

Synthesis, Structural Principles, and Reactivity of Heterometallic Alkoxides

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1. Introduction

Inorganic "materials" generally display some useful property that depends on "cooperativity" or "communication" between neighboring repeating units. Such an ensemble is useful because of the transfer of an electron, an ion, a photon, the alignment direction of an unpaired electron spin, a local dipole moment, etc., between neighbors. Such neighbors can range from (generally weakly coupled) molecules to (strongly coupled) repeating units in a polymer. To be useful, such materials must be both exceptionally pure and crystallographically perfect over macroscopic dimensions. This places extreme demands on both the selectivity of the synthetic method (and the purity of the synthetic reagents) as well as the physical process and rate of crystal growth or layer deposition. The fact that numerous of these "high-tech" materials are bimetallic (or multimetallic) oxides has resulted in intense activity in the field of bimetallic molecular precursors of oxides. Alkoxides $M(OR)_n$ ^{1,2} appear as versatile potential candidates that can meet the requirements for both sol-gel³ and MOCVD^{4,5} (metal-organic chemical vapor-phase deposition) conversion of the precursor to the final material. An attractive feature of binary alkoxides is their ability to form mixed-metal species $MM'(OR)_{n+n'}$ easily. Although this property was recognized as early as 1924 by Meerwein and Bersin⁶ on the basis of titration experiments, mixed-metal alkoxides remain poorly characterized, by contrast with organometallic heterometallic species. These alkoxides have been called "double alkoxides"⁷ or Meerwein salts; however, since compounds involving three different metals are presently known, the more general term heterometallic alkoxides is preferable and will be used here. It refers to compounds in which two or more different metallic elements are linked via μ - or μ_3 -bridging alkoxo groups or via oxo ligands of various bridging modes,⁸ the ancillary ligands being at least in part alkoxides. Metal-metal bonding is rarely involved, since the alkoxo group, acting as π -donor, favors high oxidation states and early transition metals. Exceptions to these limits will be mentioned, however, and examples of heterometallic alkoxides where the different metals are connected by chloride bridges are also known.

Since heterometallic alkoxides are potential molecular precursors of multicomponent oxides, they are thus of interest for applications in catalysis as well as in material science. Heterometallic alkoxide derivatives have been postulated to act as catalysts in Ziegler-Natta polymerization⁹ or olefin metathesis¹⁰ reactions, as well as in nitrogen activation,¹¹ but detailed characterization is lacking. Somewhat better defined heterometallic oxo alkoxides were shown to be selective catalysts for the polymerization of heterocyclic compounds¹² or for oxidation reactions¹³ if the metal is in a low oxidation state (Fe(II), Cr(II), Mo(II)). More recently, a heterometallic oxo alkoxide anion $[Mg_2Mo_3O_{22}(OMe)_6(MeOH)_4]^{2-}$, obtained in the course of nitrogen fixation ($N_2 + 3H_2 \rightarrow 2NH_3$)¹⁴ was characterized by X-ray diffraction.¹⁵ Structurally well-defined alkoxides have often been attached by specific covalent bonds (Si-O, Mg-O, Al-O, ...) to supporting surfaces, but this topic is beyond the scope of the present review.¹⁶⁻¹⁸ Another attractive property of heterometallic alkoxides is their high solubility, often in nonpolar solvents; they might thus be

used for the transport of cations such as alkali metals or act as metallic hydrocarbon-soluble Lewis acids. More generally, they could mimic some of the important properties such as synergic effects of the mixed-metal oxides commonly used in heterogeneous catalysis and thus allow the design of new, selective catalytic systems.

The choice of alkoxide as the "departing ligand" in the conversion from molecular precursors $M_aM'_b(OR)_c$, for instance $LiNb(OEt)_6$, to solid material $M_aM'_bO_{c/2}$, is not necessarily optimum (e.g., a polyalkyl $M_aM'_bR_c$ could also be considered), but it does offer the possibility of conversion by controlled hydrolysis (the so-called sol-gel process), due to the hydrolytic sensitivity of the alkoxide oxygen,^{3,19,20} or by the influence of externally supplied energy on the O-C bond, with subsequent rupture.

Various other heterometallic compounds with oxygen ligands such as catecholates,²¹ oxalates,²² squarates,²³ and carboxylates,²⁴ have been used in material science. Heterometallic alkoxides appear to cover a larger range of two or even three different metals in a single molecule, often by simple "mixing" of the homometallic species. The high solubility of the resulting heterometallic alkoxides—generally higher than that of the parent homometallic species—has been used as a way to overcome the poor solubility of d^n alkoxides,²⁵ and the formation of heterometallic species has also been considered to provide homogeneity on a molecular level for multicomponent systems.²⁶ However, often very little information is available on the real molecular composition formed simply by mixing reagents in a stoichiometry dictated by the desired solid material. The real system of use in material science often involves stoichiometry and metals different from the heterometallic alkoxides isolated and/or structurally characterized so far. Better control of the sol-gel process involves understanding of the various steps of the hydrolysis-polycondensation reactions.³ This topic is already poorly documented on homometallic alkoxides, but becomes nearly nonexistent for heterometallic species, as structural investigation prior to hydrolysis is generally lacking.

Although certain metal alkoxides may be volatile precursors of oxides, few applications of them by MOCVD techniques have been reported in the literature.⁴ The high- T_c superconductors are anisotropic materials, and it appears that, for their applications in microelectronic devices, coatings displaying high critical currents were required. This goal seems so far best achieved by metal coevaporation or by MOCVD techniques. However, the formulation of high- T_c superconductors requires three different metallic precursors for $YBa_2Cu_3O_{7-x}$, but even more source precursors are needed for systems such as the Tl-Ba-Ca-Cu-O or Bi(Pb)-Sr-Ca-Cu-O.²⁷ It is well established that, for obtaining semiconductors by MOCVD techniques, use of a "single-source" precursor (in which the different elements are incorporated in a single precursor molecule) increases the quality of the final material.²⁸ Therefore, one of today's challenges for chemists is to build heterometallic species in which heavy elements are associated in an appropriate ratio. To meet the requirements of MOCVD precursors, these heterometallics should display⁵ volatility with a sufficient vapor pressure and mass transport at reasonable tem-

perature (<200 °C); stable composition of the vapor during the evaporation process, in order to obtain a deposit homogeneous in composition, microstructure, and properties; thermal stability during prolonged heating under vacuum; and no formation of stable intermediates (residues) during the pyrolysis.

Finally, application in spray pyrolysis²⁹ might also be considered for the less volatile heterometallic alkoxides.

The purpose of this review is to outline general principles that may be used to build heterometallic species, to achieve unambiguous characterization, and to understand and perhaps predict their structures. Some considerations about reactivity and tailoring of their properties will be given.

In gathering material for this review, we put heavy emphasis on examples where product characterization includes molecular structure determination by X-ray diffraction. In the field of heterometallic alkoxides, predictive structural principles are scarce and the incorporation of unexpected groups (O²⁻, Li⁺, Cl⁻) is frequent. One is thus on uncertain ground in thinking that traditional synthetic principles *must* proceed to the "expected" product. In an attempt to avoid the myopia that might arise from succumbing to the "dictatorship of X-ray crystal structures", we also include extensive tables of reported heterometallic alkoxides that have not yet been subjected to X-ray diffraction studies. We hope that these tables will be useful for readers "shopping" for a precursor containing a particular multimetal combination and stoichiometry.

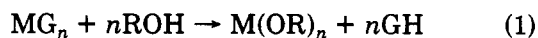
A few words are in order to give definitions to some commonly used terms, particularly since these can suffer modification over the decades of literature surveyed here. We will refer to solids and solution species as "molecular" or "ionic" or "polymeric". Molecular refers to an uncharged species. This has been called "covalent" in the many contributions of the Mehrotra group. Ionic refers to a material existing as separated charged species in solution: these will conduct electricity via independently mobile ions. Polymeric will describe materials where "many" repeat units are linked. Thus, we choose to avoid misleading "saltlike" representations³⁰ such as [Na(py)]₄[Cr₂(OPh)₃] for a molecular species.

2. Synthesis

Although the focus of this paper is heterometallic alkoxides, this field is much less mature than that of homometallic alkoxides. Consequently, many of the general principles of the chemistry of the M-OR bond are better developed for, and best exemplified by, homometallic examples. Wherever there is relevant information on heterometallic alkoxides, we have included this together with examples from cases containing a single metal elements.

2.1. Formation of the Metal-Alkoxide Bond

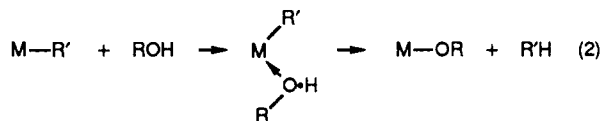
The generic reaction is eq 1. Attractive candidates for group G are hydrides, hydrocarbyls (sp³, sp², or sp carbon), and amides.³¹ Hydrocarbyl species are



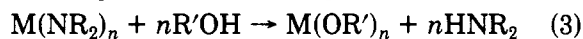
abundantly available and have been employed to a limited extent for the synthesis of metal alkoxides.^{30,32,33}

For example, RhMe(PMe₃)₃ reacts with phenols to give Rh(OAr)(PMe₃)₃.³⁴ While binary hydrides are inaccessible for most transition metals, they can be useful starting materials, as illustrated by the synthesis of a soluble zinc hydridoalkoxide,³⁵ [ZnH(O^tBu)]₄. Alcoholysis of phosphine polyhydrides MH_n(PR₃)_x as well as of metal cyclopentadienyl polyhydrides, Cp_xMH_n, warrants systematic study.³⁶ Available are Cp*₂ZrH₂, Cp₂MH₃ (M = Nb, Ta), Cp*ReH₆, Cp₂MH₂ (M = Mo, W), and CpIrH₄.³⁷ Such reactions can offer access to hydridoalkoxides,³⁶ a class of compounds that might be useful for catalysis or organic synthesis.

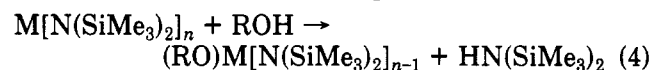
The stepwise character of eq 1 can lead to vastly different rate constants, due to different attackable species, for distinct steps. Thus, MR'_n species are little aggregated, if at all. The tendency for alkoxides to bridge makes subsequent MR'_{n-x}(OR)_x species more likely to be aggregated; the resulting approach to coordinative saturation at M will slow any alcoholysis proceeding by the mechanism in eq 2. A specific example is the alcoholysis of Me₂Zn, which stops at Me₄Zn₄(μ₃-OR)₄. Be, Mg, and Cd behave similarly.¹



Some M(NMe₂)_n species are prone to be oligo- or polymeric (i.e. insoluble) and/or decompose by β-hydrogen elimination giving MeN=CH₂.³⁹ It appears that the currently optimum amide⁴⁰ R group to employ in eq 3 is SiMe₃. This results in part from the consid-

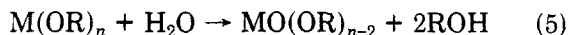


erable preexisting effort to synthesize M[N(SiMe₃)₂]_n compounds, which was motivated in turn by a desire to produce metals with low coordination numbers. This situation could of course change in the future if more NPh₂, pyrrolyl, 2,6-dimethylpiperide, etc., compounds become available. N(SiMe₃)₂ is also exceptionally attractive as a leaving group⁴¹ since HN(SiMe₃)₂ has very low Lewis basicity due to the bulky SiMe₃ groups and N-Si π-bonding. It is also a reasonably volatile by-product. In addition, the very bulk keeping M[N(SiMe₃)₂]_n monomeric also keeps M Lewis acidic for binding of ROH to initiate the alcoholysis by proton transfer to terminal amide (eq 4).



The importance of all these factors is evident from a recent study⁴² of *tert*-butyrolysis of Al₂(NMe₂)₆. In benzene with 20-fold excess of ^tBuOH at 25 °C, the reaction stops (6 h) at Al₂(O^tBu)₄(μ-O^tBu)(μ-NMe₂). After 12 h, the (nonbasic!) μ-NMe₂ group undergoes alcoholysis, but the product is the adduct Al(O^tBu)₃(NHMe₂), which exists in the solid state as a hydrogen-bonded dimer. Amine elimination requires refluxing in toluene with an N₂ purge, and finally Al₂(O^tBu)₆ is formed. Bridging amides and coordinated amines are less problematic for the bis(silyl)amide.

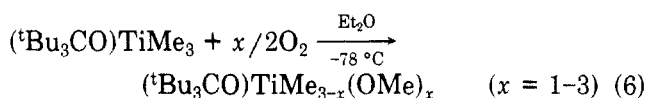
Alkoxide chemistry of the electropositive elements (early transition elements, lanthanides, actinides) has numerous examples of the unexplained appearance of oxo groups (O²⁻). While an accidental hydrolysis (eq 5) might account for this, the examples are sufficiently



numerous that this probably cannot explain all occurrences. Particularly interesting are the cases where an oxo compound is detectable even before workup, beginning with a coordinatively unsaturated and very water-sensitive compound (e.g., $M[N(SiMe_3)_2]_n$). Thus, we find⁴³ $Y_5O(O^iPr)_{13}$ is produced even upon treatment of $Y[N(SiMe_3)_2]_3$ with iPrOH in toluene at $-78^\circ C$. We speculate that such oxo production is favored by the coordinative unsaturation created by the bulky amide (eq 4). For example, possible intermediates like $Y[N(SiMe_3)_2]_2(O^iPr)$ have an unsaturation that makes them particularly prone to O–C bond heterolysis. The developing Me_2HC^+ carbonium ion could either form H^+ and propene or be trapped by iPrOH to give O^iPr_2 and H^+ .

It is a corollary of this idea that any strong Lewis acid can promote oxide and ether formation from the alkoxide even of an electron-rich metal such as lead(II) (see 2.2.1).

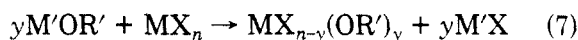
Insertion of dioxygen into σ -metal carbon MR' can offer an alternative route to metal alkoxides. The reaction proceeds via alkyl peroxide $M(\mu^2-OOR')$ ⁴⁴ and is especially interesting for obtaining mixed alkoxides $M(OR)_{n-x}(OR')_x$.^{45,46} Bulky alkoxide groups ($R = Ar, C^tBu_3, \dots$) seem desirable in order to limit side reactions such as formation of oxo derivatives.



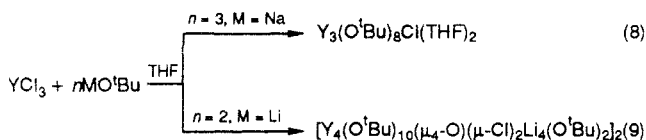
2.2. Formation of Heterometallic Alkoxides

2.2.1. Lewis Acid-Base Reactions

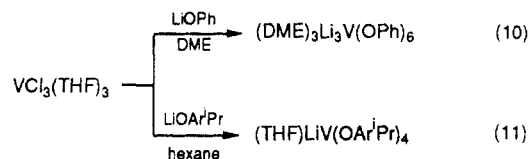
The reaction between a halide and an alkoxide—mostly an alkali-metal alkoxide—represents one of the most general synthetic routes to homometallic alkoxides or aryloxides with formation of chloro or homoleptic derivatives depending on the value of y ($<n$). In fact,



the production of compounds exhibiting low coordination number (bulky R groups) from halide reagents and alkali-metal $M'OR'$ can fail as a result of the high Lewis acidity of $M(OR)_n$, which leads to coordination of halide⁴⁷ and thus to chloroheterometallic alkoxides with retention of M' also.^{48,49} It is equally true that halide is a small ligand (compared to certain OR') that can adapt well to a μ_3 -site in an otherwise crowded molecule.⁵⁰ Retention of halide and sometimes M' is thus a fundamental problem of using the method of eq 7. Lithium is generally more readily carried along than other alkali metals as illustrated by eqs 8 and 9. The

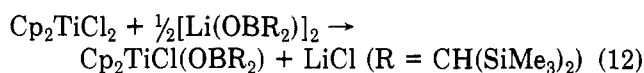


steric demand of the alkoxide or aryloxy ligands can control the stoichiometry of the resulting heterometallic alkoxide⁵¹ (eqs 10 and 11). Finally a Li_2V product, $(THF)_2Li_2V(OAr^iPr)_4$, is also obtained in high yields (77%) by allowing a V(II) derivative, $V(CF_3SO_3)_2(TH-$



$F)_4$, to react with excess $LiOAr^iPr$.⁵²

A few boron oxide derivatives⁵³ were obtained by similar routes (eq 12).



Use of more than stoichiometric amounts of alkali-metal alkoxides in eq 7 generally leads to the heterometallic alkoxides and thus represents a particular example ($X = OR'$) for obtaining heterometallic alkoxides by simple mixing (eq 13), often even at room temper-

ature, of the homometallic alkoxides. This property was first recognized by Meerwein and Bersin,⁶ using titration methods, and is based on the neutralization of acidic and basic alkoxides. However, this property is far more general, and since the metal-alkoxide bond is labile, formation of heterometallic species is observed even between alkoxides of metals as similar as aluminum and gallium⁵⁴ or niobium and tantalum.⁵⁵ However, the formation constant of the heterometallic alkoxide can then be statistical, as observed for $NbTa(OMe)_{10}$; this, in addition to dynamic equilibrium, might preclude its convenient isolation, and heterometallic alkoxides incorporating an alkali metal or derivatives of type $M[Al(OR)_4]_n$ represent so far the most important class of heterometallic alkoxide. The formulation of such derivatives is only rarely related to that of a multicomponent oxide of known utility. $MM'(OR)_6$ ($M = Li, Na, K; M' = Nb, Ta$) for $M'MO_3$ and $Mg[Al(O^iPr)_4]_2$ are among the few exceptions.^{26,56} However, heterometallic alkoxides based on alkali metals may be used as synthons for building further more tailored species.

Reactions between oxoalkoxides and alkoxides offer a route to heterometallic oxoalkoxides. $Mo_2WO(O^iPr)_{10}$, for instance, has been obtained by heating $Mo_2(O^iPr)_6$ and $WO(O^iPr)_4$ in hexane.⁵⁷ However, such reactions might be less general, especially for oxoalkoxides have a *closo* polyhedral structure: thus, $Y_5O(O^iPr)_{13}$ forms heterometallic species with $Ba(O^iPr)_2$ ⁵⁸ at room temperature, but no reaction is observed with $[Al(O^iPr)_3]_4$ even at reflux.⁴³

Experimental evidence for reactions such as depicted in eq 13 is often gained by dissolution of the less soluble alkoxide. However, more complicated reactions such as the formation of various species in which the metals display different stoichiometry and/or condensation reactions with elimination of dialkyl ether can also be observed. The reaction between $Pb_4O(OEt)_6$ and $[Nb(OEt)_5]_2$ provides an example of such behavior. $[Pb(OR)_2]_2$ can "condense" to $Pb_4O(OR)_6$ with elimination of ether. In the presence of $[Nb(OEt)_5]_2$, $Pb_4O(OEt)_6$ has been found to condense further to $Pb_6O_4(OEt)_4$, isolated as the $Nb(OEt)_5$ adduct $Pb_6O_4(OEt)_4 \cdot [Nb(OEt)_5]_4$. This derivative was the only one isolated regardless of the $Pb:Nb$ molar ratio used, although other heterometallic species could be detected in solution by ^{207}Pb NMR.⁵⁹ Mixing of the homometallic al-

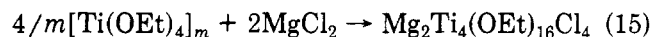
koxydes, according to the stoichiometry of the final desired material, is generally the approach used in the sol-gel process; however, even if a homogeneous solution is obtained, homogeneity at a molecular level is more doubtful, at least for systems (such as NASICON, for instance) involving three or even more different metals.

Heterometallic alkoxides involving three different metals such as $(\text{PrO})_x\text{M}(\mu\text{-O}^i\text{Pr})_2\text{Be}(\mu\text{-O}^i\text{Pr})_2\text{Al}(\text{O}^i\text{Pr})_2$ where $\text{M} = \text{Ti}(\text{IV})$, $\text{Zr}(\text{IV})$, or $\text{Hf}(\text{IV})$ for $x = 3$ or $\text{M} = \text{Nb}(\text{V})$ or $\text{Ta}(\text{V})$ for $x = 4$ have indeed been isolated by simple mixing of the homometallic species in a 1:1:1 molar ratio. The same product, along with $\text{Ti}(\text{O}^i\text{Pr})_4$, was obtained if the reaction was carried out in a 2:1:1 stoichiometry.⁶⁰ The characterization of the heterometallic derivatives rests mainly on mass spectrometry.

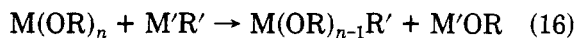
The high lability of the metal-alkoxide bonds, especially in homoleptic alkoxides, also allows the construction of heterometallic species, according to eq 14,



where Y stand for a halide (but M is different from an alkali metal, being mostly an alkaline-earth metal), a nitrate, or a hydrocarbyl. $[\text{Ti}_2(\text{OEt})_8\text{Cl}]_2\text{Mg}_2(\mu\text{-Cl})_2$, obtained by mixing $[\text{Ti}(\text{OEt})_4]_m$ and MgCl_2 in the appropriate ratio (eq 15), represents one of the few structurally characterized heterometallic chloroalkoxides.⁶¹ Similar species could be obtained with MgBr_2 or ZnBr_2 as the Lewis acids, and all products were obtained in yields higher than 50%.



Reactions of metal alkoxides with organolithium or other main-group metal alkyls such as Grignard reagents or aluminum alkyls can give either substitution (eq 16) or addition (eq 17). The volatile compound Li-



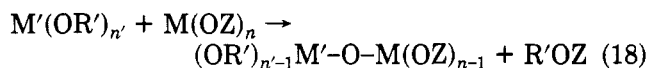
$\text{UMe}(\text{OCH}^i\text{Bu}_2)_4$ has thus been obtained in 35% yield by allowing MeLi to react with $\text{U}(\text{OCH}^i\text{Bu}_2)_4$.⁶² Heterometallic V-Mg or Ti-Al alkyl alkoxides have also been reported to be formed in the course of alkylation reactions, but since such reactions were designed to generate catalytic species for Ziegler-Natta polymerization reactions, little is known about their composition and/or structure, and more investigation is thus warranted.⁶³ A bimetallic complex, whose structure was established to be $[\text{Al}_3\text{Nd}_3(\mu\text{-Cl})_6(\mu_3\text{-Cl})_6(\mu\text{-Et})_9\text{Et}_5(\text{O}^i\text{Pr})_2]_2$, was isolated from the ternary catalytic system $(\text{O}^i\text{Pr})_3\text{Nd-AlEt}_3\text{-AlEt}_2\text{Cl}$.⁶⁴ Although alkoxides are generally difficult to reduce, the use of a strong alkylating reagent such as AlR_3 or RLi may lead to a change of the metal oxidation state. A compound formulated as $\text{LiV}(\text{O}^i\text{Bu})_3$ has, for instance, been isolated from the reaction between $\text{V}(\text{O}^i\text{Bu})_3$ and $\text{LiCH}_2\text{SiMe}_3$.⁶⁵ The low-valent titanium aluminum heterometallic alkoxides that were found to activate dinitrogen were generated by reaction between Ti(IV) alkoxides and trialkylaluminum.^{12,66}

2.2.2. Condensation Reactions

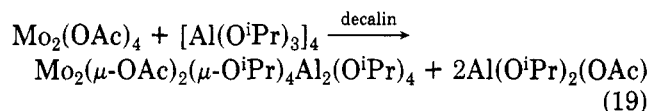
A more selective approach to the formation of heterometallic alkoxides is the elimination of small molecules (or a volatile byproduct) as well as of an insoluble

byproduct (salt, polymeric species, ...).

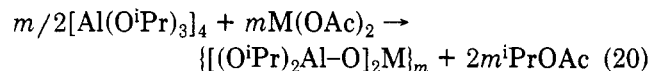
2.2.2.1. Elimination of a Volatile Product. Heterometallic oxoalkoxides can be obtained according to the general equation



where Z is most often a proton or an CH_3CO (acetyl) group. This approach has mainly been used in material science when access to the $\text{M}(\text{OR})_n$ alkoxide is difficult. The commercially available, easy to handle hydroxides (LiOH , $\text{Ba}(\text{OH})_2$, ...) or acetates ($\text{Pb}(\text{OAc})_2$, $\text{Cd}(\text{OAc})_2$, ...), have thus often been chosen, but few data are available concerning the composition of such solutions.⁶⁷ Although such reactions can proceed by simple substitution as shown for the case of Mo(II)

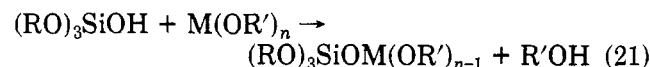


the tendency of the acetato group is to behave as an oxo donor with elimination of ester, especially toward electropositive metals. This type of thermal condensation (eq 20) was used by the group of Teyssie to build heterometallic oxoalkoxides⁶⁸ ($\text{M} = \text{Fe}$, Co , Cr , Mo , Zn).

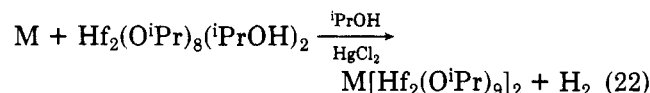


Metal hydroxides are easily available and thus often used as a source of metal oxide in the sol-gel process, but again more investigation is warranted. Since hydroxides are often used as hydrates, studies on the systems generated by eq 18 could also provide some insight into the first steps of hydrolysis-polycondensation reactions of heterometallic alkoxides. Direct hydrolysis of heterometallic alkoxides as a synthetic strategy to heterometallic oxoalkoxides remains limited to the case of the Meerwein compound $\text{Zn}[(\mu\text{-OR})_2\text{Al}(\text{OR})_2]_2$. It can be hydrolyzed to $\text{Zn}[(\mu\text{-O})\text{Al}(\text{OR})_2]_2$, which can also be obtained by thermal condensation (eq 20).

The hydroxyl functionality of $(\text{RO})_3\text{SiOH}$ (resulting from prehydrolysis of $\text{Si}(\text{OR})_4$) is required in order to build heterometallic species containing the $\text{Si}(\text{OR})_3$ moiety by alcohol elimination (eq 21) and thus to overcome the lack of reactivity of $\text{Si}(\text{OR})_4$ toward Lewis acid-base reactions. Similar reactions are involved in anchoring metal alkoxides on supporting surfaces.¹⁶⁻¹⁸



An interesting synthetic method has been reported⁶⁹ (eq 22). This oxidation of the alkaline-earth M is of interest since it may well be that $^i\text{PrOH}$ coordinated to Hf(IV) is the more acidic component of the system and thus is the site of the redox chemistry and H_2 evolution.



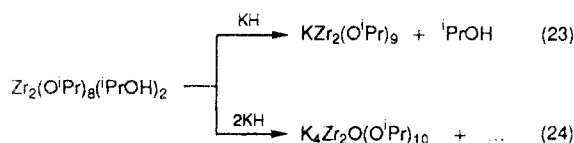
Thus, the reaction may not proceed by conversion of M to $\text{M}(\text{O}^i\text{Pr})_2$ by the solvent. It should however be noticed that such reactions involving an alkaline-earth metal might lead to reduction (at least partial) of the

TABLE I. Heterometallic Alkoxides Based on the Al(OR)₄⁻ Moiety

compound	comments
M[Al(OR) ₄] ₂ M = Be; ⁷¹ R = Me, Et, ⁱ Pr, ⁿ Pr, ⁿ Bu, ^s Bu, ² Am	IR, MW, ¹ H NMR alcoholysis, partial substitution if R bulky M[Al(OR)(OR') ₃] ₂ (R = Et, R' = ^t Bu, and M = Be, R = ⁱ Pr, R' = ^t Bu, ^t Am) tendency to association (m): Mg < Ca < Sr < Ba (Mg, m = 2; Ba, m = 3, volatile)
M = Mg, Ca, Sr, Ba; ⁷² R = Et, ⁿ Bu, (O ⁱ Pr)Be[Al(O ⁱ Pr) ₄] ₂ ⁷³	
M[Al(OR) ₄] ₂ M = Zn; ⁷⁴ R = Me, Et, ⁱ Pr, ⁿ Bu, ⁱ Bu, ^s Bu, ⁱ Am	IR, MW (monomeric), ¹ H NMR volatile for M = Cd, Zn M = Hg decomposes at RT; (O ⁱ Pr)M[Al(O ⁱ Pr) ₄] unstable for M = Cd, Hg
M = Cd, Hg; ⁷⁵ R = ⁱ Pr	
M[Al(OR) ₄] ₂ M = Co, Ni; ⁷⁶ Cu; ⁷⁶⁻⁷⁸ R = Me, Et, ⁿ Pr, ⁱ Pr, Bu	IR, UV-vis, magnetic studies M = Cu: Al(O ⁱ Pr) ₄ , tridentate ligand M = Ni: Al(OR) ₄ , tridentate or bidentate ligand, depending on R alcoholysis and substitution reactions for M = Cu disproportionates into Co[Al(O ⁱ Pr) ₄] ₂
ClCo[Al(O ⁱ Pr) ₄] ₂ ⁷⁹	IR, magnetic studies; Cl bridges IR, ¹ H NMR
M[M'(O ⁱ Pr) ₄] ₃ ⁵⁴ M = Al, Ga, In; M' = Al, Ga	IR, UV-vis, magnetic studies Al(OR) ₄ = bidentate ligand alcoholysis and substitution reactions for M = Cr Cr[Al(O ⁱ Pr) _{4-x} (OR) _x] ₃ : R = Me, x = 1, 2; R = ^t Bu, x = 2 Cr[Al(O ⁱ Pr) _{4-x} (acac) _x] ₃ : x = 1, 2, 4; disproportionation for x = 4 volatile, mass spectrometry, ¹ H NMR, monomeric formation of 1:3 heterometallic species independent of the reaction stoichiometry alcoholysis and substitution reactions for M = Ho Ho[Al(OR) ₄] ₃ : R = Me, insoluble; R = Et, disproportionates on heating Ho[Al(O ⁱ Pr) _{3-x} H _x]: x = 1, 2, X = OMe; x = 1-3, X = acac (complete dissociation by MW into the homometallic acetylacetonates for x = 3) X-ray structure determination, activation of molecular oxygen M = Zr, x = 1: dimeric in C ₆ H ₆ , monomeric in ⁱ PrOH
M[Al(OR) ₄] ₃ M = Co; ⁷⁵ R = ⁱ Pr M = Cr, ^{80,75} Mn, Fe; ⁷⁸ R = Me, Et, ⁱ Pr, ⁿ Bu, ^t Bu, CEt ₂ Me ₂ , CH ₂ CF ₃	
Lu[Al(O ⁱ Pr) ₄] ₃ Ln = Pr, Ce, Nd, Sm, Gd, Dy, ⁸¹ Ho, ⁸² Er, Yb, Lu, Y, Sc	
Mo ₂ (OAc) ₂ [Al(O ⁱ Pr) ₄] ₂ ^{83,13} (O ⁱ Pr) _{4-x} M[Al(O ⁱ Pr) ₄] _x ^{1,84} M = Hf, Zr; x = 1, 2	volatile and soluble
M[Al(O ⁱ Pr) ₄] ₄ ⁸⁵ M = U	¹ H NMR, volatile
(O ⁱ Pr) _{6-x} M[M'(O ⁱ Pr) ₄] _x ⁸⁶ M = Nb, Ta; x = 1, 2; M' = Al, Ga	

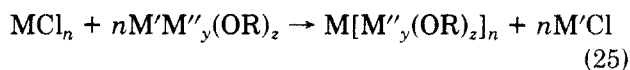
transition metal and/or favor formation of oxo species. The heterometallic species obtained might thus be different from the products resulting from the mixing of the two parent alkoxides.

The proton of the coordinated alcohol has also been used as a reacting site toward the strong base H⁻¹ as well (eq 23).⁷⁰



Elimination of small molecules such as methane or amine between two metallic species also represents potential routes for the construction of heterometallic alkoxides, but this strategy seems to have found no application, probably as a result of the few hydrocarbyl- or hydridoalkoxides available as starting material.

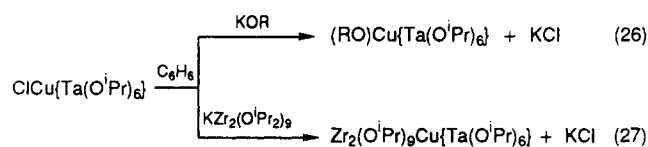
2.2.2.2. Salt Elimination Reactions. This basic reaction for the formation of organometallic heterometallics has also found large application in the field of alkoxides (eq 25), especially in the group of Mehrotra.



M' generally stands for an alkali metal, usually potassium, while the M''_y(OR)_z unit is usually Al(OR)₄, M(OR)₆ (M = Nb, Ta), or M₂(OR)₉ (M = Zr, Hf) (Tables I and II). A large variety of halides (MCl_n) has been employed, especially with the Al(OR)₄ or Ga(OR)₄ moiety. Compounds of type M[Al(OⁱPr)₄]_n (M = alkaline-earth metals, trivalent or divalent transition metals (Fe, Cr, Mn, Fe, Co, Ni, Cu, ...), lanthanides,

actinides) are known.^{1,2,110} More recently, compounds based on Sn(OR)₃ units and associated with heavy main-group elements (Pb(II), Sb(III)) have also been reported. This general, high-yield approach is particularly valuable when the homoleptic M(OR)_n alkoxides are not available or are of poor stability (Cd, Zn, Hg, Pb),¹⁰⁴ but drastic reaction conditions may be required in the case of halides of poor reactivity (Pb).¹¹¹

If reaction 25 is executed in a 1:1 stoichiometry, heterometallic alkoxides of type ClMG (M = Cu(II), Co(II)) are formed.⁷⁹ The remaining chlorine acts as a functional group and has subsequently been replaced by OR or by a second group G, thus offering heterometallic alkoxides (eqs 26 and 27). Since these



heterometallic species have been built around paramagnetic centers and no X-ray structural information has been obtained, the geometry of the central metal has been deduced solely from electronic spectra (Table II).

The isolation of an interesting copper-barium heterometallic alkoxide, Ba₂Cu₂(μ₃-OR)₄(acac)₄(ROH)₂ (R = OC₂H₄OMe), has been achieved during the first stage in preparation of thin-film precursor solutions for high-T_c superconductors.¹¹² Insoluble copper 2-methoxyethoxide forms in this reaction (eq 28) as a result

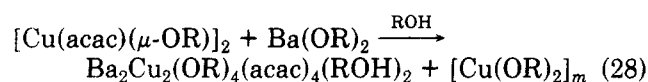


TABLE II. Heterometallic Alkoxides

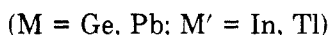
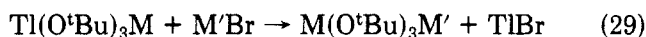
compound	comments
MM'(OR) ₆ ⁸⁷ M = Li, K, Na	(A) Based on M'(OR) ₆ ⁻ Ligands (M' = Nb, Ta) thermal stability: Ta > Nb; Li > Na > K; O ^t Bu > O ⁱ Pr > OEt, OMe
M[M'(OR) ₆] ₂ M = Mg, Ca, Sr, Ba ^{88,89} M' = Nb, Ta; R = Et, ⁱ Pr M' = Ta; R = ⁱ Pr	solubility: Mg > Ca > Sr > Ba thermal stability: Ta > Nb; Ba > Sr > Ca > Mg (Mg derivatives unstable) alcoholysis for M' = Nb M[Nb(OEt) _{6-x} (O ^t Bu) _x]: x = 3, 5; if M = Ba, x = 6 (¹ H NMR) Mg [Nb(OEt) ₆] ₂ ·2EtOH unstable under vacuum
Zn[Nb(OEt) ₆] ₂ ⁹⁰ M[M'(OR) ₆] ₂ M = Cu, ⁹¹ Ni, ⁹² Co, ⁹³ R = Me, Et, ⁱ Pr, ⁿ Pr, ⁿ Bu	no characterization or analysis soluble d ⁿ derivatives, IR, UV-vis, magnetic studies, EPR (M = Cu) axially distorted octahedron for M = Cu M = Ni: R = ² Pr equilibrium, octahedral-tetrahedral species; R = ⁱ Pr, octahedral alcoholysis and substitution reaction for Ni[M(O ⁱ Pr) ₂ (OR) ₄] ₂ (R = ^t Bu, Am; Ni[M(O ⁱ Pr) _{6-x} (acac) _x] ₂ (x = 2, 4))
ClMM'(O ⁱ Pr) ₆ M = Co, ⁷⁹ M = Cu, ⁸⁴ M' = Ta	IR substitution of Cl by OR (R = Me, ⁿ Bu)
Cr[M'(OR) ₆] ₂ ⁹⁵ R = Me, Et, ⁱ Pr	IR, UV-vis, EPR, magnetic studies; octahedral surrounding for Cr alcoholysis and substitution reactions, Cr[M'(O ⁱ Pr) ₄ (acac) ₂] ₃ disproportionation on heating for the mixed species
NaU(OEt) ₆ ⁹⁶ M[U(OEt) ₆] _n ⁹⁷ M = Ca, n = 2 M = Al, n = 3	¹³ C, EPR, crystals as EtOH solvate volatile
M[M' ₂ (O ⁱ Pr) ₉] M' = Zr ⁹⁸ M = Li, Na, K M' = Ti, M' = Li	(B) Based on M' ₂ (OR) ₉ ⁻ Ligands (M' = Zr, Hf, Sn) volatile obtain MZr(O ^t Bu) ₅ even for a 1:2 reaction stoichiometry Na ₂ Zr ₂ (OR) ₉ + CH ₃ COCl gives Zr(OR) ₄ alcoholysis
M[Zr ₂ (OR) ₉] ₂ M = Cu, ⁹⁹ Co, ¹⁰⁰ Ni; ¹⁰¹ R = Me, Et, ⁿ Pr, ⁱ Pr, ⁿ Bu, ⁱ Bu, ^t Bu M = Fe, ¹⁰¹ R = ⁱ Pr	IR, UV-vis, EPR, magnetic studies distorted-octahedral symmetry for M alcoholysis reactions for M[Zr ₂ (O ⁱ Pr) _{9-x} (OR) _x] ₂ M = Cu, Co: x = 3, R = ^t Bu, ⁱ Bu; x = 6, R = Et, ^t Bu, ^t Am, ^t Bu M = Cu: x = 7, R = Me; x = 2, R = ^t Bu; x = 5, R = ^t Am UV-vis, magnetic studies (M = Co) M = Co, alcoholysis reactions
M[Zr ₂ (O ⁱ Pr) ₉] ₂ X M = Co, ^{78,84} X = Cl M = Fe, ¹⁰¹ X = OR, acac	
(OR)M[Zr ₂ (O ⁱ Pr) ₉] M = Cu, ⁸⁴ Co; ⁷⁹ R = Me, ^t Bu, ⁱ Bu M = Co; ⁷⁹ R = ⁱ Pr, ^t Bu	ClM[Zr ₂ (O ⁱ Pr) _{9-x} (OR) _x]: x = 3, R = ^t Bu; x = 6, R = ^t Bu volatile for R = ^t Bu, ⁱ Bu (O ⁱ Pr)M[Zr ₂ (O ⁱ Pr) ₉], trigonal-bipyramidal environment for Co (UV-vis)
Fe[Zr ₂ (O ⁱ Pr) ₉] ₃ ¹⁰²	UV-vis, magnetic studies, bidentate Zr ₂ (OR) ₉ ligand alcoholysis for Fe[Zr ₂ (O ⁱ Pr) ₃ (OR) ₆] ₂ , R = Et, ⁿ Bu volatile and soluble, R = Me
M[Zr ₂ (O ⁱ Pr) ₉] ₂ ¹⁰¹ M = Ca, Ba Na ₂ Zr ₃ (O ⁱ Pr) ₁₄ ⁹⁸ MHf ₂ (O ⁱ Pr) ₉ ⁸⁴ M = Li, K M ₂ Hf ₃ (O ⁱ Pr) ₁₄ ⁸⁴ M = Li, K NaSn ₂ (O ⁱ Pr) ₉ ^{1,103}	dissociation by heating
MSn(OR) ₃ ¹⁰⁴ M = Na, K; R = Me, Et ⁿ Pr, ⁱ Pr, ⁿ Bu, ⁱ Bu, ^t Bu, ^t C ₆ H ₁₁	(C) Based on [Sn(OR) ₃] ⁻ Moieties IR, ¹ H, ¹³ C, ¹¹⁹ Sn NMR (3-coordinate Sn) poor volatility and stability
Sr[Sn(O ^t Bu) ₃] ₂ ¹⁰⁵ Sb[Sn(OR) ₃] ₃ ¹⁰⁴	X-ray structure IR, ¹ H, ¹³ C, and ¹¹⁹ Sn NMR
Pb[Sb(OR) ₄] ₂ ¹⁰⁴ R = Me, ⁿ Pr, ⁱ Pr, ^t Bu, ^t C ₆ H ₁₁	(D) Miscellaneous IR, ¹ H and ¹³ C NMR disproportionation on heating
M[Fe(OEt) ₄] _n ¹⁰⁶ M = Li, Na, K; n = 1 M = Ba; n = 2	IR, phase diagram
Ba ₃ Fe ₂ (OEt) ₁₂ ¹⁰⁶ YZr ₃ (O ⁱ Pr) ₁₅ L ₃ ¹⁰⁷ YFe ₂ (O ⁱ Pr) ₉ YFe ₃ (O ⁱ Pr) ₁₂	IR, phase diagram L = THF, ⁱ PrOH only evidence in solution
Li ₄ Zn(OMe) ₆ ¹⁰⁹ Li ₂ Zn(OEt) ₄ LiZn ₂ (OEt) ₄ X X = OEt, Cl	only analysis; dissociation in boiling MeOH (MW) alcoholysis of LiZn(OEt) ₃ (R = ⁱ Pr, ^t Bu) gives homometallic species

of the migration of some acac ligands from copper to barium. Unfortunately no data about the volatility and/or thermal stability are available. Similar reactions

(where R = ⁱPr) did not allow the isolation of Ba-Cu heterometallic species.

Simple transmetalation reactions have mainly been

applied to main-group alkoxides (eq 29).¹¹³



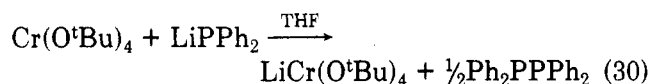
2.2.3. Miscellaneous

Various heterometallic alkyl derivatives have been reported in the literature;¹¹⁴ they mainly involve transition metals or lanthanides associated with lithium or aluminum, whose derivatives are the most commonly used as alkylating reagents. No data concerning O_2 insertion or alcoholysis on such compounds are available so far.

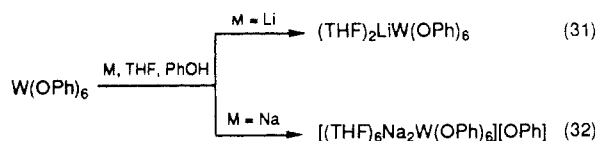
Volatile heterometallic alkyl derivatives are also potential precursors for access to multicomponent non-oxides as well as oxide materials by MOCVD techniques. Transformation to the oxide material implies use of an oxygen donor; investigation of the reactivity of oxo reactants, milder than dioxygen, such as nitrous oxide for instance,¹¹⁵ is thus desirable.

A mixed-valence Mo(V)–Mo(VI) molybdenum magnesium cluster, $\{[\text{Mg}_2\text{Mo}_3\text{O}_{22}(\text{OMe})_6(\text{MeOH})_4][\text{Mg}(\text{MeOH})_6](\text{MeOH})_6\}$, has been isolated in undefined yield from a methanolic solution resulting from MoCl_5 ("containing about 30% of Mo(VI)") and MgCl_2 ($\text{Mg}:\text{Mo} = 0.6$) after neutralization with methanolic NaOH .¹⁵

Various heterometallic alkoxides result from the reduction of transition-metal alkoxides with an alkali metal or their derivatives (Na/Hg , sodium naphthalene, lithium diphenylphosphide)¹¹⁶ (eq 30). Reduc-



tion of the tetrahedral monomer $\text{Ti}(\text{OAr}^{\text{iPr}})_4$ with 1:1 Na/Hg in THF gives $(\text{THF})_2\text{Na}(\mu\text{-OAr}^{\text{iPr}})_2\text{Ti}(\text{OAr}^{\text{iPr}})_2$, whose structure was determined by X-ray diffraction.¹¹⁷ The influence of the reductant (Li or Na , for instance) on the stoichiometry of the heterometallic alkoxides is well illustrated by the reduction of $\text{W}(\text{OPh})_6$ (eqs 31 and 32). Both compounds, obtained in high yields (85%), have been structurally characterized.¹¹⁸



3. Analytical and Spectral Methods

Alkoxide compounds, including heterometallics, have a number of characteristics that can confuse or frustrate certain analytical procedures. Heterometallics at the same time offer some special potential for other methods of characterization. It is one function of this review to consider a fairly comprehensive list of possible analytical techniques, with special reference to their application to metal alkoxides. We hope in this way to provide a standard of quality against which future workers may judge both their own work *in progress* and the reliability and unimpeachability of published

claims. While there is now an impressive arsenal of characterization techniques available, heterometallic alkoxides are sufficiently demanding (and chameleon-like!), sufficiently set with traps, that a multimethod approach is required to arrive at a correct representation of such compounds.

Elemental analysis can be discriminating of molecular formula for compounds with *small* whole number stoichiometric ratios (e.g., $\text{M}(\text{OR})_3$), but as the number of metals and of alkoxides increases, one encounters a quasi-continuum of possible formulae (e.g., $\text{CuZr}_2(\text{OR})_9$, $\text{CuZr}_2(\text{OR})_{10}$, or $\text{CuZr}_4(\text{OR})_{18}$). When one adds the possibility of the unanticipated presence of a small but stoichiometric amount of a spectroscopically "silent" group such as halides or oxides, the difficulty of establishing a formula *de novo* is formidable. Elemental analysis can thus be inconclusive or even misleading.

3.1. Molecular Weight Measurements

While hydrocarbon solubility is a crudely useful indication of molecular (nonpolymeric) character in solution, it still leaves unanswered the question of the exact degree of oligomerization m (e.g., monomer, dimer, trimer, ...). For this, careful solution-phase (or gas-phase) molecular weight measurements must be made. Cryoscopy and ebulliometry are the most used methods, although vapor-phase osmometry and isopiestic procedures are also employed. These methods, since they can operate at very different temperatures, will not necessarily give the same value. This is especially true for heterometallics, which can undergo spontaneous dissociation into homometallic species. Since such methods are counting independent particles, a small amount of a low molecular weight impurity (typically solvent) or of higher polymers (formed by adventitious hydrolysis–polycondensation reactions) can introduce dramatically large errors.

Even in favorable cases, such methods are generally accurate to no more than $\pm 10\%$ for "real world" samples. This presents a particular problem when one addresses objectively the possible coexistence of two (or more) oligomers. One is then studying the molecular weight as a function of concentration, but the accuracy obtainable rarely gives confidence in any apparent trend. Given these limitations, one is probably best advised to consider a Beer's law study when a suitable chromophore is present. The accuracy of optical spectroscopy is higher and the influence of solvent impurities is small, although the problem of growth of a new chromophore due to uncontrolled hydrolysis remains.

3.2. Electrical Conductivity

Very convincing evidence for the molecular character of heterometallic alkoxides comes from solution conductivity *titrations*.¹ Thus, during the titration of $\text{Ta}(\text{OEt})_5$ with NaOEt , no significant increase in conductivity was observed. The formulation $\text{Na}^+\text{Ta}(\text{OEt})_6^-$ was thus excluded. While this gives much needed insight into solution behavior, the need to use an electrically conducting solvent (which may also be a coordinating solvent) can alter behavior in comparison to that in a hydrocarbon.

3.3. X-ray Diffraction and Electron Diffraction

Most of the wholly unprecedented and/or unexpected structures in *any* area of chemistry today are considered secure most often if based on single-crystal X-ray (or neutron) crystallography. It is not a method where one establishes which of a finite set of models best fits the data, but instead a nearly a priori procedure.

Such a pleasant picture of course has its limitations. It holds for solids with both short- and long-range order. Certain characteristics of metal alkoxides tend to contradict these requirements, however. Heterometallic alkoxides generally have a periphery that is wholly hydrocarbon in character (or at least is dominated by the group R). This can make them extremely soluble in all available solvents (the parent alcohol can sometimes be a welcome exception to this "rule!"), frustrating all attempts at crystallization. Even when crystals are available, they can be highly plastic (deformable), and thus unsuitable for X-ray studies. Low-temperature data collection is thus desirable. A general problem of linear aliphatic chains beyond ca. C₃ is their tendency to occupy several conformations with equal probability. The R group does not experience a single deep potential well but encounters several nearly equal minima. The same is true for groups such as ^tBu (nearly conical, with the possibility of occupancy of multiple rotamers) and ⁱPr (two-thirds occupancy of each of the three possible methyl sites). Such *disorder* is localized away from the center of structural interest (the M_nO_p core), involves atoms of lesser scattering power (when M has Z > 20), and can often be modeled satisfactorily in a least-squares refinement. The structure of the M_nO_p core can then generally be obtained, but the accuracy of bond lengths and angles will probably be insufficient to permit internal and external comparisons. As a corollary, the presence or absence of several hydrogens can easily go undetected.¹¹⁹ Even when this presence has been established, the question of the *location* of those hydrogens in alkoxo compounds of lower valent metals can also be quite subtle: Is the hydrogen on an alkoxide oxygen, or is it involved in metal/hydrogen redox chemistry, giving a μ -hydrido alkoxide? Thus, the alcoholysis product of W₂(NMe₂)₆ was first considered¹²⁰ to be W₄(OⁱPr)₁₂(ⁱPrOH)₂ but was later decisively concluded to be W₄(μ -H)₂(OⁱPr)₁₄.¹²¹

The most fundamental sort of disorder arises when the periphery of the molecule is nearly spherical, or at least has one rotational symmetry axis of high order (C₄, C₅, ...). This can occur for a monomer (e.g., trigonal bipyramid or square pyramid) or an aggregate (based on an open or closed polyhedron) *when* the R groups are so large that they dominate any lower symmetry of the metal-oxygen core and give an overall globular shape to the molecule. Since the resulting disorder involves the metal-oxygen core itself, one can encounter an inability to determine the correct space group, or even the adoption of a space group of symmetry higher than permitted by this molecule itself. No satisfactory refinement of the intensity data is possible, and the structure remains undetermined. A commonly applied "solution" to this problem is to incorporate R groups with a shape conducive to rigid packing (i.e., higher lattice energy and thus lower solubility); phenyl is one example, as in O-Ph, O-CH₂Ph, or OCM₂Ph. It must be recognized, however, that this change can be quite

drastic both sterically and electronically and may thus give entirely different stoichiometry and/or structure than a purely aliphatic analog. More important, such a "molecule of convenience" may be far less suitable as a molecular precursor in material science. As is often the case in life, some compromise is required between knowledge and utility.

Twinning (intergrowth of unit cells in two distinct orientations), another crystallographic difficulty, is more frequent in high-symmetry space groups and puts such specialized demands on a crystallographer that a twinned material may be abandoned in the press of other interesting projects.

Single-crystal X-ray structure determinations are generally carried out on the "best looking" single crystal in a batch that may contain crystals of more than one morphology (shape). When subsequent studies are to be carried out on the bulk sample, it is important to establish conclusively that the crystal chosen for the single-crystal X-ray structure determination is indeed representative of the bulk sample. One effective procedure is to take an X-ray powder pattern, which samples perhaps 50 mg, and make certain that *all* observed lines have 2θ values *and intensities* in agreement with those calculated from the single-crystal unit cell and atomic positional parameters.

Finally, consideration needs to be given to the question of whether solid-state structural information remains valid in the vapor phase, where CVD studies are executed. One approach to the problem of structure determination in the gas phase is electron diffraction. This method can be informative, when the volatility is sufficient and the number of variable structural parameters is limited.¹¹⁶

3.4. Mass Spectrometry

This technique can give valuable information on the composition of heterometallic alkoxides, provided they are volatile and stable with respect to disproportionation reactions in the vapor phase. Thus, although more complete characterization of their behavior in the vapor phase is needed for their optimal use in MOCVD techniques, mass spectrometry allows a first crude selection of such precursors. The presence of heterometallic fragments is also a means of excluding the formation of mixed crystals M(OR)_n-M'(OR')_n of the homometallic compounds⁵⁵ and has been used to establish the heterotrimetallic character of the compounds of type (ⁱPrO)_xM(μ -OⁱPr)₂Be(μ -OⁱPr)₂Al(OⁱPr)₂.⁶⁰ Recent results have shown that fast atom bombardment mass spectrometry (FABMS) is of interest for the characterization of nonvolatile high molecular weight inorganic compounds¹²² and could thus be applied to some classes of heterometallic alkoxides.

3.5. Nuclear Magnetic Resonance

The current capabilities of commercial NMR spectrometers should enable considerable progress in the characterization of heterometallic alkoxides, provided that certain factors are kept in mind. Rapid site exchange yields only an average picture of structural microenvironments and thus frustrates establishing stoichiometry (by integration of distinct signals) and molecular symmetry (via comparison of model structures). NMR studies are complicated by exchange

phenomena of two types. One type of exchange obscuring structural conclusions is intramolecular bridge/terminal or terminal/terminal site permutation. In addition, the Brønsted basicity of alkoxide ligands makes them vulnerable to proton-catalyzed site exchange, as a consequence of the presence of alcohol derived from adventitious hydrolysis.¹²³ Variable-temperature studies are thus mandatory. The technique would benefit greatly if it were possible to develop a scavenging reagent for adventitious protons (KH?, MeLi?), so that the NMR tube contents could be dried in situ by addition of a 2–5 mol % scavenger. The selection of a bulky alkoxide group can complicate matters by freezing (at low temperature) the normally free rotation about M–O and O–C bonds. Thus, one obtains spectra more complex than anticipated from the MO_n substructure. This represents information that is generally unwelcome. Finally, there is evidence that NMR can be useful even if the compound is paramagnetic.^{124,125}

We have also found cases (e.g., $KZr_2(O^iPr)_6$) where the spectrum is static (and thus very useful) in C_6D_6 at 25 °C but shows rapid site exchange in THF- d_6 .¹²⁶ The “dangers” of using a coordinating solvent are to be emphasized if structural information is sought.

Since it is always true that a molecule becomes better defined when several spectroscopic probes are used, heterometallic alkoxides can offer the particular advantage of several NMR-active metal nuclei^{127,128} including in the solid state.¹²⁹ A partial listing includes ²⁷Al, ²⁹Si, ⁴⁹Ti, ⁵¹V, ⁸⁹Y, ⁹¹Zr, ⁹⁵Mo, ²⁰⁵Tl, ¹¹⁹Sn, ¹⁸³W, and ²⁰⁷Pb. When combined with studies of other nuclei that might be present (e.g., ¹H, ¹¹B, ¹³C, ¹⁷O, ¹⁹F, and ³¹P), the conditions for characterization of both structure and dynamics (i.e., site exchange) are quite good. Detection of coupling both to and between the metal nuclei should be considered. Coordination of THF to Na⁺ in $NaW_2H(O^iPr)_8$ in THF was deduced from sodium NMR.¹³⁰ It was concluded that $[Ti(OR)_4]_m$ is monomeric ($m = 1$) for R = ⁱPr and ^tBu but that $m > 1$ for R = ⁿPr and ⁿBu based on the fact that no ⁴⁹Ti NMR signal was detectable for the latter two compounds.¹³¹ Quadrupolar nuclei frequently show extremely broad (i.e., undetectable) resonances unless they are in a site of rigorous tetrahedral or octahedral symmetry.

There is presently no convincing demonstration of whether the ¹³C NMR of C_α in an alkoxide group is clearly diagnostic of whether it functions as a terminal, a μ - or a μ_3 -group, and such a study would be valuable, partly in the hope that the greater chemical shift dispersion in ¹³C NMR (compared to ¹H NMR) would be less often obscured by site exchange. Similarly, the possibility that ²⁹Si chemical shifts of OSiR₃ groups fall into distinct terminal, μ - and μ_3 -regions should be explored.

Solid-state NMR (MAS) could complement X-ray structure analysis and serve as an alternative or primary source of solid-state structural data particularly in cases where stable crystals cannot be obtained.¹³²

3.6. Electronic Spectra

Many metal alkoxides are d^0 species that, with aliphatic alkoxides, are optically transparent in the region 5000–50 000 cm^{-1} (even in the presence of an alkali metal or alkaline-earth cation). Lanthanide species may

have $f \rightarrow f$ transitions, but these can be insensitive to environment. Yet the incorporation of redox-active transition, lanthanide (Eu, ...) or actinide metals, together with redox-active cations (e.g., Tl⁺), may lead to spectroscopically accessible localized or charge-transfer bands. These may be useful as fingerprints or in establishment of oxidation state or environment. Given the pervasive question of structural retention on phase change, even the fingerprint application may be useful to provide a criterion for comparison of structure in the solid and solution. Electronic spectra have for instance been used to establish an octahedral surrounding for Cu(II) in $Cu[Ta(O^iPr)_6]_2$ and thus a tridentate coordination mode for the Ta(OⁱPr)₆ ligand.⁹¹ In this way, an equilibrium between tetrahedral and octahedral species has also been detected in solution for $Ni[Al(O^iPr)_4]_2$.⁹²

3.7. Electron Paramagnetic Resonance Spectroscopy. Magnetic Studies

Magnetic susceptibility measurements as well as EPR studies have been used as an indication of the predominantly monomeric nature of heterometallic alkoxides with d^n metal centers (Cu(II), Co(II), ...). EPR spectroscopy has been used to gain information about the stereochemistry of the paramagnetic center as well (Table II).

3.8. Vibrational Spectra

Both fingerprint and structurally diagnostic applications are in principle possible. However, the unfavorably high ratio of both the number and the intensity of (environment-insensitive) ligand-localized to metal–ligand absorptions makes this method relatively unreliable. Isotopic substitution is required to *objectively* identify *all* bands involving MO_n motions; we feel that assignment based solely on (often poorly documented) “typical spectral regions” is unreliable. Because of the limited data base and also, mainly, the problem of masking of important bands, vibrational spectra are probably at best considered as a posteriori aids, once a structure is determined with other techniques. Subsequently, vibrational spectra can be a useful criterion of structural integrity on phase change.

3.9. EXAFS and XANES

These X-ray absorption techniques are “tuned” to core excitations of preselected metal atoms. One thus knows that one observes selectively a given metal even in the presence of a large excess of another. A particular virtue of the EXAFS technique is the ability to collect data on amorphous solids as well as on solutions, providing some structural insight when classical X-ray techniques fail, and in addition it can be a test of structural integrity on dissolution.¹³³ It is also characteristic of these techniques that they perceive only the first two spheres of neighbors of the given atom, and these only according to their distance, but not their angular distribution. It is thus possible to detect not only oxide nearest neighbors but metal next-nearest neighbors; the latter requires M–M separations of less than about 4 Å. Of greatest interest are cases where instrumental resolution allows detection of distinct M–O distances, indicating terminal, μ - and μ_3 -bridges,

as well as terminal O^{2-} groups. However, an absorbing element appearing in several different environments will generally greatly complicate the interpretation of its EXAFS data, which are a superposition of bond lengths.¹³⁴ While EXAFS has been used to "count" the number of neighbor atoms (by determining empirical scattering intensity factors from compounds of known structure), this method has its severe limitations; the accuracy is currently only $\pm 30\%$. The near-edge spectral features called XANES have been used recently as an additional method for establishing the stereochemistry as well as the oxidation state of the metal.¹³³ Since the EXAFS technique is limited to short-range order ($M \cdots M'$ interactions in alkoxides are usually observed around 4.5 Å), large-angle scattering techniques (LAXS) may be used in order to obtain additional information for large interaction distances.¹³⁵

3.10. Mössbauer Spectroscopy

This technique could find application in heterometallic alkoxides containing nuclei such as ^{119}Sn , ^{121}Sb , or ^{57}Fe . The various parameters—*isomer shift*, *quadrupole splitting*, and *magnetic hyperfine splitting*—allow a detailed analysis of the chemical state, and Mössbauer spectroscopy could thus be an alternative to NMR techniques for iron compounds for which paramagnetism and the low sensitivity of ^{57}Fe may preclude the obtaining of useful information.

3.11. Electrochemical Methods

For heterobimetallic compounds containing at least one redox-active metal (the rarely studied oxidative electrochemistry of alkali-metal alkoxides themselves is generally irreversible), it is worth considering electrochemical methods of characterization. To date, inorganic chemists have used (primarily) cyclic voltammetry to establish redox reactivity. Moreover, if such electron transfer is found to be reversible on a time scale long enough for chemical or coulometric synthesis and isolation, such work is undertaken.

As an analytical method, however, cyclic voltammetry can be a useful fingerprint method for establishing solution *composition* (i.e., production of one or more electroactive oligomers in solution). Since this is most definitive if electrochemically reversible conditions are achieved, the more widespread application of microelectrodes, which permit higher potential scan rates, is to be encouraged. With respect to establishing *in situ* the presence of known (or new) products following a reaction, the group of Walton¹³⁶ has pioneered the use of cyclic voltammetry in a manner similar to that in which NMR is currently employed. In the field of alkoxide compounds, electrochemical studies remain limited to some low-valent aryloxides.^{136b}

4. Structure

Throughout this section, it will be seen that a majority of examples of heterometallic alkoxides characterized by X-ray diffraction involve alkali and alkaline-earth metals. The incorporation of alkali-metal cations M'^+ into otherwise anionic metal complexes of course extends far beyond alkoxide chemistry. Molecular species $M_aM'_bX_n$ are known when $X = \text{amide}^{137,138}$ (e.g., NMe_2), halide,¹³⁹ hydride,¹⁴⁰ sulfide,¹⁴¹

thiolate (SR),¹⁴² phosphide (PR_2),¹⁴³ arsenide (AsR_2),¹⁴⁴ β -diketonate,¹⁴⁵ and silicide.¹⁴⁶ The Lewis acidity of alkali and alkaline-earth metals is a pervasive theme, and even apparent "salts" like NaAlCl_4 and K_2CrO_4 , when they go into the gas phase, are molecular species with structures $\text{Na}(\mu\text{-Cl})_2\text{AlCl}_2$ and $\text{K}(\mu\text{-O})_2\text{Cr}(\mu\text{-O})_2\text{K}$.¹⁴⁷ This is the phenomenon underlying chemical vapor transport as a solid-state synthetic and crystal growth technique.^{148,149}

That anionic oxygen can function as a strong coordinating agent for alkali-metal ions is clear from studies of $\text{CpCo}(\text{PR}_2\text{O})_3^-$ (abbreviated L), which forms a benzene-soluble aggregate $\text{Na}_3\text{L}_3(\text{H}_2\text{O})_2$.¹⁵⁰ L also binds well to divalent and trivalent metal cations and has been used to transport Li^+ across phospholipid vesicles.¹⁵¹

It is well established that alkali metals can bind to carbon in metal alkyl derivatives,^{152–154} and strong encapsulating ligands like crown ethers are in fact necessary to separate cation and anion.^{155,156} Recognition that heterometallic compounds containing alkali metals can be hydrocarbon-soluble and molecular was made rather independently during the synthesis of organolanthanide and actinide compounds. The goal there was the production of unsaturated compounds, but the method of eq 33 frequently fails to give unsaturated



Cp_2MR . Because of the large size of M and the empty orbital in Cp_2MR , halide remains coordinated to M and Li to X (and R). One or more Lewis bases L remain attached to Li. This is often described in the literature as "difficulty to separate Cp_2MR from LiX ", when in fact "naked" Cp_2MR is not the final product.¹⁵⁷

4.1. Heterometallic Alkoxides with $M:M' = 1:1$ Stoichiometry

4.1.1. Monomeric MM' Units

Reaction of $\text{CrCl}_3(\text{THF})_3$ with four $\text{LiOCH}^t\text{Bu}_2$ in Et_2O gives $(\text{THF})\text{LiCr}(\text{OCH}^t\text{Bu}_2)_4$, which is monomeric in freezing benzene.¹⁵⁸ In the solid state this molecule has the structure $(\text{THF})\text{Li}(\mu\text{-OCH}^t\text{Bu}_2)_2\text{Cr}(\text{OCH}^t\text{Bu}_2)_2$. Both lithium and the μ -oxygens are 3-coordinate and planar, but Cr is far from planar, with cisoid angles ranging from 84.6° (within the ring) to 108.2° . A similar reaction of FeCl_3 with three(!) $\text{LiOCH}^t\text{Bu}_2$ in Et_2O gives $(^t\text{Bu}_2\text{HCOH})\text{Li}(\mu\text{-OCH}^t\text{Bu}_2)_2\text{Fe}(\text{OCH}^t\text{Bu}_2)_2$. This solid is not isomorphous with the chromium compound. While the μ -oxygens are planar, Li is definitely pyramidal and the iron is more nearly tetrahedral than chromium. The distortion at Li might originate from intermolecular hydrogen bonding.

Reaction of three LiOR ($R = \text{C}^t\text{Bu}_3$) with CrCl_3 in THF-hexane gives a Cr(II) derivative $(\text{THF})_2\text{Li}(\mu\text{-Cl})(\mu\text{-OR})\text{Cr}(\text{OR})$. While Li is 4-coordinate, Cr is only 3-coordinate. The great disparity in the size of the two different bridging groups is apparently the origin of the distortion of the geometry at chromium to "T-shaped" ($\text{O-Cr}-(\mu\text{-O}) = 157.9^\circ$, $\text{O-Cr}-(\mu\text{-Cl}) = 110.9^\circ$). LiCl is separated from the chromium upon dissolution in hexane. The Co(II) compound $(\text{THF})_3\text{Li}(\mu\text{-Cl})\text{Co}(\text{OR})_2$ differs only by an additional THF ligand, probably due to the greater steric crowding, which does not allow alkoxide coordination to lithium. Agostic interactions

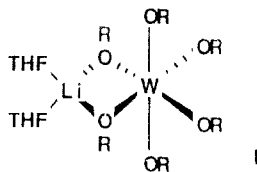
between some CH₃ groups and cobalt are observed.⁴⁹

Addition of two LiOAr^{Ph} to SnCl₄ in aromatic solvents gives, as one product, LiSn(OAr^{Ph})₃.¹⁵⁹ This minor Sn(II) product is obtained in a higher yield beginning with Sn(II). The mass spectrum shows a molecular ion, and the crystal structure shows a Li(μ-OAr^{Ph})₃Sn unit with crystallographic C₃ symmetry. This obviously leaves Li in an unusual *pyramidal* 3-coordinate environment (O–Li–O = 83.5°). Some steric shielding of Li by (or incipient bonding with) one ortho carbon (or C–H bond) of each of three phenyl groups is noted. No solution characterization was carried out. Reaction of (TlO^tBu)₄ with [Sn(O^tBu)₂]₂ gives an analogous species, Tl(μ-O^tBu)₃Sn, shown by X-ray diffraction to have pyramidal oxygen, Tl, and Sn. The compound is benzene-soluble, sublimes at 40°, and is so symmetric that there is disorder of Tl with Sn.¹⁶⁰

The heterometallic lithium–boron alkoxide (MeOH)₂Li(μ-OMe)₂B(OMe)₂ results from recrystallization in MeOH of LiB(OMe)₄.¹⁶¹ Both atoms are 4-coordinate.

The solid-state structure of LiUMe(μ-OCH^tBu)₂(OCH^tBu)₂⁶² is based upon bent 2-coordinate lithium and 5-coordinate uranium, the methyl group occupying the apical site of a square pyramid. The constitution in benzene solution is clearly different from that of the solid, and extensive dissociation is observed.

Reduction of W(OPh)₆ by Li or Na (eqs 31 and 32) gives (THF)₂LiW(OPh)₆ (toluene-soluble) and NaW(OPh)₆·NaOPh.¹¹⁸ The latter is soluble in polar organic solvents, but insoluble in toluene. Cation exchange of Na⁺ by NEt₄⁺ in methanol gives [Et₄N][W(OPh)₆] as a salt (no interaction of cation and anion) containing centrosymmetric W(OPh)₆[−] anions. The Li salt is shown in I. Lithium has a distorted tetrahedral environment, and the (μ-O)–W–(μ-O) angle is acute (79.6°). EPR spectra indicate retention of the alkoxide bridges in solution (THF, 100 K).



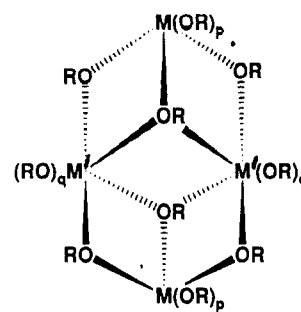
The (2,6-diisopropylphenoxy)vanadium(III) compound (THF)₂LiV(OAr^{Pr})₄ is formed from V(III) (eq 11) as well as from V(II) reagents (in reduced yields), including V₂(μ-Cl)₃(THF)₆⁺; the origin of the redox reaction is unknown. It is described as (OAr^{Pr})₂V(μ-OAr^{Pr})₂Li(THF), where attachment of Li(THF)⁺ to two of the aryloxy oxygens decreases the (μ-O)–V–(μ-O) angle to 81.6° and lengthens the V–O bonds by 0.1 Å compared to the terminal ones. The crown ether 12-crown-4 separates Li⁺ to leave a “nearly perfect” tetrahedral V(OAr^{Pr})₄[−] unit of crystallographic S₄ symmetry.⁵¹

Although the structure of NbTa(OMe)₁₀ was not established by X-ray diffraction, ¹H NMR and mass spectra give evidence for a structure analogous to that of Nb₂(μ-OMe)₂(OMe)₈,¹⁶² one niobium being substituted by a tantalum atom.⁵⁵

4.1.2. M₂M′₂ Units

A unit of common occurrence among heterometallic alkoxides with a 1:1 M:M′ stoichiometry is the struc-

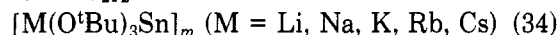
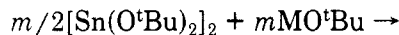
tural form^{163,164} shown in II. This unit has C_{2h} sym-



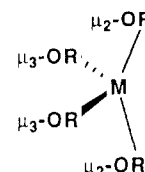
II

metry, regardless of the values of *p* and *q*, which represent terminal ligands. This symmetry would not be raised further even if M = M′, so the structure is ideal for heterobimetallics: the coordination number of M and M′ can be altered completely independently; obviously if *p* = 3 and *q* = 2, both metals are 6-coordinate and distorted-octahedral and the overall formula is M₂M′₂(OR)₁₆ (cf. M₄(OEt)₁₆, where M = Ti¹⁶⁵ or W).^{166,167} However, as *q* becomes smaller, it will be more appropriate for an alkali metal (*q* = 0) or Sn(II) (*q* = 0, but now this terminal “site” is occupied by a lone pair). With *p* = 2, a trigonal-bipyramidal geometry can easily be adopted by M′, or even a tetrahedron when *p* = 1. Various combinations of *p* and *q* can thus accommodate formulas M₂M′₂(OR)_{*r*}, where *r* = 6, 8, 10, 12, 14, and 16.

This structural principle is nicely illustrated by the products of eq 34. For M = Li and Na, the compounds [M(μ-O^tBu)₃Sn]_{*m*} are benzene- and ether-soluble and melt and sublime below 130 °C. For M = K, Rb, and



Cs, the melting point rises to above 200 °C and the solubility in benzene and ether is greatly reduced. The Li and Na compounds are dimers of formula M₂Sn₂(μ₃-O^tBu)₂(μ-O^tBu)₄, conforming nicely to the generic structure for this class of molecules.¹⁶⁸ There are no terminal alkoxides, and pyramidal Sn(II) presumably has a lone pair. The Li and Na centers are 4-coordinate, in a geometry shown schematically in III. Nevertheless,



III

the ¹H NMR shows only one singlet in benzene, where cryoscopic measurements confirm that the dimer persists. The sodium compound remains a dimer in the gas phase, but the lithium one is a monomer (by mass spectrometry).¹⁶⁹

The distinct physical properties for the light (Li, Na) vs heavy analogues originate in a polymeric structure for the potassium (and the isomorphous Rb and Cs) compound. Such polymerization is attributed to the higher coordination number demanded by the larger alkali metals. Indeed, potassium achieves coordination number 5 by forming two additional K–O bonds from

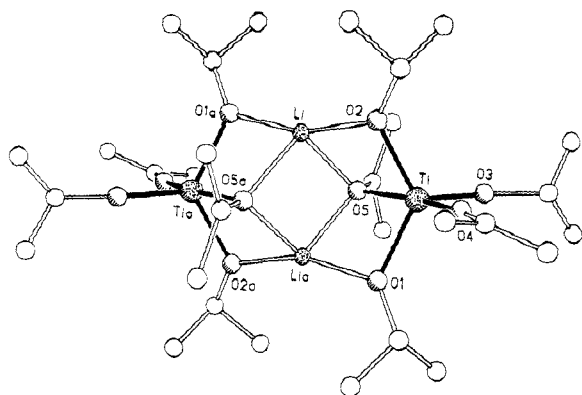
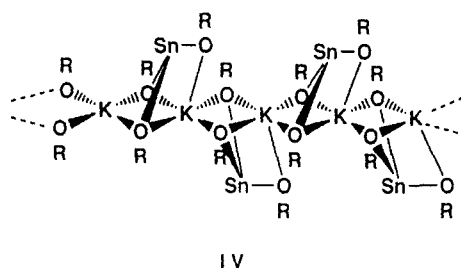


Figure 1. Molecular structure of $\text{Li}_2\text{Ti}_2(\text{O}^i\text{Pr})_{10}$. Unlabeled atoms are carbon. Hydrogen atoms have been deleted for clarity (reprinted from ref 170).

K^+ within an idealized $\text{K}(\mu\text{-O}^t\text{Bu})_3\text{Sn}$ unit (cf. TI) to two O^tBu of the next repeat unit. This gives a nearly linear chain $(\text{O}_3\text{KO}_2\text{K})_m$ polymer in which OKO angles are as small as 51° . The tin centers are on the exterior of this chain with their lone pair directed outward. Another description is as a polymeric chain of $[\text{K}(\mu\text{-O}^t\text{Bu})_2]_m^{m-}$ with $(\text{SnO}^t\text{Bu})^+$ units attached to two $\mu\text{-O}^t\text{Bu}$ oxygens and donating (by O^tBu) to K (see IV).



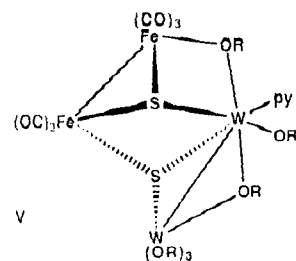
Reaction of equimolar LiO^iPr with $\text{Ti}(\text{O}^i\text{Pr})_4$ in isopropanol-pentane gives the product $[\text{LiTi}(\text{O}^i\text{Pr})_5]_2$, which is dimeric both in the solid state and in benzene (Figure 1), of generic structure II with $p = 2$ and $q = 0$. This pentane-soluble compound thus has the analogous tetrahedral geometry at Li as it does in $\text{Li}_2\text{Sn}_2(\text{O}^t\text{Bu})_6$, while the geometry at titanium is trigonal-bipyramidal with one equatorial and one axial terminal ligand. ^1H NMR shows complete site exchange of all four alkoxide types at 25° , but this is slowed in toluene-Freon 12 solution at -60 and -120°C .¹⁷⁰

The sodium analogue $\text{NaTi}(\text{O}^i\text{Pr})_5$ displays a polymeric structure in the solid state although the coordination numbers of the two metals remain unchanged.¹⁷¹

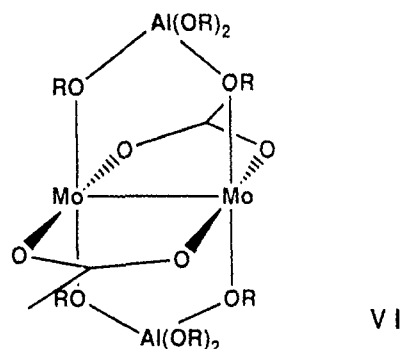
The structure of $\text{LiNb}(\text{OEt})_6$ is based on infinite helical chains composed of alternating $\text{Nb}(\text{OR})_6$ octahedra cis-linked by distorted-tetrahedral Li atoms.^{171b} In its partial hydrolysis derivative, $\text{Li}_2\text{Nb}_2(\text{OEt})_{10}(\text{OH})_2$, the metal atoms keep the same coordination numbers, the metal oxygen framework being derived from II. The hydroxo groups are in terminal position on the niobium atoms.^{171c}

Reaction of $\text{W}_2(\text{O}^i\text{Pr})_6(\text{py})_2$ with $\text{Fe}_2(\mu\text{-S})_2(\text{CO})_6$ gives $\text{W}_2\text{Fe}_2(\mu_3\text{-S})_2(\text{O}^i\text{Pr})_6(\text{CO})_5\text{py}$. This has the rhomboidal structural motif (V), with one alkoxide bridging tungsten to iron and both sulfurs bridging the irons to tungsten.¹⁷²

Reaction of $\text{Mo}_2(\text{OAc})_4$ and $[\text{Al}(\text{O}^i\text{Pr})_3]_4$, followed by sublimation (160°C) gives hydrocarbon-soluble, diamagnetic $\text{Mo}_2(\text{OAc})_2[\text{Al}(\text{O}^i\text{Pr})_4]_2$. This solid retains the



dimeric formula in benzene (cryoscopy) and in the vapor phase (mass spectrum). Both the ^{13}C and the ^1H NMR in the range -30 to $+50^\circ\text{C}$ show one acetate methyl and two types of isopropyl groups. The structure VI has a planar $\text{Al}_2\text{O}_4\text{Mo}_2$ ring with a strong



transannular interaction ($\text{Mo-Mo} = 2.079 \text{ \AA}$).⁸³ Alternatively, it can be described as the $\text{Mo}_2(\text{OAc})_4$ unit with two trans OAc bridging groups replaced by $\text{Al}(\text{O}^i\text{Pr})_4^-$ bridges. The Mo-O distances to acetate and O^iPr oxygen are essentially identical. Despite the numerous heterometallic alkoxides based on the $\text{Al}(\text{OR})_4$ ligand, $\text{Mo}_2(\text{OAc})_2[\text{Al}(\text{O}^i\text{Pr})_4]_2$ remains so far the only derivative characterized by X-ray diffraction.

The first Ba-Cu(II) heterometallic alkoxide has been obtained¹¹² according to eq 28. This compound, $\text{Ba}_2\text{Cu}_2(\mu_3\text{-OR})_4(\text{acac})_4(\text{ROH})_2$ ($\text{R} = \text{C}_2\text{H}_4\text{OMe}$), also represents one of the few structurally characterized heterometallic alkoxides with a "modified" coordination sphere. The metals are arranged in a rhomboid with two triply bridging 2-methoxyethoxide ligands above and below each of the two triangular planes defined by the two barium atoms and one copper atom (Figure 2). Each metal is also coordinated to one η^2 -acetylacetonate moiety. In addition, each barium is linked to one alcohol ligand through the ether oxygen. Finally, the geometry around the 9-coordinate Ba is a distorted capped rectangular prism; it is square-pyramidal for copper(II), as commonly found. Coordination numbers higher than 6 are observed as a result of the functional alkoxide and the chelating β -diketonate ligand.

Reduction of $\text{Ti}(\text{OAr}^{\text{Me}})_4$ with 1 equiv of Na-Hg in THF, followed by treatment with pyridine, gives deep purple (Ti^{III}) dimeric $[\text{NaTi}(\text{OAr}^{\text{Me}})_4\text{py}]_2$.¹⁷³ Half of the dimer has a trigonal-bipyramidal $[\text{Ti}(\text{py})(\text{OAr}^{\text{Me}})_4]^-$ unit (py axial) binding sodium via one axial and one equatorial aryloxy oxygen. This strongly bent 2-coordinate situation is so unsatisfactory for Na^+ that it binds to the phenyl ring of the $\mu\text{-OAr}^{\text{Me}}$ of an adjacent $\text{Ti}(\text{py})(\text{OAr}^{\text{Me}})_4^-$ unit in an η^6 -fashion ($\text{Na-C} = 2.79\text{-}2.88 \text{ \AA}$). This happens in a complementary fashion for the second sodium in the dimer (VII). This is of interest because of the Lewis acidity of (bent!) 2-coordinate sodium, as well as its ability to bind to the "soft" arene donor, even in the presence of potential oxygen donors

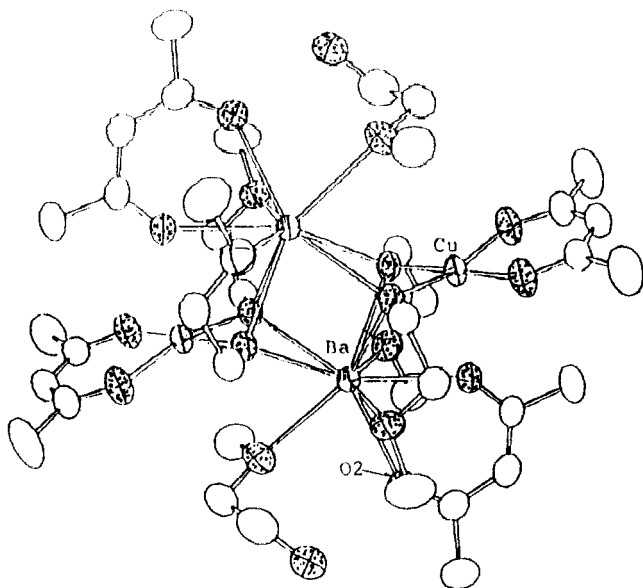


Figure 2. ORTEP view of $\text{Ba}_2\text{Cu}_2(\mu_3\text{-OC}_2\text{H}_4\text{OMe})_4(\text{acac})_4(\text{MeOC}_2\text{H}_4\text{OH})_2$ (reprinted from ref 112; copyright 1990 American Chemical Society).

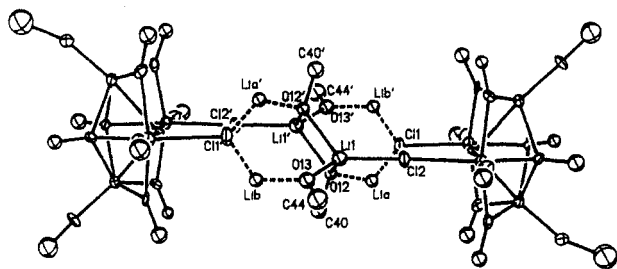


Figure 3. Molecular structure of $[\text{Y}_4(\text{O}^t\text{Bu})_{10}(\mu_4\text{-O})(\mu\text{-Cl})_2\text{Li}_4(\text{O}^t\text{Bu})_2]_2$ (reprinted from ref 174; copyright 1988 American Chemical Society).

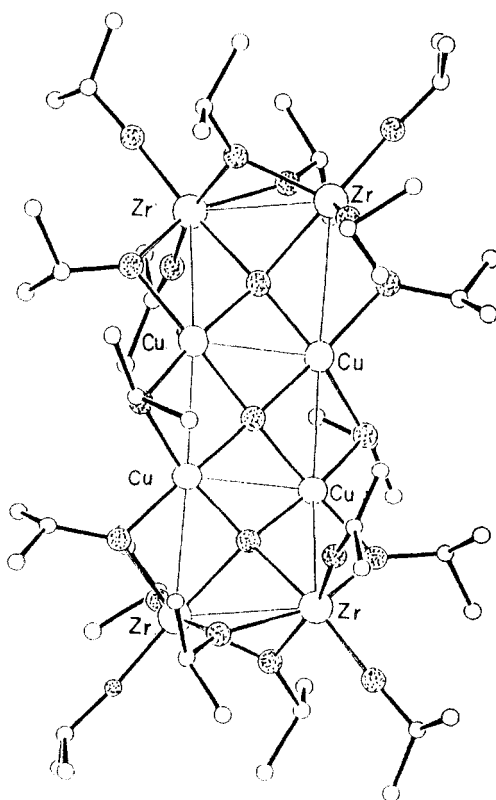
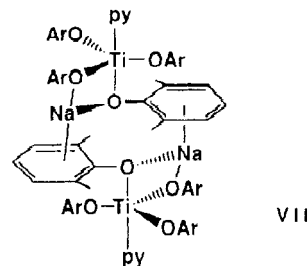


Figure 4. Molecular structure of $\text{Cu}_4\text{Zr}_4\text{O}_3(\text{O}^i\text{Pr})_{18}$.^{175a}

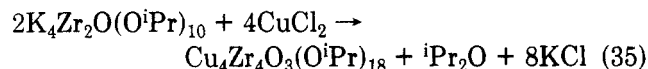


(phenoxide). The major influence of steric effects is evident from comparison with the OAr^iPr derivative. The *o*-isopropyl groups make the phenyl π -cloud inferior to alkoxide oxygen, and a monomeric compound, $(\text{THF})_2\text{Na}(\mu\text{-OAr}^i\text{Pr})_2\text{Ti}(\text{OAr}^i\text{Pr})_2$ results.¹¹⁷

4.1.3. $M_4M'_4$ Units

$[\text{Y}_4(\text{O}^t\text{Bu})_{10}(\mu_4\text{-O})(\mu\text{-Cl})_2\text{Li}_4(\text{O}^t\text{Bu})_2]_2$ obtained in low yield by metathesis of YCl_3 with LiO^tBu (eq 9) contains two $\text{Y}_4(\mu_3\text{-OR})_2(\mu\text{-OR})_4(\mu_4\text{-O})\text{Cl}_2^{2-}$ units related by a crystallographic C_2 axis linked by a complex lithium alkoxide $[\text{Li}(\text{O}^t\text{Bu})_2\text{Li}_2]_2$ unit via $\mu\text{-Cl}$ bridges (Figure 3).¹⁷⁴ The tetranuclear yttrium units can be viewed as two triangles fused along an edge, giving a butterfly arrangement of 6-coordinated metals. The lithium atoms are 4-coordinate. The overall structure can be considered as resulting from the association of several homometallic clusters.

Reaction of CuCl_2 with $\text{K}_4\text{Zr}_2\text{O}(\text{O}^i\text{Pr})_{10}$ in a 2:1 molar ratio in THF gives a high yield of $\text{Cu}_4\text{Zr}_4\text{O}_3(\text{O}^i\text{Pr})_{18}$, apparently according to eq 35. The structure of this



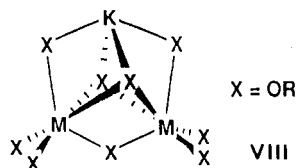
product (Figure 4) reveals an unusual planar array of four Cu(II) centers terminated on two edges by Zr_2 units and on the other two edges by O^iPr groups.^{175a} This nascent "ribbon" or sheet of CuO_4 components bears some structural similarity to the copper structural motif in copper-containing high- T_c materials.

$\text{Cd}_4\text{Sn}_4(\mu_4\text{-O})_2(\text{OAc})_{10}(\mu\text{-OCH}_2\text{CMe}_3)_4(\text{OCH}_2\text{CMe}_3)_6$ results from reaction between cadmium acetate and Sn(IV) neopentoxide in THF.^{175b} The overall centrosymmetric structure (Figure 5) can be described as two distorted $\text{Sn}_2\text{Cd}_2(\mu_4\text{-O})(\mu\text{-OAc})_3(\mu\text{-OR})_3(\text{OR})_2$ tetrahedra associated via the Cd atoms via four acetate ligands. Two of them are bridging chelating, forming a planar 8-membered Cd_4O_4 ring. The two remaining carboxylate ligands display a μ, η^4 "coat hanger" coordination mode above and below the Cd_4O_4 plane. All Sn atoms are 6-coordinate; two Cd atoms are also 6-coordinate, while those bearing the bridging chelating acetate ligands are 7-coordinate.

4.2. Heterometallic Alkoxides with $M:M' = 1:2$ Stoichiometry

4.2.1. MM'_2 Units

4.2.1.1. Closed Polyhedra (Triangular Units). Repetition of an earlier report¹⁷⁶ gave a hexane-soluble product shown to be $\text{KU}_2(\text{O}^t\text{Bu})_9$.¹²⁵ Its structure is shown in VIII, where the representation has been chosen to emphasize the metal triangle with two $\mu_3\text{-OR}$ groups, rather than to create an artificial division into $\text{U}_2(\text{O}^t\text{Bu})_9^-$ and K^+ units. Although the symmetry of



this unit is not 3-fold, but rather C_2 , the triangular representation provides a conceptual link to homometallic $M_3(OR)_n$ species. The 1H NMR of this paramagnetic species in C_6D_6 shows the 4:2:2:1 intensities expected for a static molecule. Note that K^+ is left in a very "exposed" coordination environment (i.e., no terminal ligands), with more than one hemisphere unoccupied. Spontaneous evolution into the mixed-valency $U_2(O^tBu)_9$ alkoxide is observed in solution.

Reaction of $Sr(O^iPr)_2$ with $Ti(O^iPr)_4$ (1:1 Sr:Ti ratio) in iPrOH -toluene is exothermic. The crystalline product has formula $Sr_2Ti(O^iPr)_8(^iPrOH)_5$.¹⁷⁷ This stoichiometry is attractive as a possible precursor for Sr_2TiO_4 . Its solubility is quite different from that of $Ti(O^iPr)_4$ and of $Sr(O^iPr)_2$. These crystals easily lose some of their alcohol. The solid-state structure (Figure 6) shows that two of the iPrOH molecules are lattice molecules (and not O-bound to metals). The remaining groups are linked as $Sr_2Ti(\mu_3-O^iPr)_2(\mu-O^iPr)_3(O^iPr)_3(^iPrOH)_3$. The authors describe this structure as three octahedra, with any two neighboring octahedra sharing one face. The bond lengths and angles of the octahedra around each metal are consistent only with alkoxides on Ti(IV) and the two Sr(II) centers having three terminal alcohol ligands and one terminal alkoxide. Finally the terminal ligands on Sr interact via hydrogen bonds with the two lattice iPrOH molecules. Upon heating, this compound first loses iPrOH and then $Ti(O^iPr)_4$.

This 2:1 heterobimetallic exemplifies well the problem of noncomplementarity of the number of available alkoxides (eight for two Sr(II) and one Ti(IV)) and the number of ligands needed to make each metal 6-coordinate in a triangular structure of type VIII. Neutral ligands (typically alcohols) are recruited to make up the deficit, and these are lost too readily to make this compound a viable CVD precursor. This is a situation where the use of alkoxides with neutral donor functionality (e.g., ether, amine, ...) in the side chain could be useful.¹⁷⁸

The heterometallic chloroalkoxide $BaTi_2Cl(O^iPr)_9(^iPrOH)$ displays a comparable structure; the barium atom bears the chloride as well as the isopropyl alcohol ligand.¹⁷¹

Reaction of $W_2(O^tBu)_6$ in hexane-ROH with one NaOR (R = iPr , CH_2^tBu) gives hexane-insoluble $[NaW_2H(OR)_8]_m$.¹³⁰ Addition of diglyme leads to a hydrocarbon-soluble adduct, (diglyme) $NaW_2H(O^iPr)_8$. The solid-state structure (IX) shows idealized mirror symmetry with hydride, Na, and the three diglyme oxygens on the mirror plane. The NaW_2 triangle

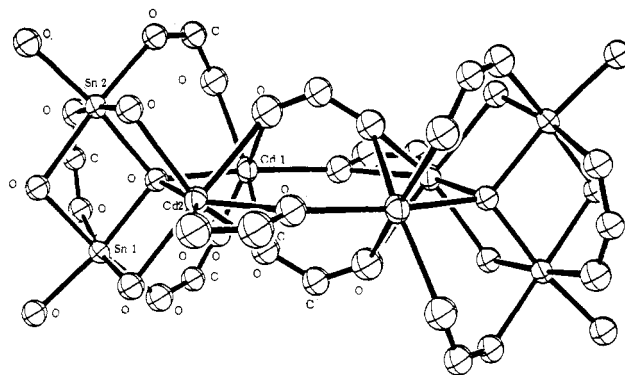
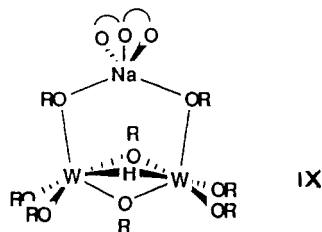


Figure 5. Molecular structure of $Cd_4Sn_4(\mu_4-O)_2(OAc)_{10}(OCH_2CMe_3)_{10}$ (only the oxygen atoms of the alkoxy groups are represented) (reprinted from ref 175b; copyright The Chemical Society).

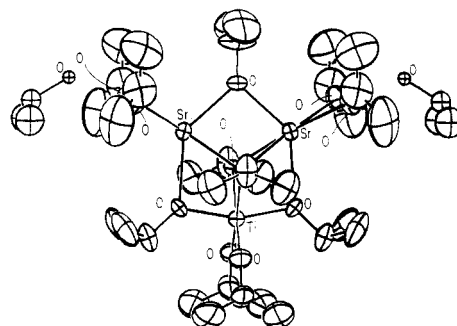
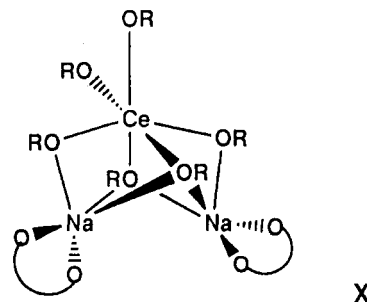


Figure 6. Molecular structure of $Sr_2Ti(O^iPr)_8(^iPrOH)_3 \cdot 2^iPrOH$. Unlabeled atoms are carbon. Hydrogen atoms have been omitted for clarity (reprinted from ref 177; copyright 1988 Pergamon).

contains a W-W multiple bond with the oxygens of three $\mu-O^iPr$ groups in the metal plane. The sodium coordination is crudely trigonal-bipyramidal. The alkoxide ligands are fluxional at 25 °C, but this migration is slowed at -45 °C in toluene. The most useful feature of the NMR of ^{23}Na (which is quadrupolar) is the line width, which is broad, as it is for Na^+ complexed by crown ethers, rather than sharp, as it is for "free" Na^+ . The ^{23}Na NMR of a mixture of $NaW_2H(O^iPr)_8$ and NaO^iPr in THF showed two signals, indicating the absence of fast exchange of sodium sites.

Reaction of $(NH_4)_2Ce(NO_3)_6$ with 8 mol of NaO^tBu in THF gave after workup 65% yield of solvent-free $Na_2Ce(O^tBu)_6$. Recrystallization from DME gave an adduct shown by X-ray diffraction to be $(DME)_2Na_2Ce(\mu_3-O^tBu)_2(\mu-O^tBu)_2(O^tBu)_2$ (X).¹⁷⁹ An-



other description of this unit is that $(DME)Na^+$ units occupy two faces of a $Ce(O^tBu)_6^{2-}$ octahedron. In that formalism, it is curious that the $(DME)Na^+$ electrophiles occupy adjacent faces of the octahedron rather than trans faces, which would give a more linear Na/Ce/Na geometry as found in $(THF)_6Na_2W(OPh)_6^+$.

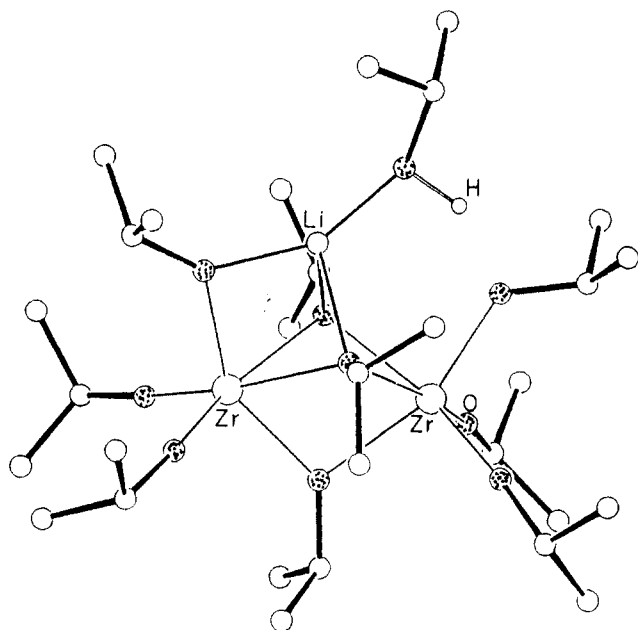


Figure 7. Molecular structure of $\text{LiZr}_2(\text{O}^i\text{Pr})_9(\text{O}^i\text{PrOH})$, omitting hydrogens on carbon: open circles, carbon; stippled circles, oxygen.⁷⁰

The sodiums adopt neither trigonal-bipyramidal nor square-pyramidal idealized geometries for coordination number 5. An alternative view of this structure, which accommodates naturally the adjacent location of the sodium ions, is that it is only a variant of the commonly adopted $\text{M}_3(\mu_3\text{-OR})_2(\mu\text{-OR})_3(\text{OR})_6$ structure with the $\mu\text{-OR}$ of the Na/Na edge omitted.

If $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ is allowed to react with 6.5 mol of NaO^tBu in THF, $\text{NaCe}_2(\text{O}^t\text{Bu})_9$ is obtained. It is isostructural with $\text{KU}_2(\text{O}^t\text{Bu})_9$ and can be written $\text{NaCe}_2(\mu_3\text{-O}^t\text{Bu})_2(\mu\text{-O}^t\text{Bu})_3(\text{O}^t\text{Bu})_4$. The ^1H and ^{13}C NMR spectra in benzene are consistent with a non-fluxional molecule.

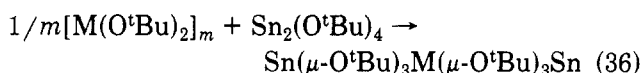
The production of Na_2Ce and NaCe_2 compounds from similar (8:1 and 6.5:1) ^tBuO to Ce mole ratios is at first remarkable. However, after allowance is made for the consumption of two O^tBu^- per Ce by reaction with NH_4^+ , the above reactions are effected with 6:1 and 4.5:1 O^tBu to Ce ratios, which are exactly the ratios found in the products.

$\text{Mo}_2\text{WO}(\text{O}^i\text{Pr})_{10}$ was found to be isomorphous with $\text{Mo}_3\text{O}(\text{O}^i\text{Pr})_{10}$ and thus has an oxo-capped cluster structure $\text{Mo}_2\text{W}(\mu_3\text{-O})(\mu_3\text{-O}^i\text{Pr})(\mu\text{-O}^i\text{Pr})_3(\text{O}^i\text{Pr})_6$. Disorder problems between the two metals precluded a detailed analysis.⁵⁷

The 1:1 reaction of LiNMe_2 with $\text{Zr}_2(\text{O}^i\text{Pr})_8(\text{O}^i\text{PrOH})_2$ in THF gives a high yield of $\text{LiZr}_2(\text{O}^i\text{Pr})_9(\text{O}^i\text{PrOH})$.⁷⁰ As shown in Figure 7, this introduces a new structural type because lithium is apparently too small to adopt a closed triangular structure. Instead, the unit $\text{Li}(\text{O}^i\text{PrOH})^+$ interacts with the face-shared bioctahedral $\text{Zr}_2(\text{O}^i\text{Pr})_9^-$ via one terminal and two $\mu\text{-O}^i\text{Pr}$ of the Zr_2 unit. This establishes coordination number 4 at lithium. The hydroxyl proton of the coordinated alcohol then hydrogen bonds to a nearby alkoxide that is terminal on the otherwise uninvolved zirconium.

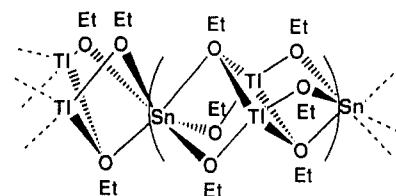
4.2.1.2. Open Structures. Veith^{105,180} has utilized a classic principle to demonstrate the formation of a heterobimetallic compound from $[\text{M}(\text{O}^t\text{Bu})_2]_m$ ($\text{M} = \text{Sr}, \text{Ba}$) and $\text{Sn}_2(\text{O}^t\text{Bu})_4$: The former compounds are insoluble in benzene but dissolve upon addition of Sn_2

$(\text{O}^t\text{Bu})_4$. The reaction stoichiometry is shown in eq 36.



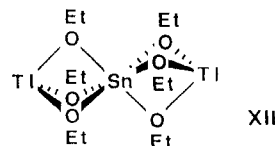
The products are hexane-soluble and show molecular ions in the mass spectra and a ^1H NMR singlet. X-ray diffraction for $\text{M} = \text{Sr}$ established the $\mu\text{-O}^t\text{Bu}$ formulation. The molecule has crystallographic S_6 symmetry, so that Sr lies on a center of symmetry with all pairs of $\mu\text{-O}$ rigorously trans. The trigonal-pyramidal tins have $\text{O-Sn-O} = 82.3^\circ$. The oxygens are coplanar with their three attached groups. Since reaction does not proceed for $\text{M} = \text{Ca}$, $\text{Sn}_2(\text{O}^t\text{Bu})_4$ is selective for separation of, e.g., Sr from Ca. The low-valent metal, Sn(II), can further react as Lewis base toward transition-metal fragments, and $\text{Cr}(\text{CO})_5\text{Sn}(\mu_3\text{-O}^t\text{Bu})_3\text{Ba}(\mu_3\text{-O}^t\text{Bu})_3\text{SnCr}(\text{CO})_5$ has been structurally characterized.¹⁰⁵

The 2:1 reaction of TlOEt with $\text{Sn}(\text{OEt})_4$ in toluene gives a quantitative yield of a compound of empirical formula $[\text{Tl}_2\text{Sn}(\text{OEt})_6]_m$.¹⁸¹ It is a one-dimensional polymer in the solid state with 6-coordinate Sn and 4-coordinate Tl. Four ethoxides are μ and two are μ_3 between Tl and Sn. The repeat unit in the chain is indicated in parentheses in XI. Note that the SnTl_2Sn unit at the right of this sketch is precisely of generic structure II with $p = 3$ and $q = 0$. The connection of four cations to *cis*- $\text{Sn}(\text{O})_2$ units makes it clear that some $\mu_3\text{-OEt}$ units are required, and the linear (rather than zig-zag) development of the catenation is thus naturally imposed. Adjacent chains are mutually separated by an exterior of radially directed ethyl groups (XI). This



XI

compound is sufficiently volatile to give an electron impact mass spectrum that shows the formula unit and dissolves in benzene to give singlets in both ^{119}Sn and ^1H NMR (temperature invariant to -90°C , showing Sn-H coupling at 25°C). The ^1H NMR spectra are too simple to agree with the repeat unit in the solid-state structure, yet formation of independent Tl^+ and octahedral $\text{Sn}(\text{OEt})_6^{2-}$ units is inconsistent with the hydrocarbon solubility. Cryoscopic measurements at two different concentrations indicate a dissolved $\text{Tl}_2\text{Sn}(\text{OEt})_6$ unit. The invariance of the ^1H NMR spectrum in benzene to added TlOEt rules out dissociation of TlOEt from $\text{Tl}_2\text{Sn}(\text{OEt})_6$. The invariance of the ^1H NMR spectrum to added EtOH was offered as evidence that only coordinatively saturated metals are present for the species in solution. The authors suggest structure XII in solution, identical with that of $\text{Sn}_2\text{Sr}(\text{O}^t\text{Bu})_6$.

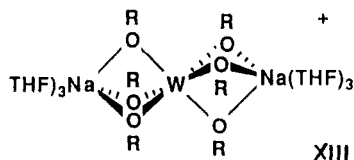


XII

This example of structural change from solid to solution or gas phase emphasizes the need to study each

phase for heterometallic alkoxides.

$[(\text{THF})_6\text{Na}_2\text{W}(\text{OPh})_6][\text{OPh}]$, obtained by reduction of $\text{W}(\text{OPh})_6$ by Na, also has the linear structure XIII.¹¹⁸ This product is different from that obtained by reduction with Li or K, but the W-O distance (average 1.995 Å) is very close to that in $(\text{THF})_2\text{LiW}(\text{OPh})_6$.



The solid-state structure of $(\text{THF})_2\text{Li}_2\text{V}(\text{OAr}^{\text{iPr}})_4$ shows a $(\text{THF})\text{Li}(\mu\text{-OAr}^{\text{iPr}})_2\text{V}(\mu\text{-OAr}^{\text{iPr}})_2\text{Li}(\text{THF})$ arrangement, with a VO_4 geometry distorted toward (but still far from) square-planar; it is farther from tetrahedral than are $(\text{THF})\text{LiV}(\text{OAr}^{\text{iPr}})_4$ or $\text{V}(\text{OAr}^{\text{iPr}})_4^-$. The distortion from a planar geometry was attributed in part to the small "bite" of the $\text{Li}(\text{OAr}^{\text{iPr}})_2^-$ unit (79°) and in part to steric effects of the bulky Ar^{iPr} groups. The compound was also characterized by solid-state EPR and visible-UV spectra.⁵²

The chloro heterometallic boroxide $(\text{THF})_2\text{Li}(\mu\text{-Cl})_2\text{Co}(\mu\text{-OBMes}_2)_2\text{Li}(\text{THF})_2$, which derives from metathesis reactions between CoCl_2 and LiOBMes_2 , displays a comparable structure.¹⁸² All metals have a distorted-tetrahedral surrounding.

Insoluble (presumably polymeric) $[\text{Cr}(\text{OAr}^{\text{Me}})_2(\text{THF})]_m$ reacts with NaOAr^{Me} in THF and TMEDA to generate $(\text{TMEDA})_2\text{Na}_2\text{Cr}(\text{OAr}^{\text{Me}})_4$.³⁰ Its structure consists of a linear array $(\text{TMEDA})\text{Na}(\mu\text{-OAr}^{\text{Me}})_2\text{Cr}(\mu\text{-OAr}^{\text{Me}})_2\text{Na}(\text{TMEDA})$, with a planar Na_2CrO_4 arrangement.

4.2.2. $M_2M'_4$ Units

Recrystallization of $\text{L}_4\text{Na}_2\text{Cr}(\text{OAr}^{\text{Me}})_4$ compounds in toluene in the presence of small amounts of L (THF, py) results in partial loss of the ligand and thus *dimerization*. For L = pyridine, the structure corresponds to centrosymmetric $(\text{py})_4\text{Na}_4\text{Cr}_2(\text{OPh})_8$. Reaction of $\text{CrCl}_2(\text{THF})_2$ with NaOPh and L in THF gives $\text{L}_x\text{Na}_4\text{Cr}_2(\text{OPh})_8$,¹⁸³ where the number of TMEDA, THF, or py ligands (L) is influenced by the crystallization solvent. X-ray diffraction of the case where one THF is coordinated to each Na revealed a *trans*- Cr_2Na_4 octahedron with one $\mu_3\text{-OPh}$ on each face. The Na^+ are square-pyramidally coordinated, with THF axial. The Cr(II) lie 0.25 Å outside the plane of their four $\mu_3\text{-O}$ neighbors and thus have a distorted square-planar coordination. A structure of similar symmetry is adopted by numerous $\text{L}_4\text{Li}_4\text{Cr}_2\text{R}_8$ compounds,¹⁸⁴ but with the large difference that these contain a quadruple (very short) Cr-Cr bond (1.98 Å, compared to 3.622 Å for the phenoxide).

$\text{Na}_2\text{Gd}_4(\mu_6\text{-O})(\mu_3\text{-O}^t\text{Bu})_8(\text{O}^t\text{Bu})_4$ has been obtained as a minor product by reaction between gadolinium chloride, sodium cyclopentadienide, and potassium *tert*-butoxide.¹⁸⁵ Only X-ray characterization has been performed. The structure corresponds to a nearly ideal octahedron whose center is occupied by the $\mu_6\text{-oxo}$ ligand, while the two sodium atoms are in apical positions. The faces of the octahedron are capped by $\mu_3\text{-alkoxo}$ ligands, which in addition to the oxo ligand ensure a coordination number of 5 for sodium, while all Gd at-

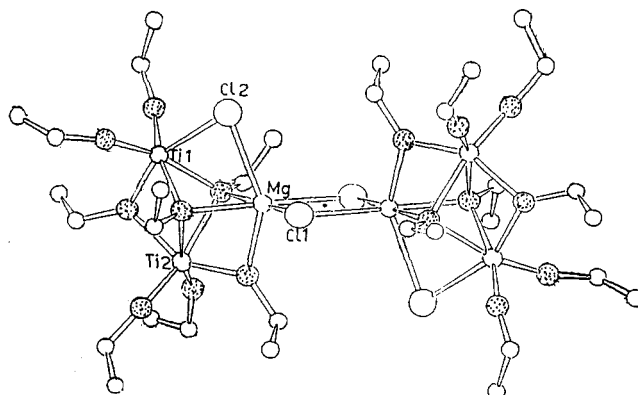
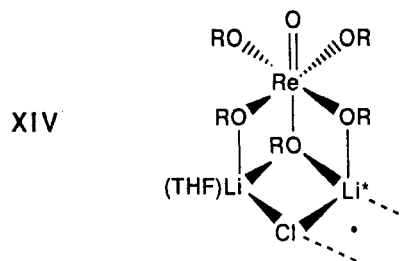


Figure 8. Molecular structure of $[\text{Ti}_2(\mu_3\text{-OR})_2(\mu\text{-OR})_4(\mu\text{-Cl})_2\text{Mg}_2(\mu\text{-Cl})_2]$ (R = Et) (reprinted from ref 61; copyright Elsevier Sequoia).

oms are 6-coordinated, as they are also linked to terminal alkoxides.

Reaction of ReOCl_4 with five LiO^{iPr} in Et_2O gives a hydrocarbon-soluble paramagnetic species. Recrystallization from THF, where the electrical conductivity is so low as to suggest a molecular ("ion-pair") species, gives the centrosymmetric dimer $[\text{LiReO}(\text{O}^{\text{iPr}})_5\text{LiCl}(\text{THF})]_2$.¹⁸⁶ The structure is best described in terms of the $\text{LiReO}(\text{O}^{\text{iPr}})_5\text{LiCl}(\text{THF})$ subunit, which has an ReLi_2 triangle connected by $\mu_3\text{-OR}$, two $\mu\text{-OR}$, and one $\mu\text{-Cl}$. Re has three terminal ligands. One lithium achieves 4-coordination by binding one THF, but Li^* achieves 4-coordination by coordination to Cl of an identical (center of symmetry shown) $\text{LiReO}(\text{O}^{\text{iPr}})_5\text{LiCl}(\text{THF})$ unit, which makes Cl become μ_3 . The two lithium centers are thus inequivalent (XIV).



The hydrocarbon-soluble compound $[\text{Ti}_2(\mu_3\text{-OR})_2(\mu\text{-OR})_2(\text{OR})_4(\mu\text{-Cl})_2\text{Mg}_2(\mu\text{-Cl})_2]$ (R = Et) has been obtained according to eq 15. The molecule is a centrosymmetric dimer (Figure 8) with two triangular Ti_2Mg cores connected via two doubly bridging chlorine atoms.⁶¹ All metal atoms are 6-coordinated, but the titanium atoms are of two different types. Ti1 is linked to a chlorine atom, while Ti2 has only alkoxide ligands. Cryoscopic measurements have confirmed the molecular complexity of the compound, which has been shown by ^1H and ^{13}C NMR to be highly fluxional, as commonly observed for alkoxides.

A similar structure is adopted by $\text{Ba}_2\text{Zr}_4(\text{O}^{\text{iPr}})_{20}$, which has been obtained in high yield by oxidation of metallic barium by the two acidic protons in $\text{Zr}_2(\text{O}^{\text{iPr}})_8(\text{iPrOH})_2$.⁷⁰ The centrosymmetric dimer (Figure 9) is composed of two triangular $\text{BaZr}_2(\mu\text{-O}^{\text{iPr}})_2(\text{O}^{\text{iPr}})_3(\text{O}^{\text{iPr}})_4^+$ units linked by the bariums via two O^{iPr} bridges.

Quite a distinct structure, a closed polyhedron, is adopted by $\text{K}_4\text{Zr}_2\text{O}(\text{O}^{\text{iPr}})_{10}$, which comes from deprotonation of $\text{Zr}_2(\text{O}^{\text{iPr}})_8(\text{iPrOH})_2$ with two KH .¹²⁶ The oxide ion, which is encapsulated in a K_4Zr_2 octahedron

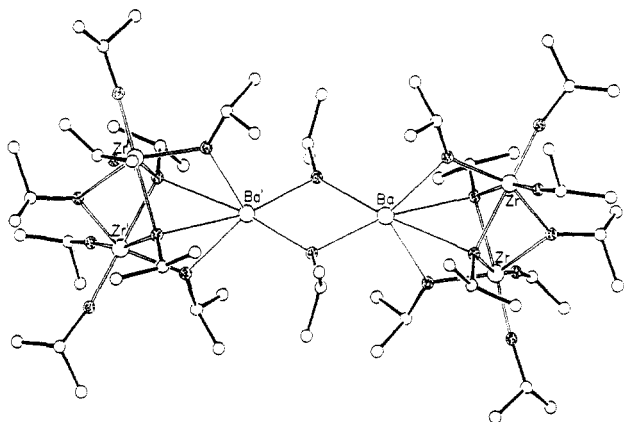


Figure 9. Structure of centrosymmetric $\text{Ba}_2\text{Zr}_4(\text{O}^i\text{Pr})_{20}$, omitting hydrogens: open circles, carbon; stippled circles, oxygen.⁷⁰

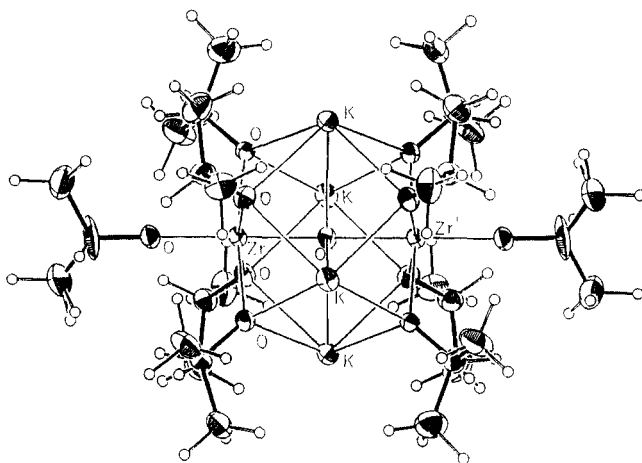


Figure 10. Molecular structure of $\text{K}_4\text{Zr}_2\text{O}(\text{O}^i\text{Pr})_{10}$.¹²⁶

(Figure 10), originates from an alkoxide group, and the overall structure is related to that of $\text{Na}_2\text{Gd}_4(\mu_6\text{-O})(\mu_3\text{-O}^t\text{Bu})_8(\text{O}^t\text{Bu})_4$.

4.3. Heterometallic Alkoxides with $\text{M}:\text{M}' = 2:3$ Stoichiometry

4.3.1. $\text{M}_2\text{M}'_3$ Units

The reaction of LaCl_3 with NaOR ($\text{R} = p\text{-tolyl}$) gives $\text{La}_2\text{Na}_3(\mu_4\text{-OR})_3(\mu\text{-OR})_6(\text{THF})_5$.¹⁸⁷ The structure is a trigonal-bipyramid of metals (La axial), each of which has a terminal THF. Each of the nine edges of the bipyramid has an aryloxy bridge. The three bridges on the equatorial/equatorial edges are also within bonding distance of the apical lanthanum centers, and are thus μ_4 . As a result, Na is 5-coordinate and La is 7-coordinate (XV).

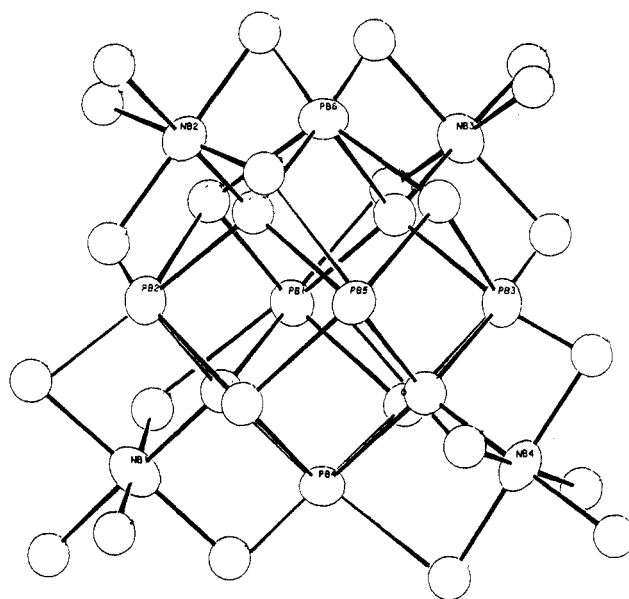
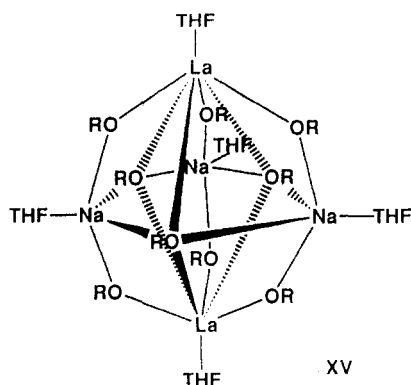


Figure 11. ORTEP view showing the metal oxygen core of $\text{Pb}_6\text{O}_4(\text{OEt})_4[\text{Nb}(\text{OEt})_5]_4$ (reprinted from ref 59; copyright The Chemical Society).

4.3.2. $\text{M}_4\text{M}'_6$ Units

Reaction between $\text{Pb}_4(\mu_4\text{-O})(\text{OEt})_8$ and $[\text{Nb}(\text{OEt})_5]_2$ offered $\text{Pb}_6\text{Nb}_4(\mu_4\text{-O})_4(\mu_3\text{-OEt})_4(\mu\text{-OEt})_{12}(\text{OEt})_8$ whose structure was established by X-ray diffraction (Figure 11).⁵⁹ The structure is based on a quite regular octahedron of lead atoms alternatively capped by μ_4 -oxo and μ_3 -ethoxide ligands. Each oxo group is connected to a $\text{Nb}(\text{OEt})_5$ moiety, and the overall structure can be viewed as $\text{Pb}_6\text{O}_4(\text{OEt})_4$ acting as a tetradentate ligand toward the $\text{Nb}(\text{OEt})_5$ Lewis acid. Disproportionation reactions are observed in solution.¹⁸⁸

4.4. Heterometallic Alkoxides with $\text{M}:\text{M}' = 1:3$ Stoichiometry

Heterometallic alkoxides having a 1:3 stoichiometry are largely represented by the derivatives involving aluminum $\text{M}[\text{Al}(\text{O}^i\text{Pr})_4]_3$ ($\text{M} = \text{Ln}, \text{Fe}, \text{Cr}$) (Table I). Unfortunately, no X-ray data are available so far, although ^{27}Al NMR could bring some evidence for 4-coordinate aluminum.

$(\text{DME})_3\text{Li}_3\text{V}(\text{OPh})_6$ synthesized according to eq 10 appears to be the only structurally characterized heterometallic alkoxide corresponding to a 1:3 stoichiometry.⁵¹ It has crystallographic 3-fold symmetry, and each $\text{Li}(\text{DME})$ group is bridged to V by two different phenoxides ($\text{O}-\text{V}-\text{O} = 77.7^\circ$).

4.5. Heterometallic Alkoxides of High Nuclearity

X-ray diffraction has established the product resulting from reaction between MoCl_5 and MgCl_2 in alcoholic-aqueous media to be $[\text{Mg}(\text{MeOH})_6]_2[\text{Mg}_2\text{Mo}_8\text{O}_{22}(\text{OMe})_6(\text{MeOH})_4](\text{MeOH})_6$. This mixed-valence ($\text{Mo}^{\text{V}}\text{Mo}^{\text{VI}}$) heterometallic oxoalkoxide dianion (Figure 12) contains μ^- , μ_3^- , and μ_4^- -oxides and μ -OMe bridges. Each Mo has one terminal oxide O^{2-} ligand, and each Mg^{2+} has two terminal methanol molecules (and two μ^- and two μ_3^- -oxides). The anion is centrosymmetric, all metals are octahedral, and metal-metal bonding between some molybdenum atoms is observed.¹⁵

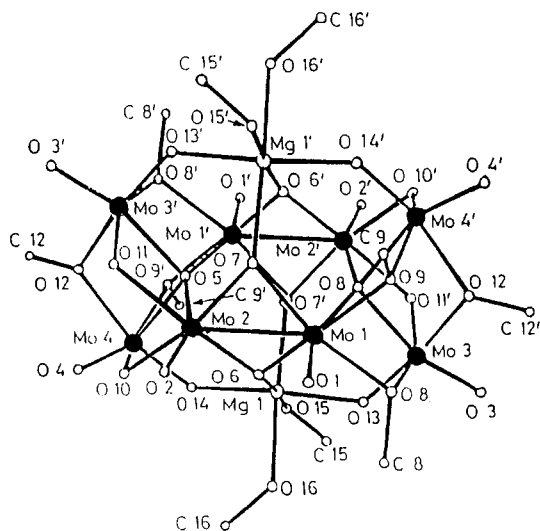


Figure 12. ORTEP view of the centrosymmetric $[\text{Mg}_2\text{Mo}_8\text{O}_{22}(\text{OMe})_6(\text{MeOH})_4]^{2-}$ anion (reprinted from ref 15; copyright 1989 The Chemical Society).

4.6. Fluorinated Heterometallic Alkoxides

Heterometallic alkoxides with fluorinated alkoxide groups are scarce and were mainly limited to $\text{M}[\text{Al}(\text{OCH}_2\text{CF}_3)_4]_n$ ($\text{M} = \text{Cu}(\text{II}), \text{Cr}(\text{III})$) and the related mixed alkoxides $\text{M}[\text{Al}(\text{O}^i\text{Pr})_{4-x}(\text{OCH}_2\text{CF}_3)_x]_n$ (Table I). The present interest in fluorinated heterometallic alkoxides stems from the higher volatility (bp 120°C compared to 215°C (0.8 mm)) for $\text{Cr}[\text{Al}(\text{OR})_4]_n$ with $\text{R} = \text{CH}_2\text{CF}_3$ and ^iPr , respectively.⁸⁰ Cesium-fluorine bonds in $\text{CsY}[\text{CF}_3\text{COCHCOCF}_3]_4$, for instance, make this compound volatile above 180°C .¹⁴⁵ However, fluorinated ligands can also lead to metallic fluorides as stable residues during MOCVD pyrolysis and thus to impurities in the final film. Such impurities might however also promote epitaxial growth,¹⁸⁹ thus increasing the value of novel fluorinated derivatives. The topic of metal binding to fluorine that is covalently bound to carbon is a newly developing but important field.¹⁹⁰ When an $\text{M}-\text{F}$ interaction exists in a precursor, it is expected to influence thermal decomposition mechanisms, and therefore product composition.

Recent results¹⁹¹ show that strong $\text{M}-\text{F}$ interactions may already be present in the precursors. Reaction of four $\text{NaOCH}(\text{CF}_3)_2$ with CuCl_2 gives sublimable (100°C (10^{-5} mmHg)), THF-soluble $\text{Na}_2\text{Cu}[\text{OCH}(\text{CF}_3)_2]_4$. This product is a polymer in the solid state (although clearly not so in the vapor phase). The polymeric repeat unit is $\text{Na}_2[(\text{CF}_3)_2\text{CHO}]_2\text{Cu}[\mu\text{-OCH}(\text{CF}_3)_2]_2$, with each sodium bridging to two alkoxides of adjacent monomer units. The $\text{Na}-\text{O}$ distances average 2.3 \AA , and the $\text{O}-\text{Na}-\text{O}$ angle is 144° . The coordination sphere of each sodium is comprised not only of two oxygens but also of five fluorines at distances of $2.48\text{--}2.79 \text{ \AA}$. Three fluorines are from two alkoxides on one copper, and two fluorines are from two alkoxides on the second copper. These complicated 7-coordinate structures for sodium are shown in Figure 13.

4.7. General Comments

The large majority of the heterometallic alkoxides characterized in the solid state correspond to derivatives in which one of the metals is lithium or sodium, the OR ligands being based either on bulky aliphatic groups

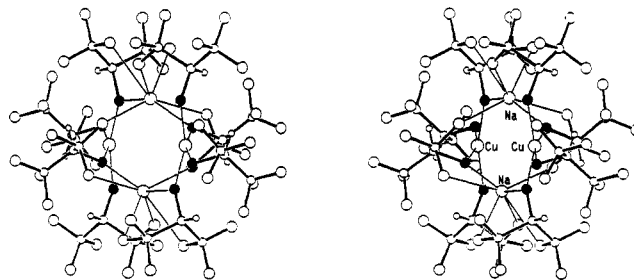


Figure 13. Stereoscopic drawing of the $\text{Na}_2[\text{Cu}\{\text{OCH}(\text{CF}_3)_2\}_4]_2$ portion of the polymeric chain in $\text{Na}_2\text{Cu}\{\text{OCH}(\text{CF}_3)_2\}_4$ viewed along the edge of the CuO_4 planes. Black circles are oxygen (reprinted from ref 191).

(C^tBu_3 , CH^iBu_2) or on aryloxides in order to minimize the tendency to polymerize and/or to give close polyhedral structures (highly soluble compounds and often crystals of poor quality). In the case of the aryloxides, the metal is also often in a low oxidation state. This represents only a small sampling of available OR groups, and there are certainly alternatives to steric blocking of polymerization. For example, alkoxide groups carrying donor functionality (tertiary amines, ethers, etc.) deserve study in homometallic alkoxide chemistry. Finally, these compounds represent only a small fraction of the heterometallic alkoxides reported in the literature (Tables I and II) and are based on $\text{M}(\text{OR})_4^-$ ($\text{M} = \text{Al}, \text{Ga}$), $\text{Zr}_2(\text{OR})_9^-$, or $\text{M}(\text{OR})_6^-$ ($\text{M} = \text{Nb}, \text{Ta}$) moieties associated to di-, tri-, tetra-, or pentavalent metals.

The coordination number of the alkali metal varies generally from 2 to 5, depending on the number of neutral ligand O (alcohol, THF, DME, diglyme, ...) or N (TMEDA) donors, and thus on the crystallization conditions, which can also affect the oligomerization of the product. An unusual coordination number of 7 for sodium is observed in $[\text{Na}_2\text{Cu}\{\text{OCH}(\text{CF}_3)_2\}_4]_m$ as a result of strong interactions with fluorine atoms. These results suggest interesting developments for alkoxides with fluorinated OR groups.

Structural data on heterometallic alkoxides involving simple alkoxide ligands (OEt, O^iPr , ...) and no alkali metal remain limited. Some derivatives with alkaline-earth metals (Mg, Ba, Sr) have been studied; the coordination number—generally 6 for these metals—is achieved by additional molecules of the parent alcohol. These solvates often display a poor stability, and thus their crystallinity is easily lost; $\text{MgNb}_2(\text{OEt})_{12}(\text{EtOH})_2$, for instance, is converted to an oil by desolvation.⁸⁸

The nuclearity of the various heterometallics varies from 2 to 16 (for $[\text{Y}_4(\text{O}^t\text{Bu})_{10}(\mu\text{-4O})(\mu\text{-Cl})_2\text{Li}_4(\text{O}^t\text{Bu})_2]_2$). In this case, the overall structure is in fact an association of homometallic clusters. The other metallic frameworks are based on linear arrays (up to three metals) or closed polyhedron, triangular M_3 units, M_4 rhombus, or bipyramidal M_5 moiety while M_6 units correspond to an octahedron of metals or result from various associations of triangular M_3 units. The coordination number of the metal is controlled by the bulk of the alkoxide ligand. Oxo O^{2-} ligands—generated during the experimental procedure—can be a means of ensuring high coordination as encapsulated ligands ($\mu_6\text{-O}$, for instance) in *closo* polyhedra.

No structure of a heterometallic alkoxide (containing three different metal elements) has been solved by X-ray so far.

5. Reactivity

5.1. Stability with Respect to Dissociation

The stabilities of heterometallic alkoxides are generally judged by their spontaneous dissociation in solution or upon heating and volatilization in the vapor phase. The factors governing these stabilities are not yet well understood, and the purification of heterometallic alkoxides by recrystallization and/or distillation must therefore be carefully considered (Tables I and II).

It has often been thought that the stability of a heterometallic alkoxide increases with the difference in the electronegativity between the two metals M and M' . This explains the stability increase in the series $MM'(OR)_6$ ($M = Nb, Ta$) going from K to Na and to Li^+ and the extensive dissociation of $NbTa(OMe)_{10}$ in solution.⁵⁵ However, the high stability of $Al[Ga(O^iPr)_4]_3$ or $Ga[Al(O^iPr)_4]_3$ is more difficult to understand on this basis.⁵⁴

Dissociation of the heterometallic species in solution leads to a loss of homogeneity at a molecular level, but the overall solution stoichiometry between the different metals is maintained, and such solutions can still be used to obtain the materials of the desired stoichiometry. The situation is more complex for MOCVD applications.⁵

Many volatile heterometallic alkoxides have been reported in the literature.⁴ It should be emphasized that the volatility of alkali or alkaline-earth metals is often considerably enhanced by combination with a higher valency metal, either a transition metal or one from group III. For instance, $Ba(O^iPr)_2$ is thermally unstable, but $BaNb_2(O^iPr)_{12}$ can be distilled unchanged at $\sim 170^\circ C$. This could thus be considered for the transport of poorly volatile elements in MOCVD conditions. $LiNb(OR)_6$, for instance, has the correct stoichiometry for obtaining lithium niobate ($LiNbO_3$). Unfortunately, partial disproportionation is sometimes observed under MOCVD conditions, leading to inhomogeneity in the final material.⁴ The problem has been overcome by using two precursors, lithium dipivaloyl-methanide and niobium pentamethoxide. Heterometallic alkoxides are also often solvated by alcohols, but the high lability of these ligands precludes the use of such derivatives in MOCVD applications. This is for instance the case of $Sr_2Ti(O^iPr)_8(^iPrOH)_5$, although its stoichiometry is attractive as a possible precursor for Sr_2TiO_4 .¹⁷⁷ Functional alkoxides might be a way to complete the coordination sphere of the metal without the need of neutral ligands, and thus improve their thermal stability. To the best of our knowledge, there is no example so far of a heterometallic alkoxide used successfully via classical MOCVD techniques to obtain a mixed-metal oxide coating.

Spray pyrolysis or flash evaporation techniques appear to be more tolerant of the properties of these heterometallic precursors. An isopropyl alcohol solution of $BaTi(O^iPr)_6$ was used as single precursor for a crystalline deposit of $BaTiO_3$.⁴

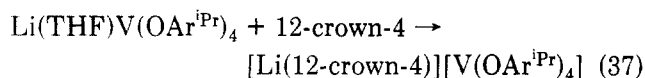
Systematic studies of the thermal stability (differential thermal analysis, influence of the addition of the free ligand or of a reactive molecule to the carrier gas, ...) of heterometallic alkoxides whose formulation could be useful for a material of technological value seems

warranted in order to "guide" the synthesis of compounds having a tailored volatility and stability.

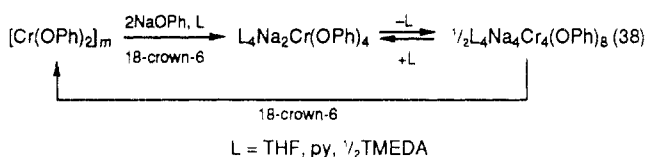
5.2. Coordination

The formation of heterometallic species can be viewed as Lewis acid-base association reactions. As such, dissociation reactions, either spontaneous or promoted by Lewis bases, can occur.

The influence of Lewis bases is most documented on low-valent transition metal-alkali metal aryloxides ($M = Ti(III), V(III), Cr(II)$). The Lewis acidity of the alkali-metal cation plays an important role in the assemblage of the heterometallic unit. Appropriate crown ethers (18-crown-6, 12-crown-4) are generally used as a means to extract the alkali metal from the transition-metal coordination sphere, giving salts (eq 37) or polymeric alkoxides.



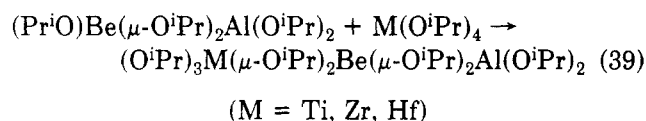
The $L_4Na_2Cr(OPh)_4$ and $L_4Na_4Cr_2(OPh)_8$ adducts are converted to insoluble polymeric $[Cr(OPh)_2]_m$ by crown ethers (eq 38).³⁰ Similar observations were made for $[(TMEDA)Na(\mu-OAr^{Me})_3Cr]_2$.



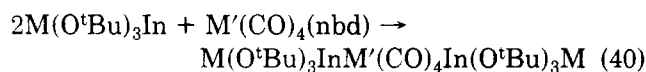
The addition of pyridine to a toluene solution of $(THF)_2NaTi(OAr^{iPr})_4$ leads to $Ti(OAr^{iPr})_3(py)_2$, showing the ability of pyridine to separate $NaOAr^{iPr}$ from the $Ti(III)$ center. The competition of different Lewis bases is thus controlling the production of heterometallic alkoxides and the condensation of these.

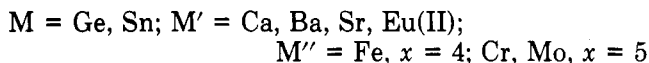
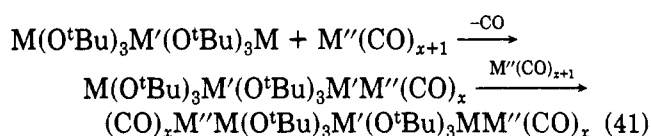
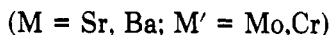
Heterometallic alkoxides containing the $Al(OR)_4$ groups might be less sensitive (with respect to dissociation of the heterometallic species), since this group is more flexible and can behave as a bidentate or tridentate ligand.⁹¹ Common Lewis bases such as pyridine or parent alcohols are less sterically hindered than a $\mu_3-Al(OR)_4$ moiety and thus may allow a metal to attain its common coordination number. According to electronic spectra, $Ni(II)$ is, in part, 4-coordinated in $NiAl_2(O^iPr)_8$ but converts to octahedral species $NiAl_2(O^iPr)_8(py)_2$ in the presence of pyridine.^{2,91} $Zr_2(O^iPr)_9^{2-}$ behaves as an ambidentate ligand as well (Table II).

Heterometallic alkoxides containing two different metals can also undergo Lewis acid-base reactions with an alkoxide, such as for example⁶⁰



Low-valent elements involved in heterometallic alkoxides have been used as Lewis bases, mainly toward metal carbonyl derivatives,¹¹³ according to reactions such as shown in eq 40.





5.3. Metathesis Reactions

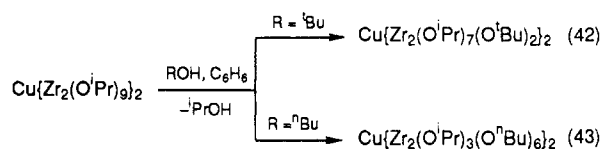
5.3.1. Reactivity of the Alkoxide Bond

One of the characteristic features of metal alkoxides is their high reactivity with water. This can be a flaw or an advantage, depending upon need. As for the homometallic derivatives, the electronegative alkoxo groups make the metal center highly prone to nucleophilic attack, but studies of the reactivity of the heterometallic alkoxides remains very limited. Substitution reactions lead to new molecular precursors displaying different volatilities, thermal stabilities, and behavior with respect to hydrolysis and condensation, and more investigation of the reactivity of heterometallic alkoxides is thus warranted.

5.3.1.1. Alcoholysis. Regarding metathesis reactions of the metal-alkoxo bond, alcoholysis reactions are the most documented, especially by the group of Mehrotra. They appear as a means to tailoring thermal stability and volatility.

As for homometallic alkoxides,¹⁵⁰ the rate of reaction of attacking alcohols increases from tertiary to secondary to primary. For instance, in the alcoholysis reactions of $\text{Cu}\{\text{Zr}_2(\text{O}^i\text{Pr})_9\}_2$ the following order of reactivity is observed: $\text{MeOH} \gg \text{EtOH}, {}^n\text{PrOH}, {}^n\text{BuOH}, {}^i\text{BuOH} \gg {}^s\text{BuOH} \gg {}^t\text{BuOH}, \text{AmOH}$.

The lower solubility of methoxide derivatives generally promotes complete substitution: Alcoholysis reactions are generally incomplete with bulky alcohols. Although few structural data are available, it seems reasonable to assume that terminal groups are the most labile.⁵²



A few alcoholysis reactions have been achieved with trifluoroethanol ($\text{CF}_3\text{CH}_2\text{OH}$), but no example of silanolysis is reported in the literature. Characterization of products is generally limited to boiling points and analytical data. Further studies of alcohol exchange reactivity are therefore necessary.

5.3.1.2. Reaction with β -Diketones. The known reactivity of heterometallic alkoxides with reactants having a hydroxyl functionality appears limited to β -diketones, more specifically acetylacetonate, and was mostly carried out on compounds of type $M[\text{Al}(\text{O}^i\text{Pr})_4]_n$ (Table I) or $\text{Ni}[\text{M}(\text{O}^i\text{Pr})_6]_2$ ($M = \text{Nb, Ta}$).⁹²

Such reactions are important in order to modify the coordination sphere of the metals. It should thus be possible to improve volatility or to adjust the hydrolytic susceptibility of the two different metals by decreasing the functionality¹⁹² of the precursor (e.g., β -diketones

are far less sensitive to hydrolysis).¹⁹³

The products mentioned in the literature are inadequately characterized. Products such as $\text{Cr}[\text{Al}(\text{O}^i\text{Pr})_{4-x}(\text{acac})_x]_3$ ($x = 1, 2, 4$) were reported.⁸⁰ Their thermal stability against disproportionation reactions in the vapor phase strongly decreases as x increases. The heterometallic nature of the product of empirical formula $\text{Cr}[\text{Al}(\text{acac})_4]_3$, mainly based on analytical data, is therefore questionable. Complete dissociation into the homometallic acetylacetonates has been reported for $\text{Ho}[\text{Al}(\text{acac})_4]_3$ on the basis of molecular weight measurement data.⁸² We have found that the substitution of alkoxide groups by β -diketonates exerts a strong destabilization on the heterometallic units. Thus, while heterometallic alkoxide- β -diketonate derivatives such as $\text{Ba}_2\text{Cu}_2(\text{OR})_4(\text{acac})_4(\text{ROH})_2$ ($\text{R} = \text{C}_2\text{H}_4\text{OMe}$) can be of interest for the sol-gel process,¹¹² their poor thermal stability will probably preclude their use in MOCVD techniques. Other routes to volatile heterometallic precursors of oxides (i.e., alternatives to β -diketonates) should thus be investigated.¹⁹⁴

5.3.1.3. Hydrolysis. Hydrolysis-polymerization reactions of alkoxides are governed by numerous factors.³ Related studies on homometallic alkoxides are limited to some oxophilic metals (tantalum, titanium, and zirconium, for instance), silicon, and aluminum. Molecular modification of the homometallic alkoxides has a strong effect on parameters such as gelation time, particle morphology, porosity, etc.²⁰ Substitution reactions by less hydrolyzable groups decrease the functionality of the precursors and thus promote a decoupling between hydrolysis and condensation. The less electronegative anionic groups are quickly removed, while the more electronegative ones are mainly removed during the condensation process. It is suggested that depending on the relative hydrolysis and condensation rates, different products can be obtained.²⁰

Although it is generally considered that materials obtained by low-temperature routes via homogeneous solutions of alkoxides are more homogeneous than those synthesized by other routes, very few data are available concerning the behavior of the heterometallic species during the sol-gel process: Is there conservation of a heterometallic unit or complete dissociation into segregated homometallic species? Is the M:M' stoichiometry modified? The most effective development of the use of heterometallic alkoxides in the sol-gel process necessitates answers to these fundamental questions.

The obtaining of spinel MgAl_2O_4 from $\text{MgAl}_2(\text{O}^i\text{Pr})_8$ (synthesized by allowing a 1:2 mixture of Mg and Al metals to react in ${}^i\text{PrOH}$) is one of the few examples of the synthesis of a material directly from a heterometallic alkoxide. Hydrolysis (H_2O - ${}^i\text{PrOH}$) of $\text{MgAl}_2(\text{O}^i\text{Pr})_8$ in the presence of triethanolamine as a "modifier" gives a gel.⁵⁶ The two metallic elements "do not break down to separate metal components during hydrolysis", and the gel is converted quantitatively to spinel in 1 h at 1500 °C. In this study,²⁷ Al NMR was useful for establishing tetrahedral geometry about Al both in the heterometallic alkoxides and during hydrolysis and gelation. Controlled hydrolysis of $\text{Zn}[(\mu\text{-OR})_2\text{Al}(\text{OR})_2]_2$ giving $\text{Zn}[(\mu\text{-O})_2\text{Al}(\text{OR})_2]_2$ has also been achieved.

For these two examples, no breakdown of the original heterometallic unit has been observed. It should how-

ever be noted that only limited hydrolysis was performed on the Meerwein product, while the complete hydrolysis of $\text{MgAl}_2(\text{O}^i\text{Pr})_8$ was achieved in the presence of an "additive", triethanolamine. This additive, a polydentate alcohol, will probably modify the precursor by alcoholysis reactions. Polydentate alcohols are also generally used to slow hydrolysis rates and to avoid formation of heterogeneous media.

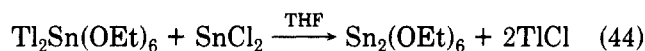
Heterometallic species may involve metals such as Y and Cu or Y and Ba, which display very different hydrolytic susceptibility or behavior. Hypercritical conditions^{195,196} can be used as a way to overcome the mismatched hydrolysis and redistribution reactions that can lead to selective precipitation en route to multi-component materials. Elimination of organic residues and the maintaining of a porous structure are further advantages of this procedure. However, adjustment of the hydrolysis rates by selective substitution of the alkoxo groups of the most electropositive metal by ligands less susceptible to hydrolysis could be another way to overcome mismatched hydrolysis rates and should thus also be considered. Ligands of interest could be aryloxide or siloxo groups, polydentate alcohols such as alkanolamines, β -diketones, carboxylic acids, As discussed above, β -diketones seem to be poor ligands; they appear to destabilize heterometallic units. Carboxylic acids seem of interest, since they were observed on homometallic alkoxides to promote controlled condensation reactions, either by acting as spontaneous oxo donor ligands or by induced hydrolysis reactions via esterification reactions.^{197,198} Their tendency to act as bridging-chelating ligands could be a favorable feature for the maintaining of the heterometallic units during the hydrolysis process.

Functional alcohols, especially such as alkoxy alcohols, seem to behave in a way comparable to carboxylic acids,¹⁷⁸ and could also be used with benefit. More generally, modification could be performed by using polyhydroxylated compounds such as bifunctional carboxylic acids ($\text{HO}_2\text{C}(\text{CH}_2)_n\text{CO}_2\text{H}$), polyols (glycerol, poly(ethanolamine), ...), or α -hydroxy acids (glycolic, ...). Such organic groups could bridge different metals, should not be removed during the hydrolysis and condensation process, and thus should also lead to mixed-metal organic-inorganic materials, a class of materials nearly unknown today.

Structural information is the most difficult to obtain during the hydrolysis-polycondensation process, and few intermediates have been characterized by X-ray diffraction for the homometallic alkoxides. NMR (²⁷Al, ²⁹Si, ⁵¹V, ...), EXAFS measurements,¹⁹⁹ light and small-angle X-ray scattering experiments,²⁰⁰ and gel chromatography appear to be valuable tools for following in situ the inorganic polymerization reactions. Hydrolysis studies of heterometallic species are even more complex; most of the above experimental methods are no longer able to decide whether heterometallic M-O-M' species are maintained during the hydrolysis process. Even for well-known nuclei such as ²⁷Al, the information available by this technique will usually be simply the coordination number. In the absence of X-ray diffraction on monocrystals, EXAFS is probably the most powerful method for establishing M-M' proximity and thus the presence of heterometallic species. This technique is also quite versatile and can

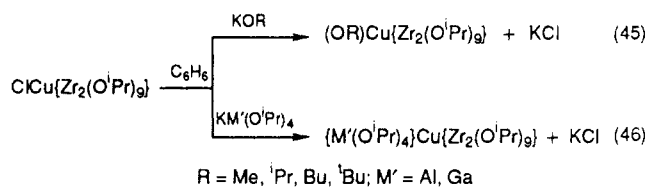
be applied on solutions, colloids, gels, and powders. FAB and EDAX techniques applied to isolated intermediates unsuitable for complete X-ray analysis can bring additional information about the stoichiometry between the different metals. LAXS techniques¹³⁵ might be useful for information on the arrangement of the metals (periodic or not) in the gel.

5.3.1.4. Transmetalation Reactions. These can be used as a way of obtaining new heterometallic alkoxides (see section 2) or mixed-valency alkoxides.¹⁸¹



5.3.2. Reactivity of Other Functional Groups (Halides, ...)

Chloride heterometallic alkoxides CIMG are limited to a few metals ($\text{M} = \text{Co}(\text{II}), \text{Cu}(\text{II})$; $\text{G} = \text{Al}(\text{O}^i\text{Pr})_4, \text{Zr}_2(\text{O}^i\text{Pr})_9$, or $\text{M}'(\text{OR})_6$ ($\text{M} = \text{Nb}, \text{Ta}$) (Tables I and II)). As already mentioned in section 2, the reactive halide group can be replaced by an alkoxide ligand (eq 45) or



allow the preparation of heterometallic species (eq 46).^{78,93} In both types of reactions, the formation of the insoluble KCl acts as a driving force and the yields are nearly quantitative; thus, chloride heterometallic alkoxides appear as interesting synthons for species involving three different metals.

5.4. Redox Reactions

5.4.1. Electrochemical Reactions

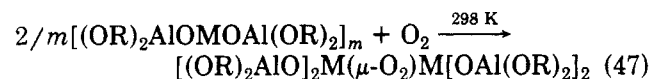
Methanolic solutions of $[\text{Mg}(\text{MeOH})_6][\text{Mg}_2\text{Mo}_8\text{O}_{22}(\text{MeO})_6(\text{MeOH})_4](\text{MeOH})_6$ are reduced electrochemically to an undefined Mo(III) complex that is an "effective catalyst for N_2 reduction" in mild conditions (room temperature, 1 atm).¹⁵

Cyclic voltammetry studies of $\text{Mo}_2\text{WO}(\text{O}^i\text{Pr})_{10}$ have shown that the reduction process is primarily centered on the Mo center while the oxidation process is predominantly W-centered. This behavior is consistent with the general difference between Mo and W.⁵⁷

5.4.2. Activation of Small Molecules

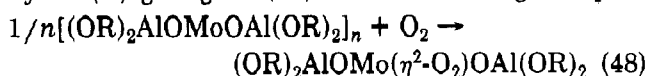
The hydrocarbon-soluble heterometallic oxoalkoxides of type $[(\text{OR})_2\text{AlOMOAl}(\text{OR})_2]_m$ ($\text{M} = \text{Cr}(\text{II}), \text{Mo}(\text{II}), \text{Fe}(\text{II})$) rapidly react with molecular oxygen at room temperature. The dioxygen coordination mode as well as the kinetics are largely a function of the metal and of the alkoxide ligand.¹³

The chromium and iron compounds react according to eq 47.

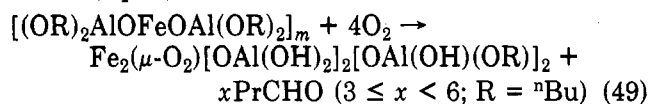


UV-visible as well as EPR spectra support the valence change to Fe(III). Activation of molecular oxygen

by Mo(II) giving Mo(IV) occurs according to eq 48.



Cryoscopic measurements were used to estimate the decrease in the degree of association, which is observed in all cases from $m = 8$ to a tetranuclear species ($m = 2$), for instance in the case of iron.²⁰¹ Excess dioxygen can lead to oxidation of the alkoxide ligands to acetone or aldehydes with concomitant formation of Al-OH bonds (eq 49).



5.5. Catalytic Activity and Organic Synthesis

Compounds of type $[M(\mu-O)_2Al_2(OR)_4]_m$ ($M = Co, Zn$) are highly active catalysts for the polymerization of oxiranes, thiranes, lactones, and even isocyanates.¹² The polymerization proceeds by specific insertion into the M-OR bond. Variation of the steric bulk of the OR groups allows modulation of the degree of association of the heterometallic alkoxides (assumed to display a *closo* polyhedral structure) and thus tailoring of a number of OR groups "accessible" and active in the polymerization process. The isotacticity of the polymers can thus be controlled. The high solubility as well as the thermal stability (up to 200 °C) makes these heterobimetallic oxoalkoxides attractive models of the frontier between homogeneous and heterogeneous catalysts.

The activity of the well-defined compound $[Ti_2(OEt)_8Cl]_2Mg_2(\mu-Cl)_2$ has been estimated for the polymerization of polyethylene or 1,3-butadiene in the presence of $AlEt_3$. Although the interaction between magnesium and titanium is certainly very different in the preceding homogeneous complex in comparison with that in the heterometallic catalyst surface formed from $MgCl_2$ and $Ti(OR)_4$, there is a similarity in the microstructure of the high molecular weight polyethylene produced by the two systems. It is thus suggested that the electron donation from the metal chloride to the titanium center promotes the propagation rate constant as well as the concomitant absence of chain-transfer reaction and thus increases the length of the macromolecular chain.⁶¹ The dimer of formula $[Al_3Nd_6(\mu-Cl)_6(\mu-Cl)_6(\mu-Et)_9Et_5(O^iPr)]_2$ was reported to display a high activity and stereospecificity for the polymerization of butadiene.

In the area of catalysis, heterometallic alkoxides are of interest since, in monometallic chemistry, OR^- groups can be replaced by R^- or even H^- . A potential route to the rational synthesis of heterometallic hydrides and hydrocarbyls is thus evident.

Finally, heterometallic alkoxides may also be useful for organic synthesis; examples are so far based on compounds involving alkali metals.^{156,201}

6. Conclusion and Outlook

Throughout this review, we have focused on a class of molecules that have been synthesized in abundance but whose further characterization and *utilization* deserves additional attention. Because the number of combinations of two or more metals is immense, this

class of molecules presently lacks many pairs for which applications can be envisioned. The synthetic methods remain available for such needs.

We have attempted to focus this paper on the manner in which, for alkali and alkaline-earth metals, the control of stoichiometry by charge balance can lead to unusual coordination geometries for such metals. Since the molecular character of heterobimetallic alkoxides originates in the strong Lewis acid behavior of "naked" alkali and alkaline-earth metals, certain of the resulting geometries are expected to leave unsatisfied Lewis acidity. This remains to be exploited in the future.

Currently, the metals present in the heterobimetallic alkoxides characterized by X-ray diffraction are most often an alkali metal and a transition or actinide metal. This is primarily for reasons of synthetic convenience: The product was formed by alkali-metal reduction or addition of alkali metal alkoxide to an unsaturated $M(OR)_n$. In fact, then, the heterometallic alkoxide is heterometallic more by chance than by design. The major other class of heterometallic alkoxides is due to contribution of Mehrotra's group, who have quite systematically employed the concept of addition and condensation of $nAl(O^iPr)_3$ units with $M(O^iPr)_n$ to form $M[Al(O^iPr)_4]_n$. One can envision extending this idea by replacing $Al(O^iPr)_3$ by $Mg(OR)_2$ to form $M[Mg(OR)_3]_n$ or $M[Mg(OR)_4]_{n/2}$. This idea, as well as its extension to heavier alkaline-earth analogues, remains unrealized in practice.

An obvious area for further synthetic development among heterometallics is the incorporation of a transition metal or a later main-group metal as the partner; i.e., two transition metals, late main group + transition metal, etc. The simple reaction of two binary alkoxides (e.g., $TiOR + Sr(OR)_2$) can be an effective synthesis, and there is room here for considerable synthetic creativity. In general, the nonaqueous chemistry of the heavier alkaline earths is neglected, with the result that synthetic reagents (and even principles) are scarce. Similarly, the needed alkoxides of lead, bismuth, etc., are little known. In this area the Mehrotra group has again served as a pioneer, reacting $NaZr_2(OR)_9$ with $CuCl$ or $CuCl_2$ to combine Cu and Zr into a single heterometallic species. The future will surely see synthetic methods proceed beyond salt (NaCl) elimination to include more of the methods outlined in section 2 (e.g., $Cu-R' + X_2M(RO-H) \rightarrow X_2M(\mu-OR)Cu + R'H$).

It is clear that the metal atom ratios in the known heterobimetallic alkoxides are determined by charge balance and thus, to date, have been achieved passively by most workers. Thus, we have $Mg[Al(OR)_4]_2$ as a spinel precursor and $BaTi(OR)_6$ as a $BaTiO_3$ precursor. To move beyond such limited stoichiometries but still with charge balance (to yield uncharged products) as the controlling principle, it becomes essential to investigate (for constant metal oxidation number) the *range* of thermodynamically accessible cluster alkoxide anions of a desired metal. Alternatively, one must change the metal oxidation number. It is the availability of several such cluster anions that will relax the constraint (relative to that for a mononuclear anion) of a single available charge. Thus, synthesis of $Ta_2(OR)_9^+$ units would make it possible to deviate from the imposed 1:1 stoichiometry when M' cations are condensed with $Ta(OR)_6^-$. Similarly, an alternative to the 2:1

stoichiometry from $M(I)$ and $Zr(OR)_6^{2-}$ is found in the combination of $M(I)$ with $Zr_2(OR)_9^-$. Manipulation of the metal atom ratio may also be possible by offering, to $Ti(OR)_6^{2-}$, either Sr^{2+} (for a 1:1 product) or $SrOR^+$ (for a 1:2 product—cf. $Sr_2Ti(OR)_8L_3$ in section 4). By partial incorporation of μ -oxo units, the charge balance could also be altered. Thus, presently unknown $Ta_2(\mu-O)(OR)_{10}^{2-}$ could generate a 1:2 compound with a divalent metal, $M(II)$; since we are currently quite ignorant of what are the attainable cluster species $M_aO_b(OR)_c^{q-}$ for elements M of known utility in material science, establishing the stability patterns of such species is a worthwhile endeavor.

The use of heterometallic alkoxides as molecular precursors also awaits further systematic development and understanding of the process of their conversion to solid materials. Chemical conversions can be imagined using water (yielding oxides), NH_3 (yielding nitrides or oxynitrides), and perhaps H_2S , PH_3 , or AsH_3 . Physical methods may include pyrolysis, photolysis, ultrasonication, and even electrooxidation as energy sources. Both the chemical and physical paths would benefit from some systematic studies of the influence of the composition, structure, and physical properties of the group R on the transformation. For sol-gel conversions, such information is beginning to appear.

While the use of molecular precursors for bulk solid materials useful for their mechanical, electronic, or optical properties is proceeding briskly, their application in the field of catalysis remains relatively unexplored. Metal carbonyls have been bound to surfaces as catalysts, as have metal alkyls. These have generally been mononuclear centers or homometallic clusters. The use of well-defined heterometallic species, which can be deposited either from solution or by their tailored volatility, offers the potential for laying down isolated multifunctional ($M_mM'_p$) centers containing the element pairs (or triplets) of choice.

In closing, we emphasize that heterobimetallic chemistry, as exemplified by alkoxides, offers many complex phenomena (fluxionality, structural modification on phase change, altered physical properties, structure down a group of the periodic table) that require multiple analytical techniques as preliminary to transforming these into applied science.

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Abbreviations

Hacac	acetylacetone (2,4-pentanedione)
Am	amyl
Ar ^R	R-substituted phenyl group, 2,6- $R_2C_6H_3$
Cp*	pentamethylcyclopentadienyl, C_5Me_5
Cp	cyclopentadienyl anion, $C_5H_5^-$
18-crown-6	1,4,7,10,13,16-hexaoxacyclooctadecane
12-crown-4	1,4,7,10-tetraoxacyclododecane
diglyme	diethylene glycol dimethyl ether

DME	1,2-dimethoxyethane
EPR	electron paramagnetic resonance
EDAX	energy dispersive X-ray analysis
EXAFS	X-ray absorption fine structure
EPR	electron spin resonance
IR	infrared
LAXS	large-angle X-ray scattering
MAS NMR	magic angle spinning nuclear magnetic resonance
Mes	mesityl
MW	molecular weight
nbd	norbornadiene
NMR	nuclear magnetic resonance
py	pyridine
TMEDA	<i>N,N,N',N'</i> -tetramethylethylenediamine
UV-vis	ultraviolet-visible spectroscopy
XANES	X-ray absorption near-edge structure

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