.D. from the University of Rajasthan, Jaipur while under the supervision of R. C. Mehrotra for a thesis entitled "Oxime Derivatives of Tri- and Tetravalent Elements". His interests in metalloorganic chemistry of f-elements were largely stimulated during three years (1979–82) of postdoctoral research with M. F. Lappert, FRS, at the University of Sussex, Brighton, U.K. His contributions in the field of sterically demanding silylated cyclopentadienyls and aryl oxides of lanthanoids and actinoids carried out in collaboration with Professor Lappert at Sussex are well recognized as outstanding achievements in a rather difficult field. Since 1968, he has been working actively in the field of organometallic/alkoxide/aryl oxide chemistry for a number of metals. For the past decade, he has been concentrating on homoleptic as well as heteroleptic heterometal alkoxides and aryl oxides. He is the author of approximately 75 research papers on various aspects of inorganic and organometallic chemistry. His book on Organometallic Chemistry coauthored with Prof. R. C. Mehrotra (Wiley Eastern: New Delhi, India, 1991) is a unique effort in presenting the subject in a unified style.



Born in 1968, Upendra M. Tripathi, received his M.Sc. degree in inorganic chemistry from the University of Rajasthan, Jaipur (India) in 1988. Since then he has been working for his Ph.D. degree under the supervision of R. C. Mehrotra and A. Singh in the Department of Chemistry at Jaipur. His thesis research involves the synthesis, characterization, and structural studies on Sc, Y, and lanthanoid alkoxo complexes.

In view of the reported[55] formation of some olefins in reaction 1, isolation of an oxide–alkoxide in this synthetic route could be ascribed to a side condensation of the tris product. The preferential crystallization of $\mathrm{Ln_5O(O\text{-}}i\text{-}\mathrm{Pr)_{13}}$ may then be a factor particularly suiting some systems only, whereas the tris products IIa and IIb have been reported in the similar reactions 2 and 3. Obviously more quantitative work is needed to explore the extent of side reactions in the interactions of lanthanoids with different alcohols under varying conditions.

The following synthesis[56] of Yb(II) aryl oxide (IV) by the interaction of ytterbium powder with $\mathrm{TlOC_6H_2\text{-}}t\text{-}\mathrm{Bu_2\text{-}2,6\text{-}Me\text{-}4}$ in tetrahydrofuran opens up a new route for aryl oxides/alkoxides of Eu(II) and Sm(II) also:

$$\mathrm{Yb} + 2\mathrm{TlOC_6H_2\text{-}}t\text{-}\mathrm{Bu_2\text{-}2,6\text{-}Me\text{-}4} \xrightarrow{\mathrm{THF}} \underset{\mathrm{IV}}{[\mathrm{Yb(OC_6H_2\text{-}}t\text{-}\mathrm{Bu_2\text{-}2,6\text{-}Me\text{-}4)_2(THF)_3}]} + 2\mathrm{Tl} \tag{4}$$

Although the use of metal atom vapors for the synthesis of metal alkoxides and phenoxides by condensation into the neat alcohol has been briefly mentioned in literature,[57] the technique does not appear to have been exploited so far for Ln metals.

Electrochemical methods[58,59] developed for many other metals (e.g., Ti, Zr, Cu, Hg, etc.) do not appear to have been pursued for Ln metals.

b. Reaction of $LnCl_3$ with Alcohols/Phenols in the Presence of Proton Acceptors

The reactions of $\mathrm{LnCl_3}$ with alcohols result in the formation of tris adducts which can often be crystallized out in an analytically pure state from the alcohols, e.g.

$$\mathrm{LnCl_3} + 3i\text{-}\mathrm{PrOH} \rightarrow \mathrm{LnCl_3}\cdot 3i\text{-}\mathrm{PrOH} \tag{5}$$

Attempts to prepare "$\mathrm{Ln(O\text{-}}i\text{-}\mathrm{Pr)_3}$" by passing anhydrous $\mathrm{NH_3}$ in the above solution were unsuccessful due to side reactions[55] of the type

$$\mathrm{Ln(OR)_3} \rightleftharpoons \mathrm{Ln(OR)_2}^+ + \mathrm{RO}^- \tag{6}$$

$$\mathrm{Ln(OR)_2}^+ + \mathrm{Cl}^- \rightleftharpoons \mathrm{Ln(OR)_2Cl} \tag{7}$$

The ammonia method, however, has been successfully employed in the preparation[60] of hexafluoroisoprop-

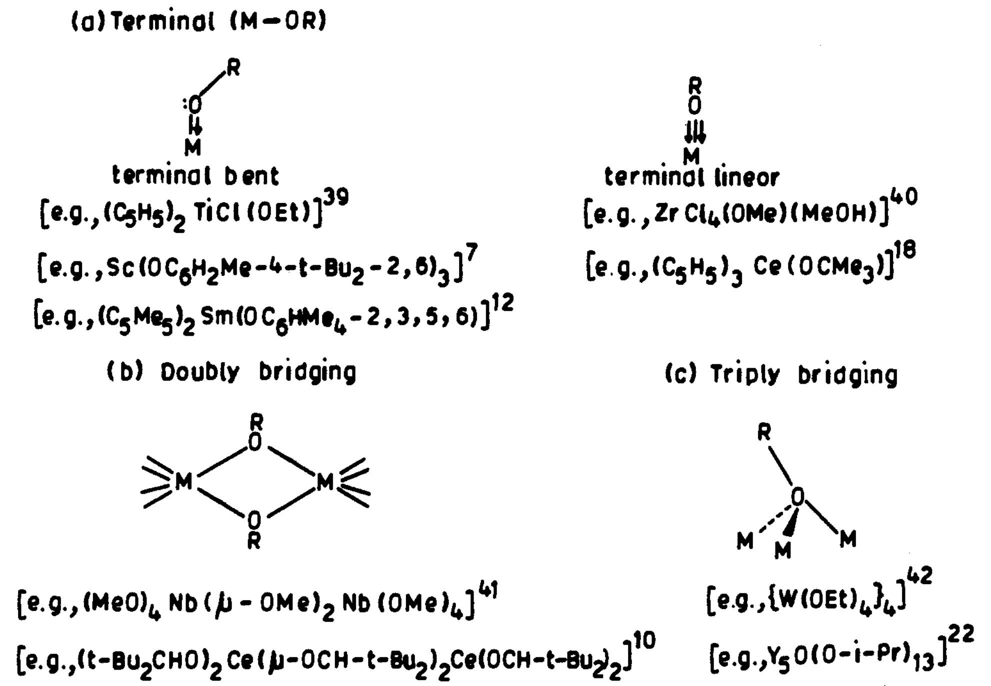


Figure 1. Modes of coordination of the alkoxo (aryloxo) ligands to a transition/lanthanoid metal center.

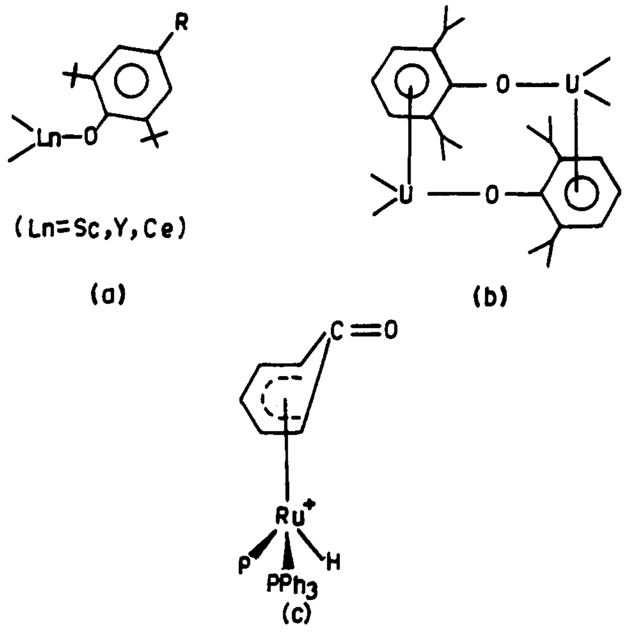


Figure 2. π or η^6-bonded aryloxo ligand.

oxide diammoniates, $[Ln\{OCH(CF_3)_2\}_3(NH_3)_2]$, as well as of $Ce(O\text{-}i\text{-}Pr)_4$ by a reaction[61,62] of the following type:

$$[(C_5H_5NH)_2]^+[CeCl_6]^- + 4i\text{-}PrOH + 6NH_3 \rightarrow [Ce(O\text{-}i\text{-}Pr)_4] + 2C_5H_5N + 6NH_4Cl\downarrow \quad (8)$$

By contrast, attempts to prepare $Y(O\text{-}i\text{-}Pr)_3$ by the reaction of YCl_3 with 3 mol of $LiO\text{-}i\text{-}Pr$ in THF was reported[55] to yield a product contaminated with LiCl.

However, the corresponding reactions of $NaO\text{-}i\text{-}Pr$/$KO\text{-}i\text{-}Pr$ with $LnCl_3{\cdot}3i\text{-}PrOH$ (prepurified by crystallization from an i-PrOH solution of $LnCl_3$, which was itself prepared in a pure (oxychloride free) state by heating a mixture of $LnCl_3{\cdot}xH_2O$ and NH_4Cl in a current of dry HCl/Cl_2) have been found to result[63-66] in a quantitative yields of "$Ln(O\text{-}i\text{-}Pr)_3$" by the simple metathetic reaction

$$LnCl_3{\cdot}3i\text{-}PrOH + 3MO\text{-}i\text{-}Pr \rightarrow \text{“}Ln(O\text{-}i\text{-}Pr)_3\text{”} + 3i\text{-}PrOH + 3MCl\downarrow \quad (9)$$

The characterization of a large number of tris(isopropoxides) and of even a larger number of other alkoxides and silyl oxides,[2] synthesized by alcoholysis and transesterification reactions described in the next section, has been carried out on the basis of chemical analyses and spectroscopic data, without any crystal structures (in spite of repeated attempts).

In fact, the only crystal structure (Figure 14) available[6] in the literature is that of a crystalline product V from the following reaction:

$$6NdCl_3 + 18NaO\text{-}i\text{-}Pr \rightarrow \underset{\text{V}}{Nd_6(O\text{-}i\text{-}Pr)_{17}Cl} + NaO\text{-}i\text{-}Pr + 17NaCl\downarrow \quad (10)$$

The qualitative observation represented by a number of workers[63-66] in the field were that the relative success of the method depends on (i) the method of preparation of $LnCl_3$, (ii) a more soluble crystalline tris adduct, $LnCl_3{\cdot}3i\text{-}PrOH$, (iii) avoiding the presence of cluster-type lanthanoid chloride species in the starting materials by the above two steps, and (iv) the greater insolubility and crystallinity of KCl resulting in its facile removal (compared to LiCl/NaCl).

In view of the above conflicting report[6] on the formation of V, the reaction has been recently repeated in our laboratories with the following results:

$$NdCl_3{\cdot}3i\text{-}PrOH + 3KO\text{-}i\text{-}Pr \xrightarrow[i\text{-}PrOH]{\text{benzene}} Nd(O\text{-}i\text{-}Pr)_3 + 3KCl\downarrow \quad (11)$$

$$6NdCl_3{\cdot}3i\text{-}PrOH + 17KO\text{-}i\text{-}Pr \xrightarrow[i\text{-}PrOH]{\text{benzene}} \text{V} + 17KCl\downarrow \quad (12)$$

The product V could be recrystallized from toluene, yielding blue, needle-shaped crystals as reported earlier.[6] Although more quantitative work is required, the purity of the tris product appears to be governed as

TABLE I. Alkoxo and Aryloxo Derivatives of Scandium Yttrium and Lanthanoids Synthesized since 1978

compounds	comments
A. Homoleptic Complexes	
[Ln(OR)$_3$]	
Ln = Y;[70] R = CMe$_2$-*i*-Pr, CMeEt-*i*-Pr, CEt$_3$	NMR (variable temperature)
Ln = La;[70] R = CMe$_2$-*i*-Pr, CMeEt-*i*-Pr	NMR (variable temperature)
Ln = Ce[10] (XXVII); R = *t*-Bu$_3$C	^{1}H NMR
[Ln$_3$(OR)$_9$(ROH)$_2$][70]	
Ln = Y; R = *t*-Bu, *t*-Am	NMR (variable temperature)
Ln = La; R = *t*-Bu	X-ray (Ln = La, R = *t*-Bu)
[{Y(OC$_2$H$_4$OMe)$_3$}$_{10}$][53] (IIb)	IR, NMR (^{1}H, ^{13}C), X-ray
[Ln(OC$_6$H$_2$-*t*-Bu$_2$-2,6-X-4)$_3$]	
Ln = Sc (IXa),[7] Y (IXb); X = H	MW, IR, ^{1}H NMR, X-ray (Ln = Y)
Ln = Sc (IXd), Y(IXe); La, Pr, Nd, Dy, Ho, Er, Yb, X = Me[7]	MW, MS, NMR (^{1}H, ^{13}C) X-ray (Ln = Sc, Figure 3)
Ln = Ce;[9] X = H (XIIIa), Me, *t*-Bu	MW, IR, ^{1}H NMR, X-ray (X = H, Figure 8)
[Ln(OC$_6$H$_3$Ph$_2$-2,6)$_3$][44] Ln = Nd, Sm, Er, Yb, Lu	IR, X-ray (Ln = Yb)
[Y(OC$_6$H$_3$Me$_2$-2,6)$_3$(THF)$_3$][20] (X)	IR, NMR (^{1}H, ^{13}C), X-ray (Figure 4)
[{Y(OC$_6$H$_3$Me$_2$-2,6)(THF)}$_2$][20] (XI)	IR, NMR (^{1}H, ^{13}C) X-ray (Figure 5)
[Ln(OC-*t*-Bu$_2$CH$_2$PMe$_2$)$_3$][67] (XII)	X-ray (Ln = Y)
[La$_3$(O-*t*-Bu)$_9$(THF)$_2$][17] (VII)	IR, NMR (^{1}H, ^{13}C)
[Ce(OC$_8$H$_{17}$)$_4$][77]	MS, ^{1}H NMR
[{Ce(O-*i*-Pr)$_4$·*i*-PrOH}$_2$][24] (XV)	IR, NMR (^{1}H, ^{13}C), X-ray (Figure 6)
[Ce(OC$_6$H$_3$-*t*-Bu$_2$-2,6)$_3$(*t*-BuNC)][9]	IR, ^{1}H NMR, X-ray
[{Ce(OCH-*t*-Bu$_2$)$_3$}$_2$][10] (XXVIII)	^{1}H NMR, X-ray (Figure 7)
[Ce(O-*t*-Bu)$_4$(THF)$_2$][19]	IR, NMR (^{1}H, ^{13}C)
[Yb(OC$_6$H$_2$-*t*-Bu$_2$-2,6-Me-4)$_2$L$_x$][56]	
L = THF, *x* = 2 (XIVa), 3(IV)	NMR (^{1}H, ^{13}C, ^{171}Yb), X-ray (IV, Figure 10; XIVa, Figure 9)
L = OEt$_2$, *x* = 2 (XIVb)	
[Yb(OC$_6$H$_3$Ph$_2$-2,6)$_3$(THF)$_2$](THF)[44]	X-ray
B. Heteroleptic Neutral Complexes	
[Ln$_5$O(O-*i*-Pr)$_{13}$]	
Ln = Y[22] (III)	NMR (^{1}H, ^{13}C, ^{89}Y), X-ray
Ln = Sc, Y, Yb[54]	X-ray (Ln = Yb)
[[Y$_7$(O-*t*-Bu)$_{14}$Cl$_5$O(THF)$_2$]$_2$][15]	IR, NMR (^{1}H, ^{13}C), X-ray
[Y$_3$(O-*t*-Bu)$_7$Cl$_2$(THF)$_2$][15] (VIII)	IR, NMR (^{1}H, ^{13}C), X-ray (Figure 12)
[Y$_3$(O-*t*-Bu)$_8$Cl(THF)$_2$][17] (VI)	IR, NMR (^{1}H, ^{13}C), X-ray (Figure 11)
[Y$_3$(OC$_2$H$_4$OMe)$_5$(acac)$_4$][23] (XXV)	MS, IR, NMR (^{1}H, ^{13}C), X-ray
[(C$_5$H$_5$)$_5$Y$_5$O(OMe)$_8$][13]	IR, ^{1}H, NMR, X-ray
[{(C$_5$H$_5$)$_2$Ln(OCH═CH$_2$)}$_2$][14]	
Ln = Y, Yb, Lu	IR, ^{1}H NMR
[{(C$_5$H$_4$Me)$_2$Y(OCH═CH$_2$)}$_2$][14]	IR, ^{1}H NMR, X-ray
[{(C$_5$Me$_5$)Ln(O-*t*-Bu)$_2$}$_2$][72]	
Ln = La, Ce	IR, NMR (^{1}H, ^{13}C), X-ray (Ln = Ce)
[(C$_5$H$_5$)$_2$Ce(O-*t*-Bu)$_2$][18]	IR, NMR (^{1}H, ^{13}C)
[(C$_5$H$_5$)$_3$Ce(O-*t*-Bu)][18] (XXII)	IR, NMR (^{1}H, ^{13}C), X-ray (Figure 13)
[(C$_5$Me$_5$)$_2$Ce(OC$_6$H$_3$-*t*-Bu$_2$-2,6)][72]	IR, NMR (^{1}H, ^{13}C)
[(C$_5$H$_5$)$_3$Ce(O-*i*-Pr)][103]	NMR (^{1}H, ^{13}C), cyclic voltammetry
[Ce(O-*t*-Bu)(NO$_3$)$_3$(THF)$_2$][19]	IR, NMR (^{1}H, ^{13}C)
[Ce(O-*t*-Bu)(NO$_3$)$_3$(*t*-BuOH)$_2$][19]	IR, NMR (^{1}H, ^{13}C)
[Ce(O-*t*-Bu)$_2$(NO$_3$)$_2$(THF)$_2$][19]	IR, NMR (^{1}H, ^{13}C)
[Ce(O-*t*-Bu)$_2$(NO$_3$)$_2$(*t*-BuOH)$_2$][19]	IR, NMR (^{1}H, ^{13}C), X-ray
[Ce(O-*t*-Bu)$_3$(NO$_3$)(THF)$_2$][19]	IR, NMR (^{1}H, ^{13}C)
[Ce$_3$O(O-*t*-Bu)$_{10}$][19]	IR, NMR (^{1}H, ^{13}C)
[Nd$_6$(O-*i*-Pr)$_{17}$Cl][6] (V)	X-ray (Figure 14)
[(Ce$_5$Me$_5$)$_2$Sm(OC$_6$HMe$_4$-2,3,5,6)][12]	IR, ^{1}H NMR, X-ray
C. Heteroleptic Cationic Complexes	
[Y$_3$(O-*t*-Bu)$_7$Cl(THF)$_3$][BPh$_4$][21] (XXIII)	IR, ^{1}H NMR, X-ray (Figure 15)
[Y$_2$(O-*t*-Bu)$_4$Cl(THF)$_4$][BPh$_4$][21] (XXIV)	IR, ^{1}H NMR, X-ray (Figure 16)
[Y(O-*t*-Bu)Cl(THF)$_5$][BPh$_4$][21] (XXV)	IR, ^{1}H NMR, X-ray (Figure 17)
D. Heterometal Alkoxo and Aryloxo Complexes	
[Ln{Zr(O-*i*-Pr)$_5$}$_3$]	
Ln = La,[121] Sm[122]	IR, NMR (^{1}H, ^{13}C)
[Ln{Zr$_2$(O-*i*-Pr)$_9$}$_x$Cl$_{3-x}$]	
Ln = La,[123] Pr, Nd,[121] Sm,[122] *x* = 1, 2, or 3	IR, NMR (^{1}H, ^{13}C)
Ln{Al(O-*i*-Pr)$_4$}$_2$Cl	
Ln = Y,[121] Sm[122]	IR, NMR (^{1}H, ^{13}C)
[LnCl$_{2-x}$(OC$_6$H$_2$-*t*-Bu$_2$-2,6-Me-4)$_x$Cl$_2$Li(THF)$_2$][125]	
Ln = Y; *x* = 2	NMR (^{1}H, ^{13}C)
Ln = Y, La, Er; *x* = 1	
[LiYbCl(OC$_6$H$_2$-*t*-Bu$_2$-2,6-Me-4)$_3$][7]	NMR (^{1}H, ^{13}C)
[La$_2$Na$_3$(OR)$_9$(THF)$_5$][109] (XXXII), R = *p*-tolyl	X-ray (Figure 19)
[Na$_2$Ce(O-*t*-Bu)$_6$(DME)$_2$][19] (XXX)	X-ray
[NaCe$_2$(O-*t*-Bu)$_9$][19] (XXIX)	X-ray (Figure 18)
[Na$_2$Gd$_4$O(O-*t*-Bu)$_{12}$][124]	X-ray

discussed earlier[63-66] by careful control of the purity of the triisopropyl alcohol adduct and use of KO-*i*-Pr resulting in the precipitation of less soluble KCl in quantitative yields.

Even more interesting products have been characterized[17] in the reactions of YCl_3 with NaO-*t*-Bu in different molar ratios.

$$3YCl_3 + 8NaO\text{-}t\text{-}Bu \xrightarrow{THF} \underset{\text{VI}}{[Y_3(O\text{-}t\text{-}Bu)_8Cl(THF)_2]} + 8NaCl\downarrow \quad (13)$$

$$3LaCl_3 + 9NaO\text{-}t\text{-}Bu \xrightarrow{THF} \underset{\text{VII}}{[La_3(O\text{-}t\text{-}Bu)_9(THF)_2]} + 9NaCl\downarrow \quad (14)$$

Yttrium(III) chloride reacts[15] with 2 equiv of NaO-*t*-Bu in tetrahydrofuran to form $[Y_3(O\text{-}t\text{-}Bu)_7Cl_2(THF)_2]$ (VIII) in 80% yield according to a reaction, which has been represented as

$$3YCl_3 + 7NaO\text{-}t\text{-}Bu \xrightarrow{THF} \underset{\text{VIII}}{[Y_3(O\text{-}t\text{-}Bu)_7Cl_2(THF)_2]} + 7NaCl\downarrow \quad (15)$$

The above yttrium complex, after being kept in toluene under nitrogen for a period of 2 weeks, is converted to $[Y_7(O\text{-}t\text{-}Bu)_{14}Cl_5O(THF)_2]_2$:

$$\text{VIII} \xrightarrow{\text{toluene}} [Y_7(O\text{-}t\text{-}Bu)_{14}Cl_5O(THF)_2]_2 + \ldots \quad (16)$$

The above change (eq 16) has been suggested as a possible mode of the manner in which alkoxides are converted into oxide alkoxide species during their use for preparation of ceramics by the sol-gel process. However, the generality of this type of change to oxide–alkoxides has to be investigated in the cases of secondary/primary alkoxy groups with lower $+I$ inductive effects.

The effect of bulkier "Ar" groups, in reducing the association of $Ln(OAr)_3$ and making oxo- and chloro-free aryloxo products, has been rather effectively demonstrated recently (eq 17) in the isolation of monomeric three coordinate (shown to be trigonal planar in the case of Sc[7] and Y[8]) aryloxides of Ln metals:

$$LnCl_3 + 3NaOAr \xrightarrow{THF} \underset{\text{IX}}{Ln(OAr)_3} + 3NaCl\downarrow \quad (17)$$

where OAr = 2,6-di-*tert*-butylphenoxide, Ln = Sc (IXa), Y (IXb), Sm (IXc); when OAr = 2,6-di-*tert*-butyl-4-methylphenoxide, Ln = Sc (IXd), Y (IXe), La, Pr, Nd, Dy, Ho, Er, Yb; and when OAr = 2,4,6-tri-*tert*-butylphenoxide; Ln = Ho, Dy, Yb, etc.

By contrast, the formation of adducts in the case of $Ln(OR)_3$ with ligands of medium steric bulk such as 2,6-dimethylphenoxide has been observed by Evans and co-workers,[20] yielding yttrium complexes $[Y(OCH_6H_3Me_2\text{-}2,6)_3(THF)_n]_x$ with enough steric flexibility to achieve six- and five-coordination, respectively, in nonbridged X and bridged XI species.

$$\begin{tikzcd}
YCl_3 + 3NaOC_6H_3Me_2\text{-}2,6 \arrow[r, "THF"] & \underset{\text{X}}{[Y(OC_6H_3Me_2\text{-}2,6)_3(THF)_3]} + 3NaCl\downarrow \arrow[d, "\text{toluene}"'] \\
 & \underset{\text{XI}}{[Y(OC_6H_3Me_2\text{-}2,6)_3(THF)]_2} \quad (18)
\end{tikzcd}$$

In this connection, it would be interesting to note that the reactions of $LnCl_3$ with $LiOC\text{-}t\text{-}Bu_2CH_2PMe_2$ has been reported[67] to be straightforward, resulting in the formation of six-coordinate species as illustrated in eq 19.

$$LnCl_3 + \tfrac{3}{2}[LiOC\text{-}t\text{-}Bu_2CH_2PMe_2]_2 \rightarrow \underset{\text{XII}}{Ln(OC\text{-}t\text{-}Bu_2CH_2PMe_2)_3} + 3LiCl\downarrow \quad (19)$$

A number of organometallic alkoxides and aryl oxides have also been prepared by the reaction of $(C_5H_5)_2LnCl$ with appropriate sodium alkoxides and aryl oxides[68,69] or lithium alkoxides:[14]

$$(C_5H_5)_2LnCl + NaOR \xrightarrow{THF} (C_5H_5)_2LnOR + NaCl\downarrow$$

$$Ln = Y, Sm, Dy, Er, Yb, Lu; \quad R = Me, t\text{-}Bu, HC{=}CH_2, Ph \quad (20)$$

$$(C_2H_4R)LnCl + LiOCH{=}CH_2 \xrightarrow{THF} (C_5H_4R)_2LnOCH{=}CH_2 + LiCl\downarrow$$

$$Ln = Y, Yb, Lu;\ R = H, CH_3 \quad (21)$$

c. Alcohol (Phenol) Interchange and Transesterification Reactions

As with other metals, the reactions of lower alkoxides (mainly isopropoxides) of Ln shown in eqs 22–24 have been reported[1,2] to yield the calculated amounts of isopropyl alcohol and the metal alkoxide/aryl oxide/silyl oxide derivative. In view of the more recent doubts about the initial product "$Ln(O\text{-}i\text{-}Pr)_3$", crystallographic investigations of the starting material as well as some of the products would add a more convincing dimension to their characterization.

$$\text{“}Ln(O\text{-}i\text{-}Pr)_3\text{”} + xROH \xrightleftharpoons{\text{benzene}} Ln(O\text{-}i\text{-}Pr)_{3-x}(OR)_n + x\,i\text{-}PrOH$$

$$R = \text{alkyl or aryl} \quad (22)$$

$$\text{“}Ln(O\text{-}i\text{-}Pr)_3\text{”} + 3MeCOOR \rightleftharpoons Ln(OR)_3 + 3MeCOO\text{-}i\text{-}Pr$$

$$R = t\text{-}Bu, SiMe_3 \quad (23)$$

$$\text{“}Ln(O\text{-}i\text{-}Pr)_3\text{”} + 3MeCOOPh \rightleftharpoons Ln(OPh)_3 + MeCOO\text{-}i\text{-}Pr \quad (24)$$

d. Reactions of Metal Disubstituted Amides with Alcohols and Phenols

Addition of an alcohol or phenol to a metal amide can set up an equilibrium as shown in eq 25.

$$Ln(NR_2)_3 + xR'OH \rightleftharpoons [Ln(OR')_x(NR_2)_{3-x}] + xHNR_2$$

$$R = \text{alkyl or trimethylsilyl group;} \quad R' = \text{alkyl or aryl moiety} \quad (25)$$

The utility of this reaction for the synthesis of an alkoxide or phenoxide derivative is largely influenced by both steric factors and relative volatilities of the alcohols or phenols and amines. The method is more convenient in view of the high volatility of the liberated amines, which are therefore, readily removable. The alkoxides, aryl oxides, and silyl oxides of yttrium and lanthanoids[7-10] in low coordination and unique geometries have been recently prepared as shown by the following equations:

$$[\mathrm{Ln\{N(SiMe_3)_2\}_3}] + 3\mathrm{ROH} \rightarrow \mathrm{Ln(OR)_3} + 3\mathrm{HN(SiMe_3)_2}$$

Ln = Y,[70] R = $\mathrm{CMe_2}$-*i*-Pr, CMeEt-*i*-Pr, $\mathrm{CEt_3}$;
Ln = La,[70] R = $\mathrm{CMe_2}$-*i*-Pr, CMeEt-*i*-Pr;
Ln = Ce,[10] R = *t*-$\mathrm{Bu_3C}$ (26)

$$\mathrm{Y\{N(SiMe_3)_2\}_3} + 3\mathrm{Ph_3SiOH} \xrightarrow[0\,^\circ\mathrm{C}]{\text{toluene}} [\mathrm{Y(OSiPh_3)_3}]_x + 3\mathrm{HN(SiMe_3)_2} \quad (27)^{11}$$

$$[\mathrm{Ln\{N(SiMe_3)_2\}_3}] + 3\mathrm{ArOH} \xrightarrow[\text{reflux}]{\text{toluene}} \underset{\text{XIII}}{[\mathrm{Ln(OAr)_3}]} + 3\mathrm{HN(SiMe_3)_2}$$

Ln = La and other lanthanoids,[7-9]
OAr = 2,6-di-*tert*-butyl-4-methylphenoxide;
Ln = Ce,[9] OAr = 2,6-di-*tert*-butylphenoxide (XIIIa), 2,6-di-*tert*-butyl-4-methylphenoxide, and 2,4,6-tri-*tert*-butylphenoxide (28)

$$[\mathrm{Yb\{N(SiMe_3)_2\}_2(L)_2}] + 2\mathrm{ArOH} \rightarrow [\mathrm{Yb(OAr)_2(L)_2}]$$

OAr = 2,6-di-*tert*-butyl-4-methylphenoxide,
L = THF (XIVa) or $\mathrm{OEt_2}$ (XIVb) (29)[56]

By contrast, in reactions of $\mathrm{Ln\{N(SiMe_3)_2\}_3}$ (Ln = Y, La) with an excess of *tert*-butyl and *tert*-amyl alcohols, the alcoholates of the type $[\mathrm{Ln_3(OR)_9(ROH)_2}]$ (Ln = Y, R = *t*-Bu, *t*-Am; Ln = La, R = *t*-Bu) have been isolated and the product $[\mathrm{La_3(O}$-*t*-$\mathrm{Bu)_9}$(*t*-$\mathrm{BuOH)_2}]$ has been characterized[70] by X-ray crystallography.

e. Metal–Carbon Bond Cleavage Reactions

Organometallic alkoxo (aryloxo) derivatives of lanthanoids[71,72] have been prepared by the reactions of an appropriate organometallic compound with a suitable alcohol (phenol), e.g.

$$\mathrm{Ln(C_6F_5)_2} + 2\mathrm{ArOH} \xrightarrow{\text{THF}} [\mathrm{Ln(OAr)_2}] + 2\mathrm{C_6F_5H}$$

Ln = Yb; OAr = 2,6-di-*tert*-butylphenoxide and 2,4,6-tri-*tert*-butylphenoxide; Ln = Eu, Yb, OAr = 2,6-di-*tert*-butyl-4-methylphenoxide (30)

$$\mathrm{Hg(C_6F_5)_2} + 2\mathrm{ArOH} + \mathrm{Yb} \xrightarrow{\text{THF}} [\mathrm{Yb(OAr)_2}] + 2\mathrm{C_6F_5H} + \mathrm{Hg}\downarrow$$

OAr = 2,6-di-*tert*-butyl-4-methylphenoxide (31)

Interestingly the above reaction (eq 31) with 2,6-diphenylphenol has been shown to form tris(2,6-diphenylphenoxo)lanthanoid(III) derivatives,[44] $[\mathrm{Ln(OC_6H_3Ph_2\text{-}2,6)_3}]$ (Ln = Nd, Sm, Er, Yb, Lu), and the X-ray structure of $[\mathrm{Yb(OC_6H_3Ph_2\text{-}2,6)_3}]$ contained on intramolecular chelate Yb···π-arene interaction. The same product can also be prepared by using $\mathrm{Hg(C{\equiv}CPh)_2}$ instead of $\mathrm{Hg(C_6H_5)_2}$ in the above reaction or by the interaction of $\mathrm{Ln(C_5H_5)_3}$ with the 2,6-diphenylphenol.

It would be interesting to extend the studies of the above type for synthesis of lanthanoid(II) alkoxides, of which no authentic example appears to have been reported so far.

Recently,[72] treatment of $[\mathrm{(C_5Me_5)_2LnCH(SiMe_3)_2}]$ (Ln = La or Ce) with *t*-BuOH has been reported to yield the novel derivatives, $[\mathrm{C_5Me_5Ln(OCMe_3)_2}]$ (eq 32).

$$2[\mathrm{(C_5Me_5)_2LnCH(SiMe_3)_2}] + 4t\text{-}\mathrm{BuOH} \rightarrow [\mathrm{C_5Me_5Ln(O\text{-}}t\text{-}\mathrm{Bu)_2}]_2 + 2\mathrm{C_5Me_5H} + 2\mathrm{CH_2(SiMe_3)_2} \quad (32)$$

Further reaction of $[\mathrm{(C_5Me_5)_2CeCH(SiMe_3)_2}]$ with an excess of 2,6-di-*tert*-butylphenol at room temperature gives[72] the product as shown in eq 33.

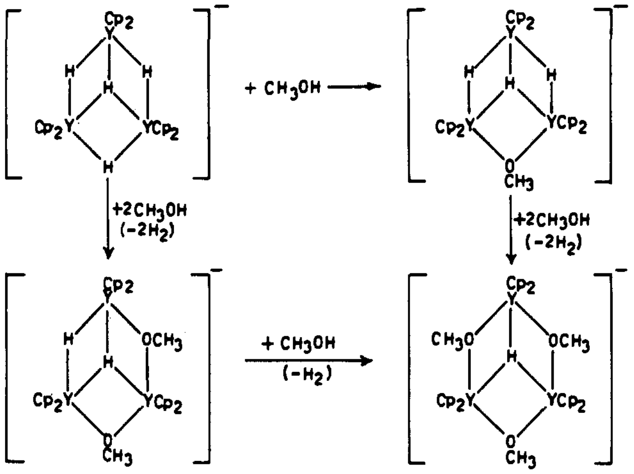
$$\mathrm{(C_5Me_5)_2CeCH(SiMe_3)_2} + \mathrm{HOC_6H_3\text{-}}t\text{-}\mathrm{Bu_2\text{-}2,6} \xrightarrow{\text{room temperature}} [\mathrm{(C_5Me_5)_2Ce(OC_6H_3\text{-}}t\text{-}\mathrm{Bu_2\text{-}2,6)}] + \mathrm{CH_2(SiMe_3)_2} \quad (33)$$

f. Metal–Hydrogen Bond Cleavage and Related Reactions

The prototypical organometallic alkoxide complex, dicyclopentadienylyttrium methoxide,[13] can be produced in the reaction

$$[\mathrm{(C_5H_5)_2Y(\mu\text{-}H)(THF)}]_2 + 2\mathrm{CH_3OH} \rightarrow [\{\mathrm{(C_5H_5)_2Y(\mu\text{-}OMe)}\}_2] + 2\mathrm{H_2}\uparrow \quad (34)$$

Further, synthesis of organoyttrium methoxy hydride anions[16] has been achieved by the interaction of trimetallic organoyttrium hydride complexes with methanol in appropriate stoichiometric ratio as illustrated in eq 35. Recently,[73] interaction of $[\mathrm{(C_5H_5)_2Lu(\mu\text{-}H)(THF)}]_2]$ with PhCHO has been shown to produce $[\mathrm{(C_5H_5)_2Lu(OCH_2Ph)(THF)}]$.



(35)

g. Redox Reactions

The $\mathrm{Ln^{3+}/Ln^{2+}}$ redox potentials [vs normal hydrogen electrode (NHE)], −1.04 V for Yb, and −1.50 V for Sm, indicate that these divalent ($\mathrm{Sm^{2+}}$, $\mathrm{Yb^{2+}}$) ions would be strong reducing agents, and cyclopentadienyl derivatives such as $\mathrm{Sm(C_5Me_5)_2}$ or $\mathrm{Yb(C_5Me_5)_2}$ may serve as a versatile hydrocarbon-soluble source of a single electron. This property has been exploited in the synthetic procedure involving cleavage of phenolic O–H[12] and peroxide[74] bonds, e.g., the aryl oxide $[\mathrm{(C_5Me_5)_2Sm(OC_6HMe_4\text{-}2,3,5,6)}]$ is readily prepared from $\mathrm{HOC_6HMe_4\text{-}2,3,5,6}$ and $\mathrm{Sm(C_5Me_5)_2(THF)_2}$:

$$\mathrm{(C_5Me_5)_2Sm(THF)_2} + \mathrm{HOC_6HMe_4\text{-}2,3,5,6} \xrightarrow{\text{toluene}} [\mathrm{(C_5Me_5)_2Sm(OC_6HMe_4\text{-}2,3,5,6)}] + \tfrac{1}{2}\mathrm{H_2}\uparrow \quad (36)$$

Similarly organoytterbium *tert*-butoxide[74] can readily be prepared by the cleavage of peroxide bonds:

$$2(C_5Me_5)_2Yb(NH_3) + t\text{-BuOO-}t\text{-Bu} \xrightarrow{\text{toluene}} 2[(C_5Me_5)_2YbO\text{-}t\text{-Bu}] \quad (37)$$

The formation of lanthanoid(III) alkoxide derivatives has been accomplished[75] recently by oxidation of metal or a lanthanoid(II) iodide:

$$2LnI_2 + t\text{-BuOO-}t\text{-Bu} \rightarrow 2Ln(O\text{-}t\text{-Bu})I_2$$

$$Ln = Sm, Yb \quad (38)$$

$$Ce + I_2 + i\text{-PrOH} \xrightarrow[20\ ^\circ C]{THF} Ce(O\text{-}i\text{-Pr})I_2 + \tfrac{1}{2}H_2\uparrow \quad (39)$$

h. From Metal Carboxylates

The use of lanthanoid trichloroacetates along with an appropriate sodium alkoxide has been successful in the synthesis of a large number of lanthanoid alkoxides,[76] typically in alcohol–benzene solvent mixture, as exemplified by the following reaction:

$$Ln(OCOCCl_3)_3 + 3NaOR \rightarrow Ln(OR)_3 + 3NaOCOCCl_3\downarrow$$

$$Ln = Pr, Nd, Sm \quad (40)$$

i. Reactions of Lanthanoid Ammonium Nitrates with Alcohols or Their Alkali Metal Salts

In the lanthanoid series, cerium ($4f^25d^06s^2$) shows a predominant tendency for oxidation state 4+; cerium(III), which has been reported recently,[10] has been shown to be extremely oxygen sensitive. In spite of the expected higher stability of Ce(IV) alkoxides, recourse had to be taken[1] to pyridinium hexachlorocerate(IV) for the synthesis of $Ce(OR)_4$ derivatives, since $CeCl_4$ itself is not stable.

An interesting and convenient alternative route for ceric alkoxides has been shown[77] (eq 41) by using ammonium hexanitratocerate(IV) (commonly known as ceric ammonium nitrate, CAN). If in reaction 41 iso-

$$(NH_4)_2Ce(NO_3)_6 + 5MeOH + 4NH_3 \rightarrow Ce(OMe)_4{\cdot}MeOH + 6NH_4NO_3\downarrow \quad (41)$$

propyl alcohol is used instead of methyl alcohol (eq 42), the reaction hardly gets completed because of an apparent equilibrium in which ammonium nitrate reacts with $Ce(O\text{-}i\text{-}Pr)_4$ in DMF liberating NH_3 and i-PrOH.

$$(NH_4)_2Ce(NO_3)_6 + 4NH_3 + 4i\text{-PrOH} \rightarrow Ce(O\text{-}i\text{-}Pr)_4 + 6NH_4NO_3\downarrow \quad (42)$$

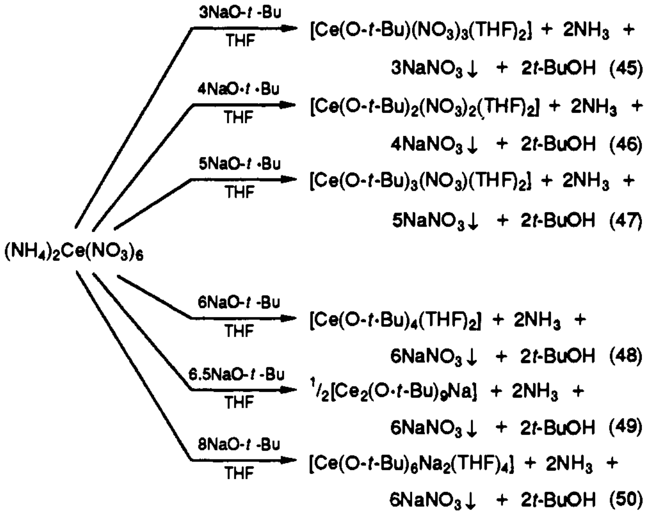
$$Ce(O\text{-}i\text{-}Pr)_4 + NH_4NO_3 \rightleftharpoons Ce(O\text{-}i\text{-}Pr)_3NO_3 + NH_3 + i\text{-PrOH} \quad (43)$$

However, quantitative yields of $Ce(O\text{-}i\text{-}Pr)_4$ have been achieved[78] by the reaction of $(NH_4)_2Ce(NO_3)_6$ and sodium isopropoxide in presence of isopropyl alcohol and dimethoxyethane (DME) (eq 44). The improvement

$$(NH_4)_2Ce(NO_3)_6 + 4NaO\text{-}i\text{-Pr} \rightarrow Ce(O\text{-}i\text{-}Pr)_4 + 2NH_4NO_3\downarrow + 4NaNO_3\downarrow \quad (44)$$

of an earlier method[78] for synthesizing $[Ce(O\text{-}i\text{-}Pr)_4(i\text{-}PrOH)]_2$ (XV) has been reported[24] recently.

SCHEME I



Evans and co-workers[19] have extended this procedure for the synthesis of a wide range ceric *tert*-butoxide derivatives, according to the reactions in Scheme I. More recently, Gradeff, Evans, and co-workers[79] have exploited this procedure for the synthesis of Ce(IV), Ce(III), and other lanthanoid silyloxy complexes, as shown in eqs 51–53.

$$(NH_4)_2Ce(NO_3)_6 + 6NaOSiPh_3 \xrightarrow{DME} [Ce(OSiPh_3)_4(DME)] + 6NaNO_3\downarrow + 2NH_3 + 2Ph_3SiOH \quad (51)$$

$$(NH_4)_2Ce(NO_3)_6 + 6NaOSiEt_3 \xrightarrow{CH_3CN} [Ce(OSiEt_3)_4] + 6NaNO_3\downarrow + 2NH_3 + 2Et_3SiOH \quad (52)$$

$$(NH_4)_xLn(NO_3)_{3+x} + (3 + x)NaOSiPh_3(THF) \xrightarrow{THF} [Ln(OSiPh_3)_3(THF)_3](THF) + (3 + x)NaNO_3\downarrow + xPh_3SiOH + xNH_3$$

$$Ln = Ce, Pr, Nd, x = 2; Ln = Y, x = 4 \quad (53)$$

3.2. Chemical Properties

Lanthanoid alkoxides/aryl oxides are in general highly reactive. The large electronegativity difference between oxygen and lanthanoids would tend to induce a high polarity on the lanthanoid–oxygen bonds, rendering metal atoms more prone to nucleophilic attack and oxygen atoms to electrophilic attack. However, a number of alkoxides and aryl oxides (specially derived from bulky ligands) of lanthanoids exhibit significant volatility and solubility in organic solvents. These apparently covalent characteristics of alkoxo (aryloxo) derivatives of lanthanoids may be rationalized in terms of the $+I$ effects of the alkyl (aryl) group on the oxygen–metal π-bonding.

a. Reactions with Protic Reagents

Similar to other alkoxides,[1] lanthanoid alkoxides/aryl oxides[1,2] also react readily with protic reagents, e.g., water, alcohols, silanols, β-diketones, β-ketoamines, Schiff bases, amino alcohols, glycols, organic acids, etc. The alkoxide method has proved to be exceptionally successful in the preparation of anhydrous tris-β-diketonates which can not be synthesized successfully in most of the cases[1] by any other route:

$$\text{“}Ln(O\text{-}i\text{-}Pr)_3\text{”} + xHacac \rightleftharpoons Ln(O\text{-}i\text{-}Pr)_{3-x}(acac)_x + xi\text{-PrOH} \quad (54)$$

The method has also been extended to the preparation of a variety of derivatives of lanthanoids with chelating ligands such as β-ketoamines, Schiff bases,[80-90] heterocarboxylic acids,[91,92] furfuryl alcohol,[93] 2-thenoate,[94] ethanolamines,[95] thioglycols,[96] secondary amides,[97] thiosemicarbazones,[98] 2-(*o*-hydroxyphenyl)benzoxazole,[99] and β-amidoamines.[100] These derivatives have shown interesting plausible stoichiometries and coordination states, in view of the varying functionalities of the ligands used and recent doubts about the composition of starting metal alkoxides "$\mathrm{Ln(O\text{-}\mathit{i}\text{-}Pr)_3}$" and their X-ray crystallographic authentication would be highly interesting and meaningful.

b. Reaction with Organometallics

Alkoxo/aryloxo ligands play an important role in the chemistry of organolanthanoid compounds, as illustrated by the following equations:[101,102]

$$\mathrm{2Ce(O\text{-}\mathit{i}\text{-}Pr)_4{\cdot}\mathit{i}\text{-}PrOH + 10AlEt_3 + 3C_8H_8 \xrightarrow[140\ ^\circ C]{C_8H_8} \underset{\text{XVI}}{Ce_2(C_8H_8)_3} + 10AlEt_2O\text{-}\mathit{i}\text{-}Pr + 2C_2H_6 + 8(Et)} \quad (55)$$

$$\mathrm{Ce(O\text{-}\mathit{i}\text{-}Pr)_4{\cdot}\mathit{i}\text{-}PrOH + 5AlEt_3 \xrightarrow[110\ ^\circ C]{2C_8H_8} \underset{\text{XVII}}{Ce(C_8H_8)_2} + 5AlEt_2O\text{-}\mathit{i}\text{-}Pr + C_2H_6 + 4(Et)} \quad (56)$$

$$\mathrm{Ce(O\text{-}\mathit{i}\text{-}Pr)_4{\cdot}\mathit{i}\text{-}PrOH + 4AlEt_3 \xrightarrow[100\ ^\circ C]{C_8H_8,\ toluene} \underset{\text{XVIII}}{Ce(C_8H_8)(O\text{-}\mathit{i}\text{-}Pr)_2AlEt_2{\cdot}{}^1\!/\!_4C_7H_8} + C_2H_6 + 3(Et)} \quad (57)$$

$$\mathrm{2Ce(O\text{-}\mathit{i}\text{-}Pr)_4 + 3Mg(C_5H_5)_2 \xrightarrow{benzene} \underset{\text{XIX (4\% yield)}}{2Ce(C_5H_5)_3(O\text{-}\mathit{i}\text{-}Pr)} + 3Mg(O\text{-}\mathit{i}\text{-}Pr)_2} \quad (58)$$

$$\mathrm{Ce(O\text{-}\mathit{i}\text{-}Pr)_4 + 3Me_3SnC_5H_5 \xrightarrow[65\ ^\circ C]{toluene} \underset{\text{XX (67\% yield)}}{(C_5H_5)_3Ce(O\text{-}\mathit{i}\text{-}Pr)} + 3Me_3Sn(O\text{-}\mathit{i}\text{-}Pr)} \quad (59)^{103}$$

$$\mathrm{[Ce(O\text{-}\mathit{t}\text{-}Bu)_2(NO_3)_2(THF)_2] + 2NaC_5H_5 \rightarrow \underset{\text{XXI}}{(C_5H_5)_2Ce(O\text{-}\mathit{t}\text{-}Bu)_2} + 2NaNO_3 + 2THF} \quad (60)$$

$$\mathrm{[2Ce(O\text{-}\mathit{t}\text{-}Bu)_2(NO_3)_2(THF)_2] + 6NaC_5H_5 \rightarrow XXI + \underset{\text{XXII}}{(C_5H_5)_3Ce(O\text{-}\mathit{t}\text{-}Bu)} + 6NaNO_3\downarrow + other\ products} \quad (61)^{18}$$

Earlier attempts to prepare homoleptic alkyls of lanthanoids generally resulted[5] in products containing coordinated LiCl. In order to obtain LiCl-free compounds, alternative starting reagents have been investigated as illustrated by the following reactions:

$$\mathrm{Er(O\text{-}\mathit{t}\text{-}Bu)_3 + 3Li\text{-}\mathit{t}\text{-}Bu \xrightarrow{TMEDA} Er(\mathit{t}\text{-}Bu)_3(TMEDA)_2 + 3LiO\text{-}\mathit{t}\text{-}Bu\downarrow} \quad (62)^{104}$$

$$\mathrm{(C_5Me_5)_2Sm(OC_6HMe_4\text{-}2,3,5,6) + LiR \rightarrow (C_5Me_5)_2SmR + LiOC_6HMe_4\text{-}2,3,5,6\downarrow}$$

$$\mathrm{R = Ph,\ CH_2SiMe_3} \quad (63)^{12}$$

$$\mathrm{(C_5H_5)_2Sm(O\text{-}\mathit{t}\text{-}Bu) + LiCH_2SiMe_3 \rightarrow (C_5H_5)_2SmCH_2SiMe_3 + LiO\text{-}\mathit{t}\text{-}Bu\downarrow} \quad (64)^{69}$$

More recently,[105] coordinatively unsaturated highly reactive three coordinate alkyls of lanthanoids free from LiCl have been isolated upon treatment of a pentane solution of the lanthanoid aryloxide, $\mathrm{Ln(OAr)_3}$ with LiR at room temperature:

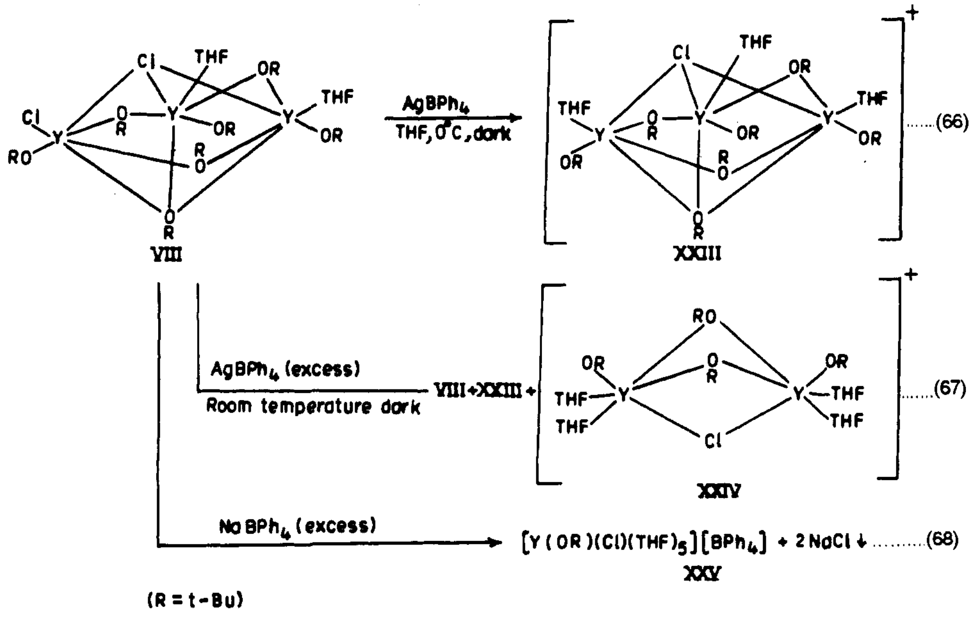
$$\mathrm{Ln(OAr)_3 + 3LiR \xrightarrow{pentane} LnR_3 + 3LiOAr\downarrow}$$

$$\mathrm{Ln = Y,\ La,\ Sm;\ R = CH(SiMe_3)_2,\ Ar = 2,6\text{-}di\text{-}\mathit{tert}\text{-}butylphenoxide} \quad (65)$$

c. Reactions of Yttrium Chloride tert-Butoxide Complexes

Recently,[21] the reactions shown in Scheme II have considerable attention in view of the interesting structural feature of the products. For example, interaction of $\mathrm{[Y_3(O\text{-}\mathit{t}\text{-}Bu)_7Cl_2(THF)_2]}$ with $\mathrm{AgBPh_4}$ or $\mathrm{NaBPh_4}$ affords a new class of cationic yttrium alkoxides, e.g., $\mathrm{[Y_3(O\text{-}\mathit{t}\text{-}Bu)_7Cl(THF)_3][BPh_4]}$ (XXIII), $\mathrm{[Y_2(O\text{-}\mathit{t}\text{-}Bu)_4Cl(THF)_4][BPh_4]}$ (XXIV), and $\mathrm{[Y(O\text{-}\mathit{t}\text{-}Bu)(Cl)(THF)_5]^+}$ (XXV), of varying composition depending upon many factors. Chloro–alkoxy replace-

SCHEME II



ment reactions[15] of the yttrium *tert*-butoxide complexes have also been investigated:

$$\underset{\text{VIII}}{Y_3(O\text{-}t\text{-}Bu)_7Cl_2(THF)_2} + NaO\text{-}t\text{-}Bu \rightarrow \underset{\text{VI}}{Y_3(O\text{-}t\text{-}Bu)_8Cl(THF)_2} + NaCl\downarrow \quad (69)$$

$$\text{VI} + NaO\text{-}t\text{-}Bu \rightarrow \text{insoluble products} \quad (70)$$

$$5Y_3(O\text{-}t\text{-}Bu)_7Cl_2(THF)_2 \rightarrow [Y_7O(O\text{-}t\text{-}Bu)_{14}Cl_5(THF)_2]_2 + 6THF + \text{“}Y^{3+} + 5t\text{-}BuO^- + 2t\text{-}Bu^{+}\text{”} \quad (71)$$

d. Reactivity of Oxide Alkoxides

The reactivity of metal oxides toward alcohols has been so far considered to be limited to nonmetals and metalloids, e.g., R_2GeO, R_2SnO, SeO_2. In view of the above, the following diversified reactions of $Y_5O(O\text{-}i\text{-}Pr)_{13}$, with ligands such as Ph_3SiOH,[79] $Al(O\text{-}i\text{-}Pr)_3$,[22] and Hacac,[106] appear to be of significant interest:

$$Y_5O(O\text{-}i\text{-}Pr)_{13} + Ph_3SiOH(\text{excess}) \xrightarrow{THF} [Y(OSiPh_3)_3(THF)_3](THF) + i\text{-}PrOH \quad (72)$$

$$Y_5O(O\text{-}i\text{-}Pr)_{13} + Al(O\text{-}i\text{-}Pr)_3 \rightarrow \text{no reaction [cf., reaction of “}Y(O\text{-}i\text{-}Pr)_3\text{”]} \quad (73)$$

The recent report[106] about the formation and characterization of $[Y_2(\mu_2\text{-}OAc)_2(acac)_4(H_2O)_2]$ by unexpected cleavage of acetylacetone during its reaction with $Y_5O(O\text{-}i\text{-}Pr)_{13}$ is highly exciting and much work is needed to investigate mechanism of its formation.

e. Adduct Formation

Although metal alkoxides generally prefer to attain higher coordination states by formation of alkoxy bridges (μ_2 or μ_3) rather than adducts with Lewis bases,[1,2,4] yet in addition to exceptional cases, e.g., $Ce(O\text{-}i\text{-}Pr)_4 \cdot i\text{-}PrOH$ and $[Ln_3(OR)_9(ROH)_2]$[70] (Ln = Y, La, R = *t*-Bu, *t*-Am) a few more instances of adduct formation have been described:

$$[Y\{OSiPh_3\}_3]_n + L \rightarrow [Y(OSiPh_3)_3(L)_3] \cdot L_x$$

$$L = THF,\ x = 1;\ L = Py,\ x = 0 \quad (74)^{11}$$

$$\underset{\text{X}}{Y(OC_6H_3Me_2\text{-}2,6)_3(THF)_3} \xrightarrow[THF]{toluene} \underset{\text{XI}}{[Y(OC_6H_3Me_2\text{-}2,6)_3(THF)]_2} \quad (75)^{20}$$

The above reaction showed steric flexibility in achieving five/six coordination states.

Another example to illustrate the tendency of a lanthanoid metal alkoxide and aryloxide to form a complex with Lewis bases was provided by NMR spectral studies.[9] The addition of THF to C_6D_6 solution of the compound resulted in a change in the NMR spectrum consistent with the formation of a 1:1 adduct in accordance with the following equation:

$$Ce(OC_6H_3\text{-}t\text{-}Bu_2\text{-}2,6)_3 + L \rightleftharpoons LCe(OC_6H_3\text{-}t\text{-}Bu_2\text{-}2,6)_3$$

$$L = THF,\ Ph_2CO,\ Et_3PO,\ n\text{-}BuNH_2,\ Et_2NH, MeCN,\ t\text{-}BuNC,\ \overline{CH_2CH_2CH_2CH_2S} \quad (76)$$

f. Reaction with Metal β-Diketonates

Recently the reaction between $[Y(OC_2H_4OMe)_3]_{10}$ and $Cu(acac)_2$ (1:3 molar ratio) (eq 77) at room temperature has been reported[23] to yield several products, out of which the derivative $[Y_3(\mu_3,\eta^2\text{-}OC_2H_4OMe)_2(\mu_2,\eta^2\text{-}OC_2H_4OMe)_2(\mu_2,\eta^1\text{-}OC_2H_4OMe)(acac)_4]$ has been characterized by X-ray crystallographic studies.

$$\underset{\text{IIb}}{[Y(OC_2H_4OMe)_3]_{10}} + 30Cu(acac)_2 \rightarrow \underset{\text{XXVI}}{3[Y_3(OC_2H_4OMe)_5(acac)_4]} + [Cu(OC_2H_4OMe)(acac)]_m \quad (77)$$

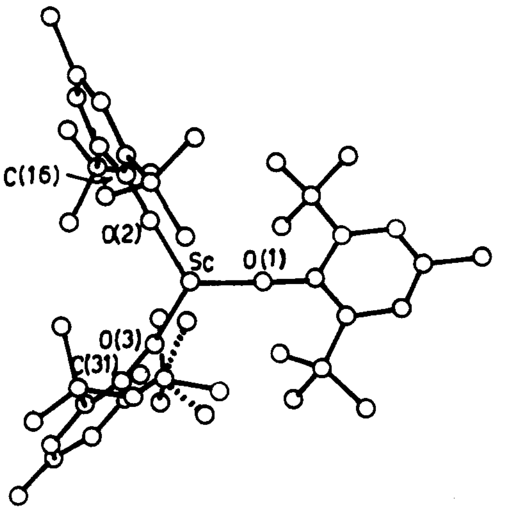


Figure 3. Molecular structure of IXd (reproduced from ref 7; copyright 1983 The Chemical Society).

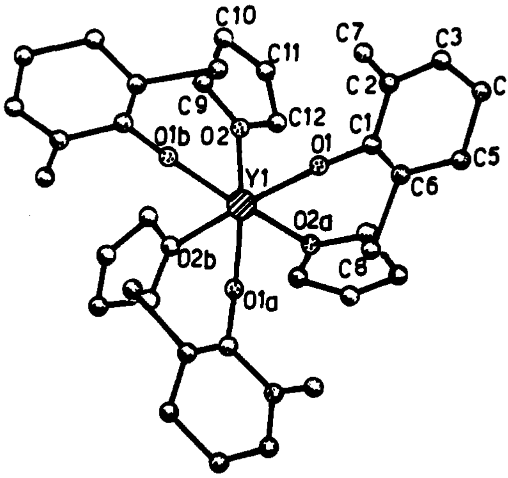


Figure 4. Molecular structure of X (reproduced from ref 20; copyright 1989 American Chemical Society).

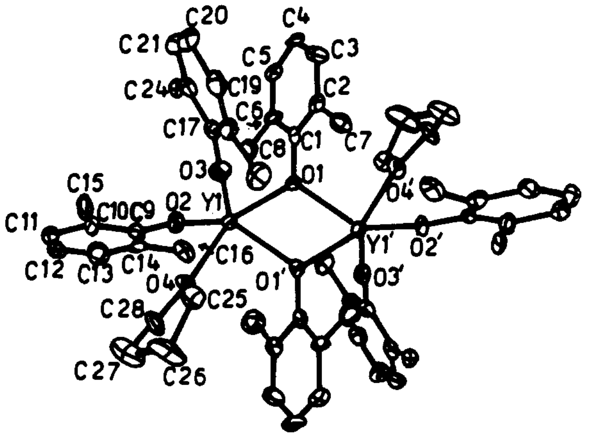
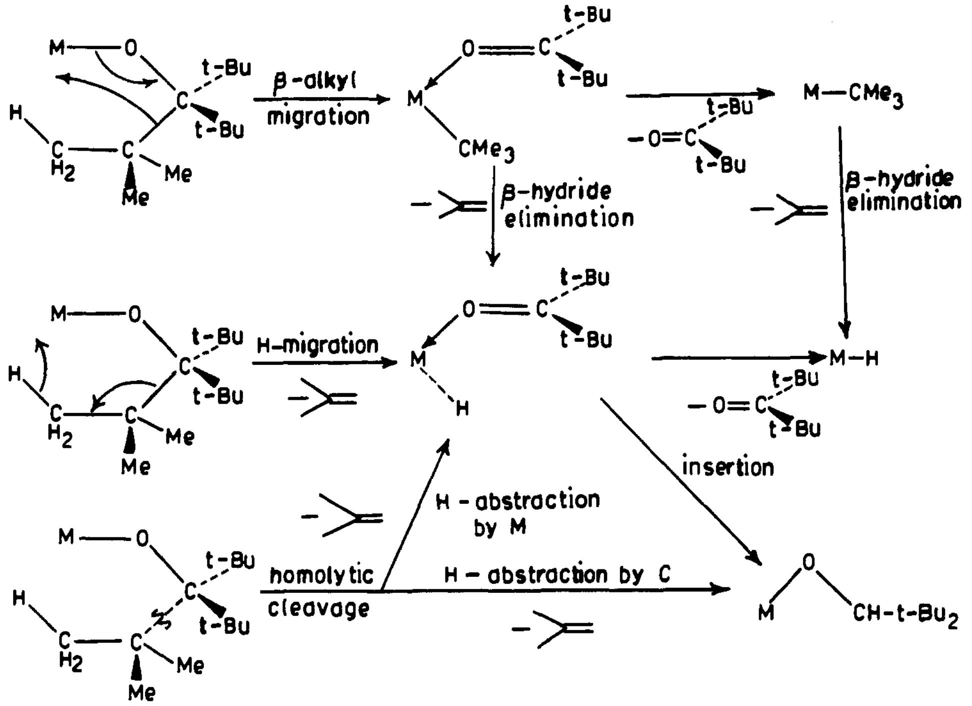


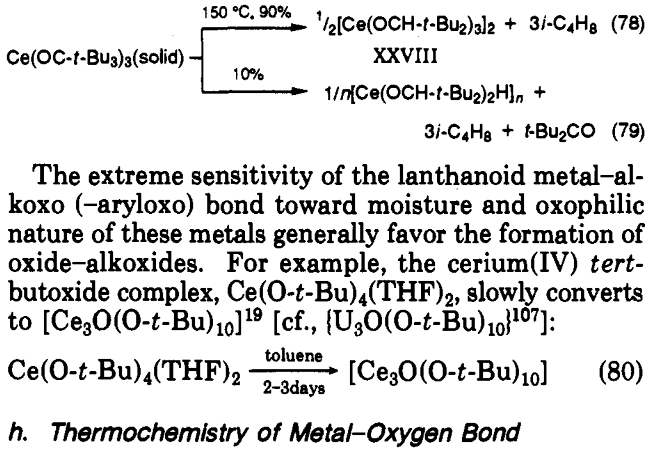
Figure 5. ORTEP diagram of XI (reproduced from ref 20; copyright 1989 American Chemical Society).

SCHEME III



g. Thermal Stability

Most of lanthanoid alkoxides are thermally stable and can be volatilized under reduced pressure and higher temperatures in low yields and in fact, some of these decompose, leading to the formation of a different alkoxide, a hydrido alkoxide, isobutylene and a ketone. For example, thermolysis of $Ce(OC\text{-}t\text{-}Bu_3)_3$ (XXVII) at 150 °C under vacuum results[10] in its decomposition to $[Ce(OCH\text{-}t\text{-}Bu_2)_3]_2$ (XXVIII) and isobutylene, in addition, the detection of a small quantity of $t\text{-}Bu_2CO$ indicates the formation of a Ce(III) hydride (eq 79). A plausible mechanism for the formation of these products has been suggested (see Scheme III).



$$Ce(OC\text{-}t\text{-}Bu_3)_3(\text{solid}) \xrightarrow{150\ ^\circ C,\ 90\%} {}^1/_2[Ce(OCH\text{-}t\text{-}Bu_2)_3]_2 + 3i\text{-}C_4H_8 \quad (78)$$

XXVIII

$$\xrightarrow{10\%} 1/n[Ce(OCH\text{-}t\text{-}Bu_2)_2H]_n + 3i\text{-}C_4H_8 + t\text{-}Bu_2CO \quad (79)$$

The extreme sensitivity of the lanthanoid metal–alkoxo (–aryloxo) bond toward moisture and oxophilic nature of these metals generally favor the formation of oxide–alkoxides. For example, the cerium(IV) *tert*-butoxide complex, $Ce(O\text{-}t\text{-}Bu)_4(THF)_2$, slowly converts to $[Ce_3O(O\text{-}t\text{-}Bu)_{10}]$[19] [cf., $\{U_3O(O\text{-}t\text{-}Bu)_{10}\}$[107]]:

$$Ce(O\text{-}t\text{-}Bu)_4(THF)_2 \xrightarrow[\text{2–3days}]{\text{toluene}} [Ce_3O(O\text{-}t\text{-}Bu)_{10}] \quad (80)$$

h. Thermochemistry of Metal–Oxygen Bond

Thermochemical data on lanthanoid alkoxides (aryl oxides) are limited to only organosamarium alkoxides[126] wherein observed average D (Sm–OR) value has been shown to be ~82 kcal/mol (R = t-Bu, CH-t-Bu_2, this value is to some extent influenced by the nature of ancillary ligand(s) present in the molecule. In view of the utility of the bond energy data in predicting reactivity trends, measurements on other lanthanoid alkoxides (aryl oxides) should provide a useful subject of further research.

3.3. Physical and Spectroscopic Properties

a. Infrared Spectra

Although both fingerprint and structurally diagnostic applications are in principle possible, infrared spectroscopy has so far proved to be of limited practical utility in lanthanoid alkoxo (aryloxo) chemistry. However, terminal and bridging alkoxo (aryloxo) groups can often be distinguished.[1,3]

b. Nuclear Magnetic Resonance Spectra

NMR spectroscopy has provided a convenient technique for identifying terminal, doubly and triply bridged alkoxo groups[2,8,10,19,74] in metal alkoxides. The ^1H NMR spectra of lanthanoid alkoxide clusters, as expected, follow the general trend that methyl proton signals of the μ_3-OR appear at lower fields than μ-OR which in turn are at lower fields than terminal OR groups. These studies tend to be complicated by (i) exchange phenomena of two types, i.e., intramolecular terminal/bridge or terminal/terminal site permutation, and (ii) proton-catalyzed site exchange, as a consequence of the presence of alcohol resulting from accidental hydrolysis.[109]

It may be mentioned that in addition to diamagnetic species such as Sc, Y, La, and Lu (in III oxidation states), Ce(IV) as well as Yb(II), some paramagnetic lanthanoid (e.g., Sm(III)[12]) complexes exhibit rather sharp signals in their ^1H and ^{13}C spectra at ambient temperatures, due to the rapidity of electronic spin lattice relaxation in these systems. The conventional techniques may not be applicable for species like Gd(III)[108] which tend to give highly broadened resonances due to long relaxation time. However, these types of problems are being successfully resolved by special irradiation multipulse techniques applied to other NMR active metal nuclei.

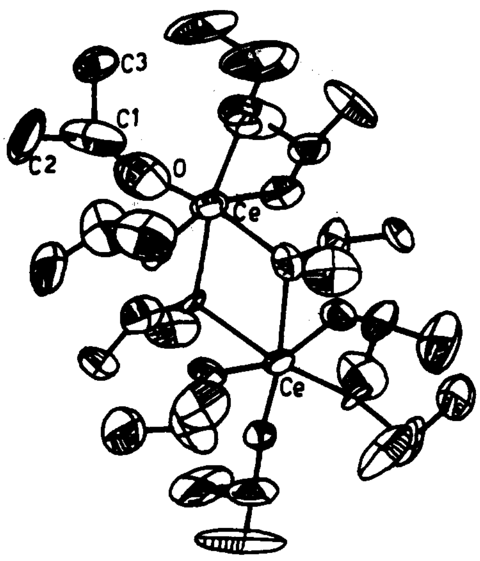


Figure 6. ORTEP view of XV (reproduced from ref 24; copyright 1990 American Chemical Society).

c. Electronic Spectra

Although the observed f–f transitions tend to be rather insensitive to environmental variations, yet in view of useful information derived from the intensity changes and broadening of absorption bands for organolanthanoid[110] species, similar detailed and quantitative studies for $Ln(OR)_3$ type derivatives should be of considerable value in elucidating metal–ligand interactions. For example, investigations in such directions as f–f as well as 4f–5d transitions, in addition to some charge-transfer absorptions in $Ln(OR)_3$ type derivatives, have been initiated by Misra et al.[111]

d. Mass Spectra

Mass spectrum of isopropoxides of neodymium, terbium, erbium, and lutetium have been reported[112] in the literature, and the molecular ion peaks correspond to the molecular weight of the tetramer.

In view of the inefficacy of conventional methods of molecular weight determination, the mass spectrometry should have greater potential for the heterometal alkoxo (aryloxo) systems, in which molecular weight is often greater than 1500.

3.4. Structures

The X-ray crystallographic studies of metal alkoxides have been reported[113] to be in general frustrated by factors such as (i) difficulties in crystallization due to high solubility in common organic solvents including parent alcohols, (ii) crystallographically unsuitable crystals, (iii) disorder phenomenon, and (iv) twinning problems, in addition to the extreme sensitivity to atmospheric moisture. Even if suitable single crystals are available, it is important to establish that the particular crystal chosen for the single-crystal structure determination is indeed representative of the bulk sample. Therefore, it may be desirable to support the conclusion(s) by X-ray powder diffraction studies.

In spite of the above limitations, structural studies have been carried out for a variety (e.g., homoleptic, heteroleptic, and cationic) of alkoxy and aryloxy derivatives of Sc, Y, and lanthanoids, and a few of these

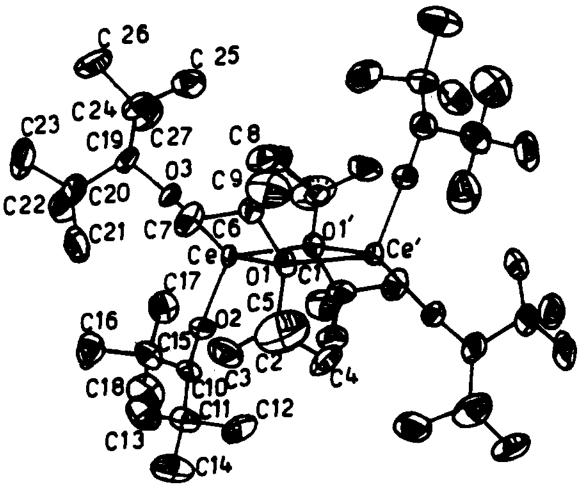


Figure 7. Molecular structure of XXVIII (reproduced from ref 10; copyright 1989 American Chemical Society).

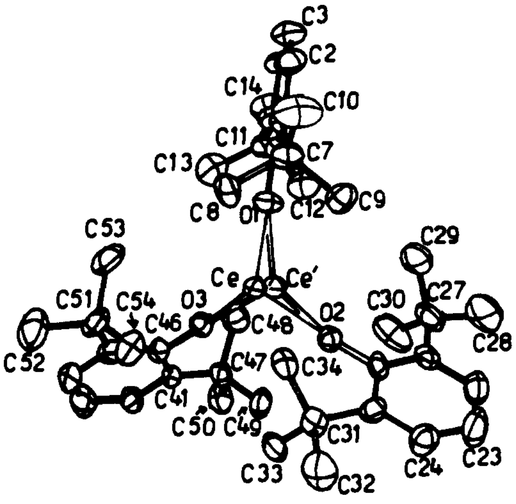


Figure 8. Thermal ellipsoid diagram of XIIIa (reproduced from ref 9; copyright 1988 American Chemical Society).

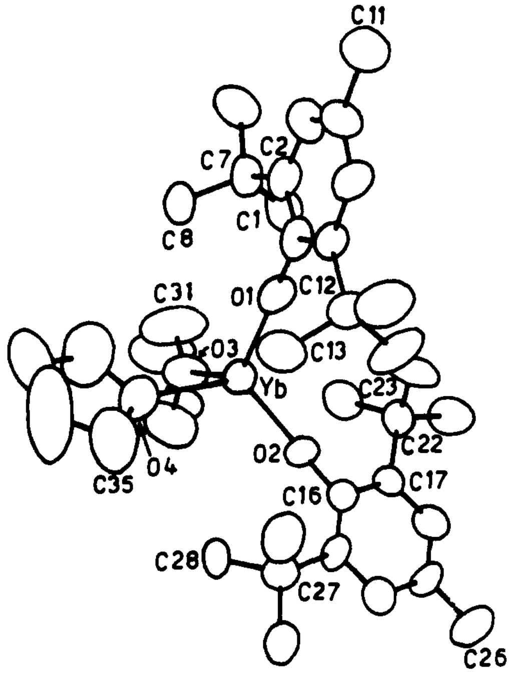


Figure 9. X-ray structure of XIVa (reproduced from ref 56; copyright 1989 The Chemical Society).

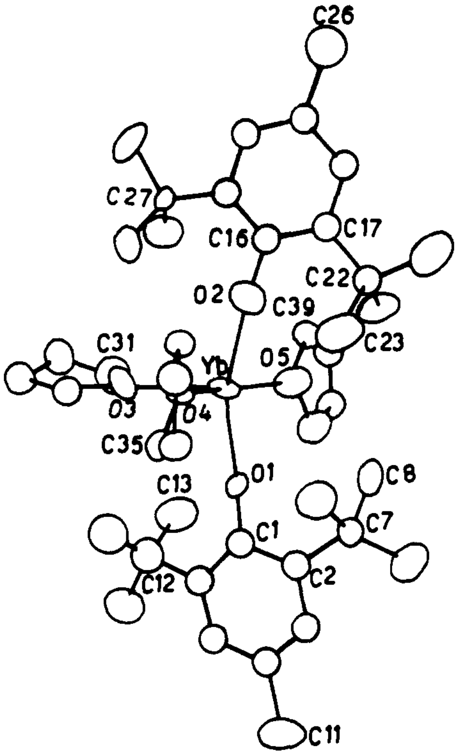


Figure 10. X-ray structure of IV (reproduced from ref 56; copyright 1989 The Chemical Society).

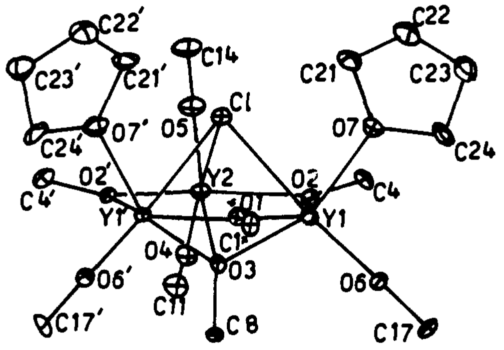


Figure 11. ORTEP drawing of VI (reproduced from ref 17; copyright 1988 American Chemical Society).

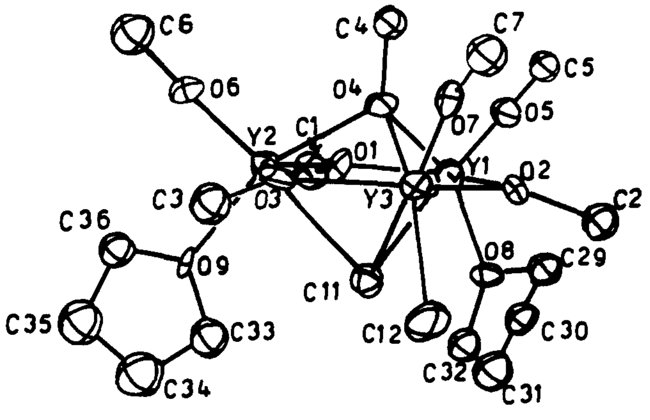


Figure 12. Molecular structure of VIII (reproduced from ref 15; copyright 1988 American Chemical Society).

are illustrated in Figures 3–17 (with the formulae of the compounds in brackets): 3 [$Sc(OC_6H_2$-t-Bu_2-2,6-Me-4$)_3$, IXd], 4 [$Y(OC_6H_3Me_2$-2,6$)_3(THF)_3$, X], 5 [$\{Y(OC_6H_3Me_2$-2,6$)_3(THF)\}_2$, XI], 6 [$\{Ce(O$-i-$Pr)_4 \cdot i$-$PrOH\}_2$, XV], 7 [$\{Ce(OCH$-t-$Bu_2)_3\}_2$, XXVIII], 8 [$Ce(OC_6H_3$-t-Bu_2-2,6$)_3$, XIIIa], 9 [$Yb(OC_6H_2$-t-Bu_2-2,6-Me-4$)_2(THF)_2$, XIVa], 10 [$Yb(OC_6H_2$-t-Bu_2-2,6-Me-4$)_2(THF)_3$, IV], 11 [$Y_3(O$-t-$Bu)_8Cl(THF)_2$, VI]; 12 [$Y_3(O$-t-$Bu)_7Cl_2(THF)_2$, VIII], 13 [$(C_5H_5)_3Ce(O$-t-$Bu)$, XXII], 14 [$Nd_6(O$-i-$Pr)_{17}Cl$, V], 15 [$\{Y_3(O$-t-$Bu)_7Cl(THF)_3\}\{BPh_4\}$, XXIII], 16 [$\{Y_2(O$-$t$-$Bu)_4Cl(THF)_4\}\{BPh_4\}$, XXIV], and 17 [$\{Y(O$-$t$-$Bu)Cl(THF)_5\}\{BPh_4\}$, XXV].

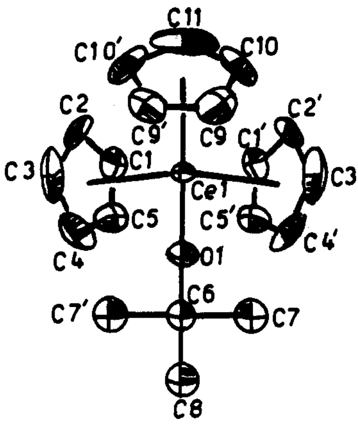


Figure 13. ORTEP plot of XXII (reproduced from ref 18; copyright 1989 American Chemical Society).

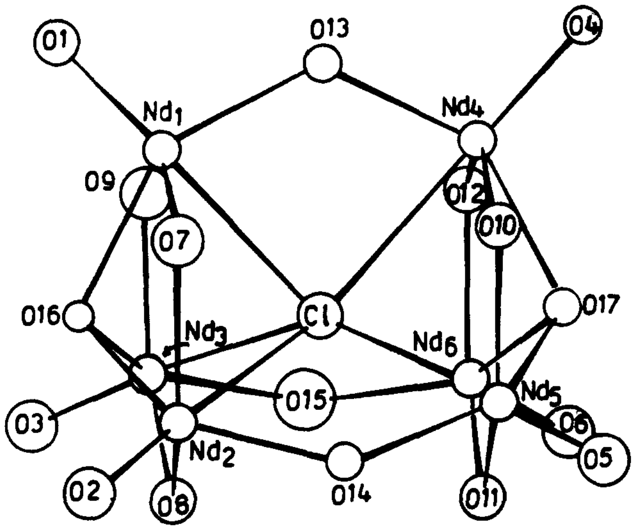


Figure 14. ORTEP drawing of V (reproduced from ref 6; copyright 1978 American Chemical Society).

Salient features of the available structures are (i) the metal–oxygen bond distances increase as expected from terminal to doubly to triply bridging modes; (ii) the terminally bonded alkoxides (aryl oxides) exhibit greater opening of Ln–O–C bond angles, in some cases approaching to 180°, probably as a consequence of both the steric and metal–oxygen bond multiplicity factors; (iii) the monomeric nature of some three coordinate species is reflected in the observed bulk of the ligands, e.g., 2,6-di-*tert*-butylphenoxide, hindering sterically the formation of "OR" bridges (such a situation would obviously be favored with the smaller size of the lanthanoid, e.g., Sc, Y, Yb, and Lu); and (iv) the use of less sterically demanding, for example, 2,6-dimethylphenoxide, ligand provides complexes with enough flexibility to achieve higher coordination by forming adducts/OR-bridged homo- and heterobimetallic derivatives.

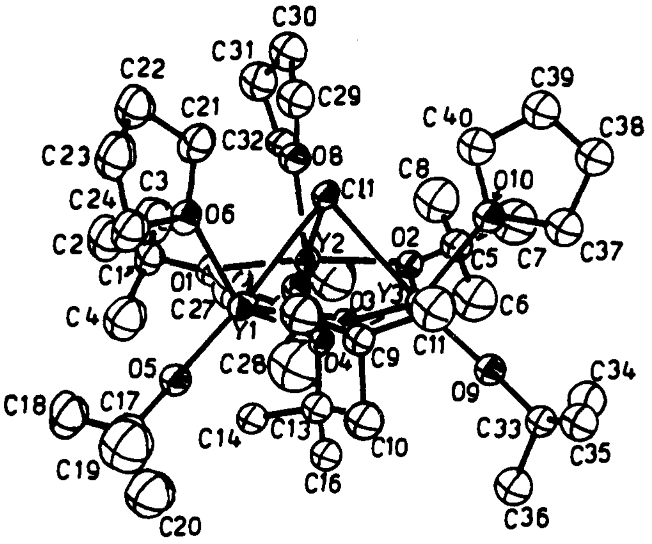


Figure 15. ORTEP diagram of XXIII (reproduced from ref 21; copyright 1990 American Chemical Society).

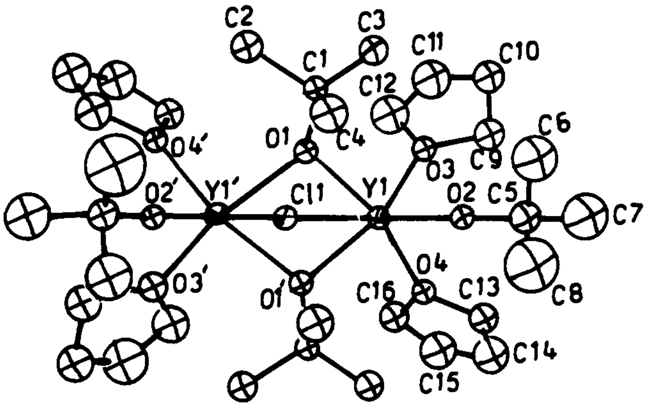


Figure 16. ORTEP diagram of XXIV (reproduced from ref 21; copyright 1990 American Chemical Society).

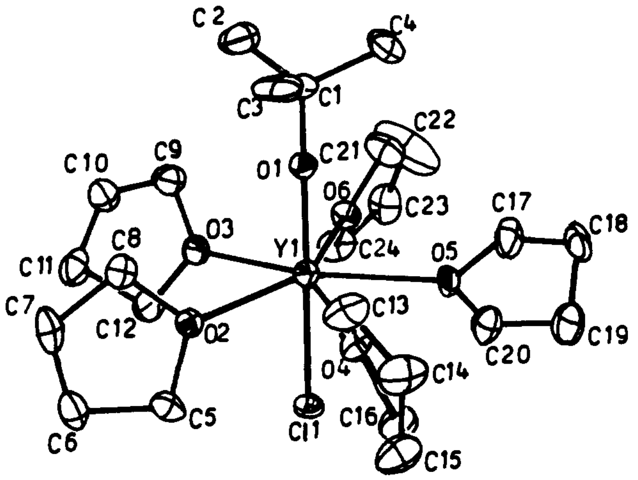


Figure 17. ORTEP diagram of XXV (reproduced from ref 21; copyright 1990 American Chemical Society).

4. Heterometal Alkoxo and Aryloxo Derivatives

4.1. Introduction

Besides the chemical and spectroscopic evidence, actual structures of some of the exciting heterometal alkoxides[19,109] as well as, more recently, a chloride-bridged heterometal species,[114] $[\mathrm{ClCd\{Zr_2(O\text{-}}i\mathrm{\text{-}Pr)_9\}]_2}$, have been determined.

In addition to earlier reviews[2,51,115,116] on heterometal alkoxide systems, the latest review[109] on the topic is limited to $[\mathrm{Ln\{Al(O\text{-}}i\mathrm{\text{-}Pr)_4\}_3}]$ type derivatives only and does not include the more recently investigated other hetero bi- and trimetallic lanthanoid alkoxides which will be examined in the following presentation.

4.2. Preparative Methods

Equations 81–84 represent the methods commonly employed earlier[1,115] for the synthesis of heterometal alkoxides of lanthanoids:

$$\mathrm{LnCl_3} + 3\mathrm{KM(O\text{-}}i\mathrm{\text{-}Pr)_4} \rightarrow [\mathrm{Ln\{M(O\text{-}}i\mathrm{\text{-}Pr)_4\}_3}] + 3\mathrm{KCl}\downarrow \quad (81)$$

$$\mathrm{LnCl_3} + 3\mathrm{MCl_3} + 12\mathrm{K} + 12i\mathrm{\text{-}PrOH} \rightarrow [\mathrm{Ln\{M(O\text{-}}i\mathrm{\text{-}Pr)_4\}_3}] + 12\mathrm{KCl}\downarrow \quad (82)$$

$$\mathrm{Ln(O\text{-}}i\mathrm{\text{-}Pr)_3} + 3\mathrm{M(O\text{-}}i\mathrm{\text{-}Pr)_3} \rightarrow [\mathrm{Ln\{M(O\text{-}}i\mathrm{\text{-}Pr)_4\}_3}] \quad (83)$$

$$[\mathrm{Ln\{M(O\text{-}}i\mathrm{\text{-}Pr)_4\}_3}] + xt\mathrm{\text{-}ROH} \rightarrow xi\mathrm{\text{-}PrOH} + [\mathrm{Ln\{M_3(O\text{-}}t\mathrm{\text{-}R)}_x\mathrm{(O\text{-}}i\mathrm{\text{-}Pr)}_{12-x}\}]$$

$$\mathrm{M = Al\ or\ Ga;\ R = Bu\ or\ Am} \quad (84)$$

Most of the above derivatives have been characterized by analytical data, molecular weight determinations, as well as physicochemical techniques including mass-spectroscopic studies as well as by their reactivity with reagents like tertiary alcohols and β-diketones, e.g.

$$[\mathrm{Ln\{(\mu\text{-}O\text{-}}i\mathrm{\text{-}Pr)_2Al(O\text{-}}i\mathrm{\text{-}Pr)_2\}_3}] + 9t\mathrm{\text{-}BuOH} \xrightarrow{-9\cdot i\text{-PrOH}} [\mathrm{Ln\{(\mu\text{-}O\text{-}}i\mathrm{\text{-}Pr)(\mu\text{-}O\text{-}}t\mathrm{\text{-}Bu)Al(O\text{-}}t\mathrm{\text{-}Bu)_2\}_3}] \quad (85)$$

$$[\mathrm{Ln\{(\mu\text{-}O\text{-}}i\mathrm{\text{-}Pr)_2Al(O\text{-}}i\mathrm{\text{-}Pr)_2\}_3}] + 6\mathrm{MeOH} \xrightarrow{-6\cdot i\text{-PrOH}} \underset{\text{(transient insoluble precipitate)}}{[\mathrm{Ln\{(\mu\text{-}O\text{-}}i\mathrm{\text{-}Pr)_2Al(OMe)_2\}_3}]} \rightarrow \underset{\text{(soluble monomeric volatile)}}{[\mathrm{Ln\{(\mu\text{-}OMe)_2Al(O\text{-}}i\mathrm{\text{-}Pr)_2\}_3}]} \quad (86,87)$$

$$[\mathrm{Ln\{(\mu\text{-}O\text{-}}i\mathrm{\text{-}Pr)_2Al(O\text{-}}i\mathrm{\text{-}Pr)_2\}_3}] + 6\mathrm{Hacac} \xrightarrow{-6i\text{-PrOH}} \underset{\text{(volatile soluble monomeric)}}{[\mathrm{Ln\{(\mu\text{-}O\text{-}}i\mathrm{\text{-}Pr)_2Al(acac)_2\}_3}]} \quad (88)$$

In all the above reactions (eqs 85–88), the tetraisopropoxyaluminate ligand has been assumed to be bidentate. Some $\{\mathrm{Al(OR)_4}\}^-$ ligands have been shown to depict tridentate behavior with transition metals like cobalt,[117,118] nickel,[117,119] and copper.[117,120] Since chemical reactions of the types shown above as well as spectroscopic techniques are sometimes unable to distinguish unambiguously between the two possibilities (bi- and tridentate behavior), and in view of the tendency of lanthanoids to attain "high" coordination states, concerted efforts are called for the determination of the actual structures of the above types of lanthanoid derivatives.

A recent report[22] on the distillation of $[\mathrm{Y\{Al(O\text{-}}i\mathrm{\text{-}Pr)_4\}_3}]$ from the reaction of the crude reaction mixture of yttrium chips with isopropyl alcohol (from which the species, $\mathrm{Y_5O(O\text{-}}i\mathrm{\text{-}Pr)_{13}}$, has been characterized) with 3 mol of $\mathrm{Al(O\text{-}}i\mathrm{\text{-}Pr)_3}$ shows the greater stability of the bimetallic system.[33]

During the last few months, the work has been extended (eqs 89–92) to a number of other systems:

$$\mathrm{LnCl_3{\cdot}3\textit{i}\text{-}PrOH + 3KO\text{-}\textit{i}\text{-}Pr + 3Zr(O\text{-}\textit{i}\text{-}Pr)_4{\cdot}\textit{i}\text{-}PrOH \xrightarrow[\text{reflux}]{\text{benzene}} [Ln\{Zr(O\text{-}\textit{i}\text{-}Pr)_5\}_3] + 3KCl\downarrow + 6\textit{i}\text{-}PrOH}$$

$$\mathrm{Ln = La,^{121}\ Sm^{122}} \qquad (89)$$

$$\mathrm{LnCl_3{\cdot}3\textit{i}\text{-}PrOH + \textit{x}KZr_2(O\text{-}\textit{i}\text{-}Pr)_9 \xrightarrow{\text{benzene}} [Cl_{3-\textit{x}}Ln\{Zr_2(O\text{-}\textit{i}\text{-}Pr)_9\}_\textit{x}] + \textit{x}KCl\downarrow + 3\textit{i}\text{-}PrOH}$$

$$\mathrm{Ln = La,^{123}\ Pr,^{121}\ Nd,^{121}\ Sm;^{122}}\ x = 1, 2, \text{ or } 3 \qquad (90)$$

$$\mathrm{LnCl_3{\cdot}3\textit{i}\text{-}PrOH + K_2Zr_3(O\text{-}\textit{i}\text{-}Pr)_{14} \xrightarrow{\text{benzene}} [ClLn\{Zr_3(O\text{-}\textit{i}\text{-}Pr)_{14}\}] + 2KCl\downarrow + 3\textit{i}\text{-}PrOH}$$

$$\mathrm{Ln = La,^{121}\ Sm^{122}} \qquad (91)$$

$$\mathrm{2LnCl_3{\cdot}3\textit{i}\text{-}PrOH + 3K_2Zr_3(O\text{-}\textit{i}\text{-}Pr)_{14} \xrightarrow{\text{benzene}} [Ln_2\{Zr_3(O\text{-}\textit{i}\text{-}Pr)_{14}\}_3] + 6KCl\downarrow + 6\text{-}\textit{i}\text{-}PrOH}$$

$$\mathrm{Ln = La, Pr, Nd;^{121}\ Sm^{122}} \qquad (92)$$

An interesting heterobimetallic alkoxide of gadolinium, $Na_2Gd_4(\mu_6\text{-}O)(\mu_3\text{-}O\text{-}t\text{-}Bu)_8(O\text{-}t\text{-}Bu)_4$, has been obtained as a minor product[124] by the reaction between $GdCl_3$, NaC_5H_5, and KO-*t*-Bu.

Recently, a number of heterobimetallic alkoxides of cerium(IV) have also been prepared[19] by the reactions of ceric ammonium nitrate with sodium *tert*-butoxide:

$$\mathrm{2(NH_4)_2Ce(NO_3)_6 + 13NaO\text{-}\textit{t}\text{-}Bu \xrightarrow{\text{THF}} \underset{\text{XXIX}}{[NaCe_2(O\text{-}\textit{t}\text{-}Bu)_9]} + 4NH_3 + 12NaNO_3\downarrow + 4\textit{t}\text{-}BuOH} \qquad (93)$$

$$\mathrm{(NH_4)_2Ce(NO_3)_6 + 8NaO\text{-}\textit{t}\text{-}Bu \xrightarrow{\text{THF}} \underset{\text{XXX}}{[Na_2Ce(O\text{-}\textit{t}\text{-}Bu)_6(THF)_4]} + 2NH_3 + 6NaNO_3\downarrow + 2\textit{t}\text{-}BuOH} \qquad (94)$$

$$\mathrm{[Na_2Ce(O\text{-}\textit{t}\text{-}Bu)_6(THF)_4] \xrightarrow{\text{DME}} \underset{\text{XXXI}}{[Na_2Ce(O\text{-}\textit{t}\text{-}Bu)_6(DME)_2]}}$$

$$\text{DME} = \text{dimethoxyethane} \qquad (95)$$

Almost all the above examples corroborate the well-known tendency of lanthanoids to attain "high" coordination states. However, Lappert and co-workers[7,125] have isolated complexes in low coordination states by using sterically hindered ligands such as 2,6-*t*-$Bu_2C_6H_3OH$, 2,6-*t*-Bu_2-4-MeC_6H_2OH, 2,4,6-*t*-$Bu_3C_6H_2OH$, 2,6-*i*-$Pr_2C_6H_3OH$, and 2,6-$Ph_2C_6H_3OH$ as illustrated by the following examples:

$$\mathrm{YbCl_3 + LiOC_6H_2\text{-}\textit{t}\text{-}Bu_2\text{-}2,6\text{-}Me\text{-}4(OEt_2) \xrightarrow{\text{toluene}} Li\{YbCl(OC_6H_2\text{-}\textit{t}\text{-}Bu_2\text{-}2,6\text{-}Me\text{-}4)_3\} + 2LiCl\downarrow} \qquad (96)$$

$$\mathrm{LnCl_3 + 4NaOC_6H_2\text{-}\textit{t}\text{-}Bu_2\text{-}2,6\text{-}Me\text{-}4(OEt_2) \xrightarrow{\text{THF}} [Ln(OC_6H_2\text{-}\textit{t}\text{-}Bu_2\text{-}2,6\text{-}Me\text{-}4)_4Na(THF)_2] + 3NaCl\downarrow}$$

$$\mathrm{Ln = La, Yb} \qquad (97)$$

$$\mathrm{LnCl_3 + \textit{x}LiOC_6H_2\text{-}\textit{t}\text{-}Bu_2\text{-}2,6\text{-}Me\text{-}4(OEt_2) \xrightarrow{\text{THF}} LnCl_{2-\textit{x}}(OC_6H_2\text{-}\textit{t}\text{-}Bu_2\text{-}2,6\text{-}Me\text{-}4)_\textit{x}(\mu\text{-}Cl)_2Li(THF)_2}$$

$$\mathrm{Ln = Y,}\ x = 2;\ \mathrm{Ln = Y, La, Er,}\ x = 1 \qquad (98)$$

Very recently,[109] Evans and co-workers, synthesized $La_2Na_3(\mu_4\text{-}OR)_3(\mu\text{-}OR)_6(THF)_5$ (XXXII) by the interaction of $LaCl_3$ with NaOR (R = *p*-tolyl).

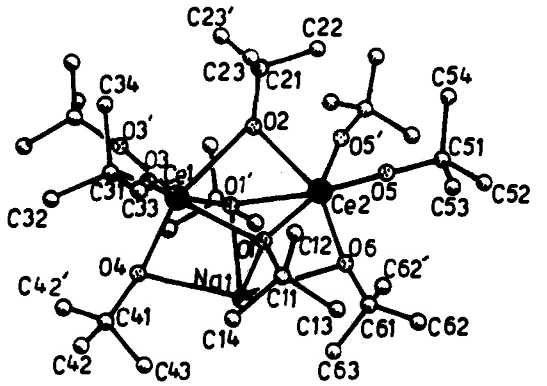


Figure 18. The structure of $[NaCe_2(O\text{-}t\text{-}Bu)_4(\mu\text{-}O\text{-}t\text{-}Bu)_3(\mu_3\text{-}O\text{-}t\text{-}Bu)_2]$ (reproduced from ref 19; copyright 1989 American Chemical Society).

4.3. Physical and Chemical Properties

The heterometal alkoxides and aryloxides of lanthanoids are highly moisture-sensitive solid or viscous materials, the color of which varies with the nature of the lanthanoid metal. All these derivatives are generally soluble in common organic solvents; they depict volatility and monomeric behavior ebullioscopically in benzene. However, some mixed derivatives appear to be dimeric in nature.

Alcoholysis reactions of lanthanoid alkoxides are generally rather slow. Compared to simple alkoxides, their heterometal alkoxides and aryloxides tend to undergo facile alcoholysis, leading to the formation of the products of interesting composition and structures; this has been explained to be due to much more facile reactivity at the Al/Zr/Ta centers.

The chloro complexes such as $[Cl_{3-x}Ln\{Zr_2(O\text{-}i\text{-}Pr)_9\}_x]$ (Ln = Y, La, Pr, Nd, and Sm) are proving to be convenient and versatile precursors for the synthesis of novel heterotrimetallic alkoxides of lanthanoids:[121,122]

$$\mathrm{Cl_{3-\textit{x}}Ln\{Zr_2(O\text{-}\textit{i}\text{-}Pr)_9\}_\textit{x} + (3-\textit{x})KAl(O\text{-}\textit{i}\text{-}Pr)_4 \rightarrow \{Al(O\text{-}\textit{i}\text{-}Pr)_4\}_{3-\textit{x}}Ln\{Zr_2(O\text{-}\textit{i}\text{-}Pr)_9\}_\textit{x} + (3-\textit{x})KCl\downarrow}$$

$$x = 1 \text{ or } 2 \qquad (99)$$

The high-yield synthesis, volatility, and hydrocarbon solubility of heterotrimetallic isopropoxides has opened a new dimension in the lanthanoid alkoxo (aryloxo) chemistry.

Another noteworthy reaction illustrating the formation of oxo-alkoxide[19] is given in eq 100.

$$\mathrm{NaCe_2(O\text{-}\textit{t}\text{-}Bu)_9 \xrightarrow[\text{2 weeks at room temperature}]{\text{toluene}} \{Ce_3O(O\text{-}\textit{t}\text{-}Bu)_{10}\}} \qquad (100)$$

4.4. Spectroscopy and Structures

IR and NMR studies[2,53,123] have been used for the elucidation of the structures of these novel types of heterometal derivatives.

An interesting variation in the rate of exchange of terminal and bridging isopropoxy groups along the lanthanoid series, $[Ln\{Al(O\text{-}i\text{-}Pr)_4\}_3]$, has been explained on the basis of decreasing radii:[127] La → Lu → Sc.

It is logical to expect that a molecule becomes better defined when several spectroscopic probes are used. In view of the heterometal alkoxides (aryl oxides) offering the advantage of the presence of more than one NMR-active metal nucleus (e.g., ^{27}Al, ^{29}Sc, ^{49}Ti, ^{89}Y, ^{91}Zr, ^{205}Tl,

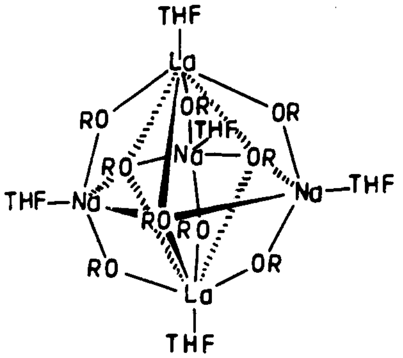


Figure 19. The structure of $[La_2Na_3(\mu_4\text{-}OR)_3(\mu\text{-}OR)_6(THF)_5]$ (R = *p*-tolyl) reproduced from ref 109; copyright 1990 American Chemical Society).

^{119}Sn, ^{207}Pb, etc.), which when combined with the NMR studies of other active nuclei (e.g., ^{13}C, ^{17}O, ^{19}F, and ^{31}P), which might be present in the molecule, the conditions for characterization of both structure and dynamics (i.e., site exchange) tend to be ideal.

The interesting data on the mass spectral studies of only a few lanthanoid tetraisopropoxyaluminates[128,129] indicate that the technique has greater potential in the development of heterometal alkoxide (aryl oxide) of lanthanoids. Unfortunately, very few X-ray structures[19,109] of these derivatives (Figures 18 and 19) appear to have been carried out, pointing a direction for future investigations.

The earlier (in the section dealing with homometallic systems) indicated techniques (Table I) such as high-resolution solid-state MAS NMR, XPS, EXAFS have also greater potential in future developments of heterometal alkoxide (aryl oxide) chemistry of 4f elements as revealed recently in the case of alkoxides of transition metals like titanium.[130]

5. Addendum

This section, added in proof, provides information on four additional papers that have come to our attention since the submission of the manuscript. Caulton et al.[131] have prepared a number of yttrium and lanthanum siloxides, e.g., $[Ln(OSiPh_3)_3]_n$ (Ln = Y, La) and $[\{Y(OSiMe_2CMe_3)_2(HOSiMe_2CMe_3)\}\{Y(OSiMe_2CMe_3)_2\}(\mu\text{-}OSiMe_2CMe_3)_2]$ by the reactions of $[Ln\{N(SiMe_3)_2\}_3]$ with Ph_3SiOH. These have been shown to form kinetically labile monomeric molecular adducts of the types $[Ln(OSiPh_3)_3L_n]\cdot xL$ (L = THF, $n = 3$, $x = 1$; L = pyridine, $n = 3$, $x = 0$; L = $OPBu_3$, $n = 2$, $x = 0$) and $[Y(OSiMe_2CMe_3)_3(THF)_3]$. Single-crystal X-ray data have been provided for five compounds: $[Y(OSiPh_3)_3(THF)_3]\cdot THF$, $[La(OSiPh_3)_3(THF)_3]\cdot THF$, $[Y(OSiPh_3)_3\{OPBu_3\}_2]$, $[\{Y(OSiMe_2CMe_3)_2(HOSiMe_2CMe_3)\}\{Y(OSiMe_2CMe_3)_2\}(\mu\text{-}OSiMe_2CMe_3)_2]$, and $[K(\eta^2\text{-}DME)_3(\eta^1\text{-}DME)][Y(OSiPh_3)_4(\eta^2\text{-}DME)]$.

Another report by Caulton et al.[132] deals with photoreduction of the cerium complex, octakis(isopropoxo)bis(2-propanol)dicerium to the mixed-valence derivative $[Ce_4O(O\text{-}i\text{-}Pr)_{13}(i\text{-}PrOH)$, the structure of which has been established as $[Ce_4(\mu_4\text{-}O)(\mu_3\text{-}O\text{-}i\text{-}Pr)_2(\mu_2\text{-}O\text{-}i\text{-}Pr)_4(O\text{-}i\text{-}Pr)_7(i\text{-}PrOH)]$.

Evans and co-workers[133] have reported the synthesis of organosamarium alkoxides by a novel route, involving the reactivity of the samarium complex $[(C_5Me_5)_2Sm(\mu\text{-}H)]_2$ toward ether solvents such as Et_2O or THF to yield $(C_5Me_5)_2Sm(OEt)(OEt_2)$ and $(C_5Me_5)_2Sm(OBu)(THF)$, respectively.

More recently, Mehrotra et al.[134] have succeeded in characterizing (by single-crystal X-ray diffraction) a novel heptacoordinated heterobimetallic isopropoxide of praseodymium(III), $[\{Pr\{Al(O\text{-}i\text{-}Pr)_4\}_2(i\text{-}PrOH)(\mu\text{-}Cl)\}_2]$, which can be converted to complexes of the type $[\{Pr\{Al(O\text{-}i\text{-}Pr)_4\}_2(L)(\mu\text{-}Cl)\}_2]$ (L = THF or Py), and a hexacoordinated derivative, $[\{Pr\{Al(O\text{-}i\text{-}Pr)_4\}_2(\mu\text{-}Cl)\}_2]$ (on distillation at ca. 200 °C (10^{-2} Torr)).

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