

# Homo- and Hetero-metallic Alkoxides of Group 1,2, and 12 Metals

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## 1 Introduction

The discovery of high  $T_c$  superconducting properties of a number of oxide-ceramic materials like  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  involving alkaline earth metals, led to an unprecedented search for their soluble and volatile alkoxy derivatives which could serve as precursors for ceramic materials by the sol-gel/MOCVD process.<sup>1</sup>

Interestingly, the use of chelating alkoxometallate ligands,<sup>2,3a,3b</sup> like  $\text{Al}(\text{OR})_4^-$ ,  $\text{Zr}_2(\text{OR})_6^-$ ,  $\text{Nb}(\text{OR})_6^-$ , and  $\text{Ta}(\text{OR})_6^-$  in the laboratories of the authors had already resulted in solubilization of insoluble simple alkoxy derivatives of bivalent metals. Similar successful results on solubilization, obtained with the use of chelating alcohols like aminoalkanols, have since been extended to alkoxyalkanols. In addition to the potential use of these soluble hetero- and homo-metallic alkoxy derivatives as precursors in the sol-gel process,<sup>3</sup> these have exhibited rather unique structural features,<sup>3-8</sup> which has prompted more detailed investigations on similar alkoxy derivatives of strongly electro-positive monovalent group 1 metals also.

The chemistry of the alkali and alkaline earth metals can be understood in terms of an ionic model. These metal ions exhibit 'hard' or class 'A' character and are more prone to bind 'hard' or class 'A' ligands. With the increase in ionic size down each group coordination number increases; for example there is an increase in coordination number (shown in parentheses) going from  $\text{Li}^+$  (4), through  $\text{Na}^+$  (6) to  $\text{K}^+$ ,  $\text{Rb}^+$ ,  $\text{Cs}^+$  (8) and from  $\text{Be}^{2+}$  (4) through  $\text{Mg}^{2+}$  (6) to  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Ba}^{2+}$  (8). The ionic potential (charge/ionic radii) decreases in moving from top to bottom in each group and this is reflected in the more covalent characteristics found in compounds of Li, Be, and Mg relative to their heavier congeners.

The presence of the filled  $(n-1)d$  and to a lesser extent  $4f$

shells in the electronic configurations of group 12 metals causes two effects: (i) the poor shielding characteristics of  $d$  and  $f$  orbitals reduce the size of  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ , and  $\text{Hg}^{2+}$  ions relative to  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ , and  $\text{Ba}^{2+}$ ; and (ii) the filled  $(n-1)d$  orbitals are more easily polarized by ligand electrons than the  $np$  orbitals. These two effects contribute to higher stability of complexes formed by Zn, Cd, and Hg relative to their counterparts (the alkaline earth metals).

Although group 12 ( $d^{10}s^2$ ) metals (Zn, Cd, and Hg) are much less electropositive, yet they resemble group 2 metals in forming polymeric alkoxides which are insoluble in organic solvents. By contrast, group 11 ( $d^{10}s^1$ ) metals (Cu, Ag, and Au) have hardly any similarity with group 1 metals and are therefore not included in this review; in fact the alkoxide chemistry of these metals (particularly that of Cu) is generally treated along with that of other transition metals. The main focus of attention in this review article is therefore on the chemistry of strongly electro-positive group  $s^2$  and  $s^1$  (group 2 and 1) metals along with that of group 12 elements, laying particular emphasis on the work done during the last decade.

## 2 Homo-metallic Alkoxides of Group 1,2, and 12 Metals

### 2.1 Synthesis

These metal alkoxides have been prepared by the following routes illustrated by representative recent chemical reactions, emphasizing points of special interest/further investigations.

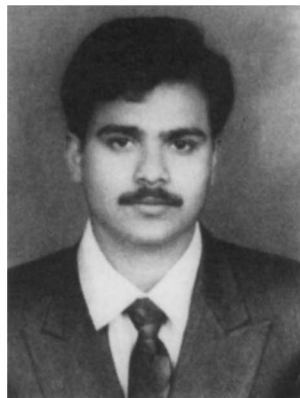
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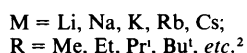
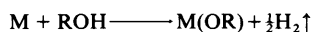
*University of Sussex, followed by 3 months in 1987 as a Visiting Scientist. Dr. Singh is an inorganic and organometallic chemist with particular current interests in molecular design and characterization of homo- and hetero- metallo-organic precursors for better ceramic and catalytic materials. He is the author/co-author of over 90 research papers, review articles, and course-work for Open Universities in areas of his speciality. With Professor R. C. Mehrotra he co-authored the widely appreciated book 'Organometallic Chemistry: A Unified Approach'.*

*With more than four decades of research experience on M-O-C derivatives, synthesis and characterization of a large variety of heterometallic alkoxides has been the unique contribution from the research school of Professor Emeritus R. C. Mehrotra [M.Sc., D.Phil. (Alld.), Ph.D., D.Sc. (London)] during the past two decades. Author/co-author of more than 600 research papers, dozens of review articles, and chapters in well-known treatises, Mehrotra has supervised the research work of more than 100 scholars, who have themselves won coveted honours in their own careers.*



### 2.1.1 Reactions of Metals and Alcohols

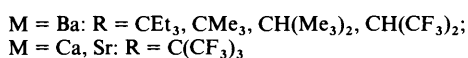
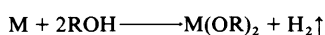
This type of direct reaction is naturally more facile with more electropositive alkali metals as compared with alkaline earths, in which case the insolubility of the bivalent alkoxides also becomes a hindering factor. In the latter cases also, derivatives with sterically demanding as well as with monofunctional chelating alcohols tend to be soluble:



Reactions of alkaline earth metals with alcohols may be classified under two headings:

#### (a) Reactions of metals with monodentate alcohols

Reactions of bulky alcohols<sup>4</sup> with alkaline earth metals have been recently reported to yield soluble bis-derivatives:

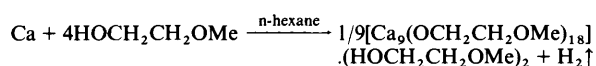


By contrast, the formation of an oxo-alkoxide cluster  $H_3Ba_6(O)(OCMe_3)_{11}(OCEt_2CH_2O)(thf)_3$  has been identified by X-ray crystallography in the reaction of  $Me_3COH$  with Ba in tetrahydrofuran (thf) by Caulton and co-workers.<sup>5</sup> Formation of the diolate ligand  $OCEt_2CH_2O$ , in the above reaction, despite its low concentration (relative to  $Bu^iOH$  and thf) illustrates the preferential formation of this moiety suited to a desired molecular configuration, it is also significant that the above reaction between Ba and  $Bu^iOH$  in toluene does not generate this ligand, which gives a clue that the diolate is probably formed in a reaction involving the solvent thf molecules.

Interestingly, the  $NH_3$ -catalysed reaction of Ba granules with  $Ph_3COH$  in thf does not form an oxo-alkoxide derivative, but yields<sup>6</sup> dimeric  $[Ba(OCPh_3)_2]_2$  which has been characterized by single crystal X-ray study.<sup>6</sup> Some siloxide derivatives of Ba such as  $[Ba_3(OSiPh_3)_6]_2 \cdot 0.5thf^7$  and  $[Ba_2(OSiBu_3)_4(thf)]^6$  have also been synthesized similarly. It is interesting to note<sup>6</sup> that there appeared to be no reaction between Ba granules and either  $Ph_3COH$  or  $Bu^iSiOH$  in refluxing thf over 3 days, even in the presence of  $I_2$  or  $HgCl_2$  catalyst. However, the rate of the heterogeneous reaction of Ba metal with these alcohols in thf was significantly increased by adding catalytic amounts of dry ammonia.<sup>6</sup> It was assumed that ammonia reacts with barium to produce  $H_2$  and  $Ba(NH_2)_2$ ; the latter then undergoes proton transfer and anion metathesis to give alkoxide and siloxide derivatives.

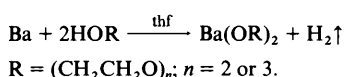
#### (b) Reactions of metals with chelating alcohols

Reactions of calcium filings and 2-methoxyethanol in refluxing n-hexane yields<sup>8</sup> X-ray crystallographically characterized molecular calcium dialkoxide with a large  $Ca_9$  aggregate size:



By contrast, similar reaction with barium granules followed a different course, yielding<sup>9</sup> X-ray crystallographically characterized oxo-alkoxide cluster,  $[H_4Ba_6(O)(OCH_2CH_2OMe)_{14}]$ .

Furthermore, it has been reported<sup>10</sup> recently that reaction of Ba with oligomeric alcohols in thf produced monomeric  $Ba[O(CH_2CH_2O)_n]_2$  ( $n = 2$  or  $3$ ):

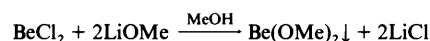


The parameters determining the variation in the nature of products in the reaction of Ca/Ba with chelating alcohols obviously needs further probing. Similar remarks would apply to the role of catalyst, side reactions with the solvent, etc., and

the formation of oxide alkoxide/diolate products in the reactions of Ba with alcohols [cf. Section 2.1.1 (a)] under slightly varying condition.

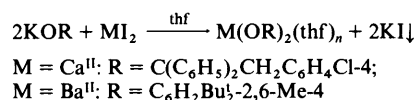
### 2.1.2 Reactions of Metal Halides with Alkali Metal Alkoxides

Initially this method was used<sup>2</sup> for the synthesis of insoluble beryllium methoxide according to the following reaction:



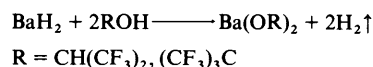
Similar reactions with  $ZnCl_2$  and  $CdCl_2$  are not straightforward;<sup>2</sup> the initially formed dialkoxides tended to react with  $Li(OCH_3)$  to give soluble heterobimetallic methoxides of the type  $Li_xZn(OMe)_{2+x}$  which, however, could not be separated from the reaction mixture.

Recently, soluble monomeric alkoxides or aryloxides of Ca and Ba also have been prepared<sup>11</sup> from the reactions of potassium salts of the alcohols and phenols with alkaline earth diiodides:



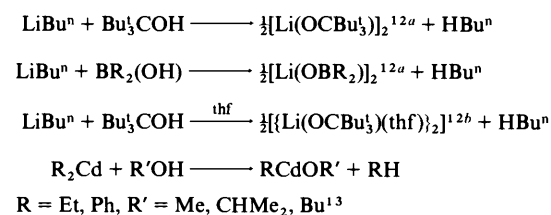
### 2.1.3 Reactions of Metal Hydrides with Alcohols

Reactions of  $BaH_2$  with sterically demanding fluorinated alcohols have been shown to produce<sup>4</sup> soluble dialkoxides of Ba:



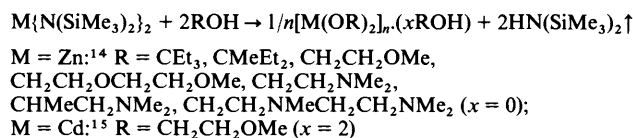
### 2.1.4 Metal-Carbon Bond Cleavage Reactions

The high reactivity of metal alkyls ( $M^{\delta+} - C^{\delta-}$ ) has been exploited for the synthesis of alkali metal alkoxides and also for alkylmetal alkoxides of Be, Mg, Zn, and Cd metals as illustrated by the following recent examples:



### 2.1.5 Reactions of Metal Dialkyl Amides with Alcohols

The alcoholysis reactions of metal amides, which appear to be more straightforward and facile, have been used for the synthesis of group 12 (Zn, Cd) metal alkoxides more extensively in the past few years:



## 2.2 General Properties

### 2.2.1 Group 1: Li, Na, K, Rb, Cs

Amongst the alkoxides of alkali metals, derivatives of lithium are expected to be the least ionic as depicted by their solubility in organic solvent and volatility of lithium tertiary butoxides.

The degree of associability tends to be lower with decreasing ionic size and ramification of alkyl group involved. Although

more detailed investigations under comparative conditions are still not available, yet the effect of these factors may be illustrated by the following few available data:<sup>1,2,16</sup>

**Table 1** Degree of association of different alkali metal alkoxides

	OMe ( <i>n</i> )	OPr <sup>i</sup> ( <i>n</i> )	OBu <sup>t</sup> ( <i>n</i> )	OCMePh <sub>2</sub> ( <i>n</i> )	OCBu <sub>3</sub> <sup>t</sup> ( <i>n</i> )
Li	large	11	4/6	6	2
Na	large	—	6/9	—	2
K	large	—	4	—	—

### 2.2.2 Group 2: Be, Mg, Ca, Sr, Ba

Simple  $[M(OR)_2]_n$  ( $R = Me, Et, Pr^n, Pr^i$ ) alkoxides of group 2 metals are generally polymeric, insoluble in organic solvents (including parent alcohols), and non-volatile.<sup>2</sup>

A noteworthy property of beryllium alkoxides is the volatility and solubility of  $[Be(OBu^t)_2]_3$ . Furthermore, it is interesting to note that alkyl metal alkoxides,  $RMOR'$  ( $M = Be, Mg$ ) are less associated and depict higher volatility compared with those of the corresponding dialkoxides.<sup>2</sup> The role of steric factors on the extent of oligomerization could be further demonstrated by the following alkoxides and aryloxides of beryllium.

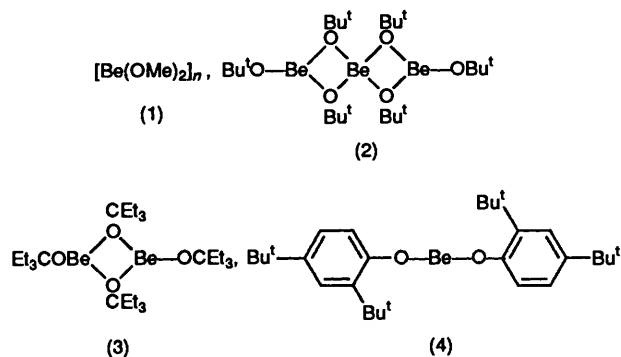


Figure 1

Recently, the strategy of using sterically demanding ligands<sup>11</sup> such as  $2,6-Bu^t_2C_6H_3O^-$ ,  $Et_3CO^-$ ,  $C(Me_3)_2CHO^-$ ,  $4-ClC_6H_4-CH_2(C_6H_5)_2CO^-$ , etc., and chelating ligands such as  $Me_2NCH_2CH_2O^-$ ,  $ROCH_2CH_2O^-$ ,  $CH_3(OCH_2CH_2)_nO^-$ , etc., has led to the formation of the least associated species, such as:

(i)  $Ba(O(CH_2CH_2O)_nCH_3)_2$  ( $n = 2$  or  $3$ ) which exhibits<sup>10</sup> monomeric behaviour in solution; (ii)  $M(BHT)_2(thf)_3$  ( $M = Ca, Ba$ ;  $BHT = OC_6H_2-Bu^t_2-2,6-Me-4$ ), and  $Ca[OC(C_6H_5)_2CH_2C_6H_4Cl-4](thf)_3$ ,<sup>11</sup> which are monomeric even in solid state; (iii) the derivative  $[Ca(OC(C_6H_5)_2CH_2C_6H_4Cl-4)_2(thf)_2]$  which is dimeric,<sup>11</sup> and soluble (in organic solvents), and shows volatile behaviour. During the past few years, the bulky alkoxides of group 2 metals, especially those of Ca and Ba, have been found to exhibit<sup>5-11</sup> some unusual structural patterns in the solid state. A systematic comparison of structural relationships among these complexes suggests that it is not only the metal radii that play a key role in determining metal–ligand distances, but that packing of ligands around the metal is just as critical and can lead to isostructural molecules even with large differences in radii, as in the case of  $M(BHT)_2(thf)_3$  ( $M = Ba, Ca$ ;  $BHT = OC_6H_2-Bu^t_2-2,6-Me-4$ ).<sup>11</sup>

It is interesting that soluble dialkoxides of barium such as  $Ba(OEt)_2$ ,  $Ba(OCMeEtPr)_2$ ,  $Ba(OCMe_3)_2$ , and  $Ba(OCH(CMe_3)_2)_2$  on attempted sublimation have been reported<sup>4</sup> to yield oxide-alkoxides, e.g.,  $[Ba(OR)_2]_x(BaO)_y$ . Tertiary alkoxides,  $Ba(OEt)_2$ ,  $Ba(OCMeEtPr)_2$ , and  $Ba(OCMe_3)_2$  have been reported to eliminate alkene and parent alcohol during

sublimation, but in case of the alkoxide  $Ba[OCH(CMe_3)_2]_2$ , the ketone  $[(Me_3C)_2C=O]$  appears to be eliminated.

### 2.2.3 Group 12: Zn, Cd

Similar to the group 2 bivalent metal alkoxides,  $Zn^{II}$  and  $Cd^{II}$  normal dialkoxides are also polymeric, insoluble in organic solvents, and non-volatile in nature. Even their *t*-butoxide derivatives are insoluble, in contrast to  $Be^{II}$  and  $Ba^{II}$ . Many soluble heteroleptic compounds  $[RM(OR')_n]$  ( $M = Zn, R = alkyl^2$  or  $H^{16a}$ ;  $M = Cd, R = Et, Ph^{13}$ ) are known; some of which like  $[EtZn(OBu^t)]_n$  have been used to obtain zinc oxide through the sol-gel process.

As in the case of group 2 metals, the strategy of using sterically demanding and chelating ligands such as  $^-OC_6H_2Bu^t_2-2,6-Me-4$ ,  $^-OCEt_3$ ,  $^-OCHC(Me_3)_2$ ,  $^-OCH_2CH_2NMe_2$ ,  $^-OCH_2CH_2OR$ , etc., has resulted in the formation of hydrocarbon-soluble, generally volatile, and less associated species. For example,  $[Zn(OEt)_2]_n^{14}$  ( $n = 2.5$ ) has been found to be readily soluble and volatile ( $10^{-4}$  Torr,  $220-225^\circ C$  bath temperature), whereas species of the type  $Zn(OAr)_2(thf)_2^{17}$  and  $Cd(OAr)_2(thf)_2^{18}$  have been shown to be monomeric.

## 2.3 Spectroscopic Studies

### 2.3.1 Infrared Spectra

Infrared spectral studies have revealed some structurally significant absorptions in the region  $1360-200\text{ cm}^{-1}$  due to  $\nu(OR)$ ,  $\nu(C-O)$ , and  $\nu(M-O)$ . The  $M-O$  stretching frequencies for group 2 and 12 metals ( $Mg, Ca, Sr, Ba, Zn, Cd$ ) have generally been observed in the region  $400-460\text{ cm}^{-1}$ , whereas  $\nu Be-O$  is seen in the region  $800-700\text{ cm}^{-1}$ .

### 2.3.2 NMR Spectra

An account of  $^1H$  NMR spectral behaviour of alkali and alkaline earth metal alkoxides has already been summarized in an earlier publication.<sup>2</sup> Recently, efforts have been made<sup>14-15</sup> to elucidate structural features of some soluble alkoxides of group 2 and 12 metals by this technique, but in a large number of cases no significant conclusions could be drawn owing to fast exchange between different types of alkoxide groups involved.

## 2.4 X-Ray Crystallographic Studies

In spite of inherent difficulties in studying alkoxides by this technique, *X*-ray diffraction studies have been carried out recently on a few homo-metallic alkoxides of group 1, 2, and 12 metals, e.g., (i)  $[Li(\mu-OCBu_3^t)]_2^{12a}$ , (ii)  $[Li(OCBu_3^t)(thf)]_2^{12b}$ , (iii)  $[LiOCMe_2Ph]_6^{12c}$ , (iv)  $[MOBu^t \cdot Bu^tOH]_\infty$  and  $[MOBu^t]_4^{12d}$  ( $M = K, Rb$ ), (v)  $[NaOCH(CF_3)_2]_4^{12e}$ , (vi)  $[Ca_9(OCH_2CH_2OMe)_{18} \cdot (HOCH_2CH_2OMe)_2]^8$ , (vii)  $[H_4Ba_6(\mu_6-O)(OCH_2CH_2OMe)_{14}]^9$ , (viii)  $[H_3Ba_6(O)(OBu^t)_{11}(OCEt_2CH_2O)(thf)_3]^5$ , (ix)  $Ba_2(OCPh_3)_4(thf)_3^6$ , (x)  $[Ba_3(OSiPh_3)_6(thf)_{0.5}thf]^7$ , (xi)  $[Ba_2(OSiBu_3)_4(thf)]^6$ , (xii)  $[Ca(\mu-OR)(OR)(thf)]_2^{11}$  ( $R = C(C_6H_5)_2CH_2C_6H_4Cl-4$ ), (xiii)  $Zn(\mu-OEt_3)(N(SiMe_3)_2)_2^{14}$ , (xiv)  $[Zn(1,4,7-\eta^3-OCH=CHNMeCH_2CH_2NMe_2)_2]^{14}$ , (xv)  $[Cd_6(OCH_2CH_2OMe)_{18} \cdot (HOCH_2CH_2OMe)_2]^{15}$ . Structures for some of the above derivatives with special features are shown in Figures 1–9.

### 2.4.1 Comments on Structures Determined by X-Ray Crystallography

Some noteworthy novel structural features recognized in the above *X*-ray diffraction studies could be summarized as:

- In the structures of Li organic compounds, Li is generally four-coordinated. However, in appropriately tuned environments sterically and electronically, rare coordination states of three and two can also be achieved (*cf.* Figures 2 and 3).
- The alkaline earth metal alkoxides containing sterically compact groups (e.g. MeO, EtO, etc.) exhibit low solubility

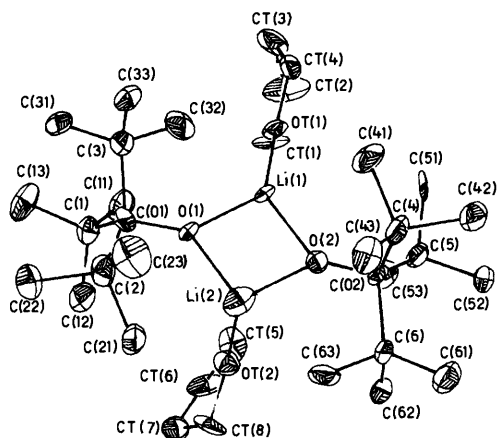


Figure 2 Molecular structure of  $[\text{Li}(\text{OCBu}_3)(\text{thf})_2]_2$ .<sup>12b</sup>

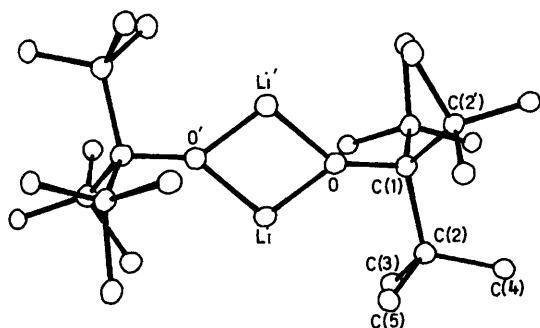


Figure 3 X-Ray structure of  $[(\text{Li}(\mu\text{-OCBu}_3))_2]$ .<sup>12a</sup>

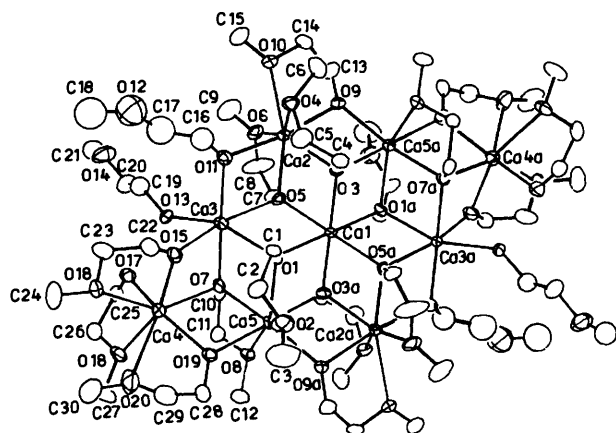


Figure 4 An ORTEP of  $[\text{Ca}_9(\text{OCH}_2\text{CH}_2\text{OMe})_{18}(\text{HOCH}_2\text{CH}_2\text{OMe})_2]$ .<sup>9</sup>

and volatility, and presumably oligomeric or polymeric structures. Being large in size these metal ions tend to form larger molecular aggregates (*cf.* Figures 4, 5, and 6) with higher (6 to 8) coordination environment around the metal ion. However, with the use of sterically demanding ligands like  $^-\text{OC}_6\text{H}_2\text{Bu}_2$ -2,6-Me-4- $\text{OC}(\text{C}_6\text{H}_5)_2\text{CH}_2\text{C}_6\text{H}_4\text{Cl}$ -4, less associated molecular species in lower coordination states can be obtained. The almost linear  $\text{M}-\text{O}-\text{C}$  angles and shortened  $\text{M}-\text{O}$  bonds may be due to combined effects of steric demand and  $\pi$  bonding (*i.e.*  $\text{M}=\text{O}=\text{C}$ ) contributions.<sup>11</sup> From recent studies on monomeric and dimeric alkaline earth alkoxides, it appears that packing of ligands around the metal may be more critical and can lead to isostructural molecules even with large changes in radii.<sup>11</sup>

(iii) It has long been known that the energetic difference between trigonal bipyramidal and square pyramidal geometries is small enough that crystal packing forces become more effective.

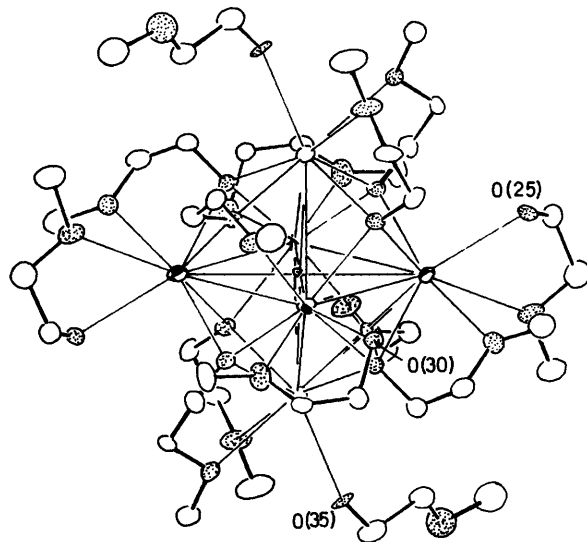


Figure 5 An ORTEP of  $[\text{H}_4\text{Ba}_6(\mu_6\text{-O})(\text{OCH}_2\text{CH}_2\text{OMe})_{14}]$ .<sup>9</sup>

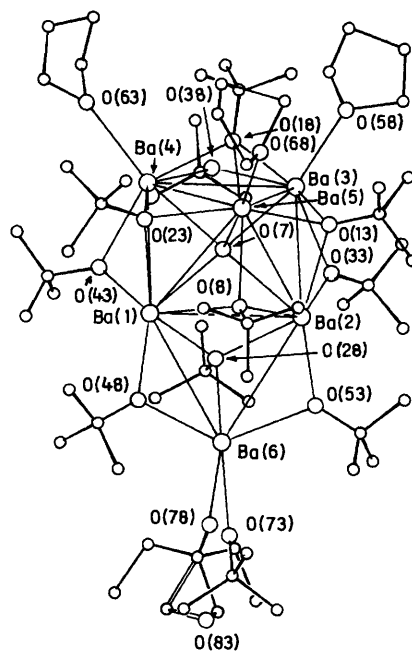


Figure 6 An ORTEP diagram of  $[\text{H}_3\text{Ba}_6(\text{O})(\text{OBu})_{11}(\text{OEt}_2\text{CH}_2\text{O})(\text{thf})_3]$ .<sup>5</sup>

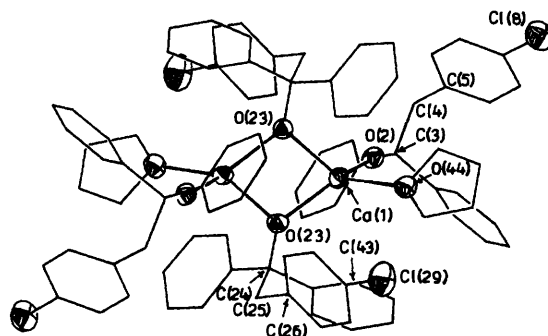


Figure 7 An ORTEP diagram of  $[\text{Ca}(\mu\text{-OR})(\text{OR})(\text{thf})_2]_2 \cdot 2$  toluene<sup>11</sup> ( $\text{R} = \text{C}(\text{C}_6\text{H}_5)_2\text{CH}_2\text{C}_6\text{H}_4\text{Cl}$ -4).

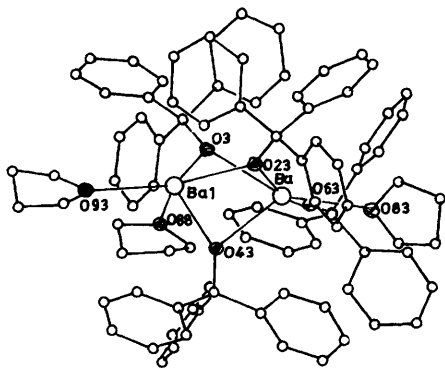


Figure 8 An ORTEP diagram of  $\text{Ba}_2(\text{OCPh}_3)_4(\text{thf})_3$ .<sup>6</sup>

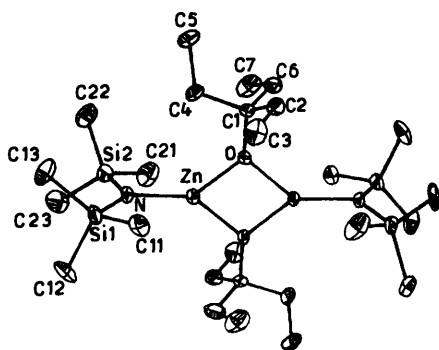


Figure 9 An ORTEP view  $[\text{Zn}(\mu\text{-OCEt}_3)\{\text{N}(\text{SiMe}_3)_2\}]_2$ .<sup>14</sup>

The presence of a square-based pyramidal core  $\text{Ba}_5(\mu_5\text{-O})$  is supported by  $\mu_3$ - and  $\mu_2$ -butoxide ligands in  $\text{H}_3\text{Ba}_6(\text{O})(\text{OBu}^t)_{11}(\text{OCEt}_2\text{CH}_2\text{O})(\text{thf})_3$  (Figure 6). The apical as well as two of the barium atoms in the basal plane are each ligated by one terminal thf molecule. The two other barium atoms in the basal plane are bonded to the six barium atom *via* three  $\mu$ -OR bridges. This type of ligand arrangement creates a six-coordinate environment around each barium associated with the  $\text{Ba}_5(\mu_5\text{-O})$  pyramid, while the sixth barium atom is ligated to only five oxygen atoms.

The coordination number five for barium is unusual. The pyramidal  $\text{Ba}_5$  unit may be viewed as fusing of four triangular subunits  $(\text{M}_3(\mu_3\text{-O})_2(\mu\text{-O})_3\text{L})$ , a type which is more common in metal-cluster and -oxide structures.

In contrast to the structure of the above derivative, the structure of  $\text{H}_4\text{Ba}_6(\mu_6\text{-O})(\text{OCH}_2\text{CH}_2\text{OMe})_{14}$  (Figure 5) contains a fully encapsulated oxo-ligand and the molecule has a crystallographically imposed centre of inversion; each barium attains eight-coordination by arranging around it an oxo-group, four oxygen atoms from  $\mu_3$ -OR ligands, two ether oxygens, and one  $\text{OCH}_2\text{CH}_2\text{OCH}_3$  oxygen atom which is either a terminal ( $\eta^1$ ) group (the apical Ba atoms), or a chelating ( $\eta^2$ ) ligand (four Ba atoms in equatorial plane).

(iv) Simple alkoxide and aryloxide derivatives of Zn and Cd are oligomeric leading to higher coordination environments around these metal ions. However, with sterically hindered ligands, molecular species in interesting and rare coordination geometries can be obtained. These are illustrated in the crystal structures of  $[\text{Zn}(\mu\text{-OCEt}_3)\{\text{N}(\text{SiMe}_3)_2\}]_2$ <sup>14</sup> (Figure 9),  $\text{Zn}(\text{OAr})_2(\text{thf})_2$ <sup>17</sup> and  $\text{Cd}(\text{OAr})_2(\text{thf})_2$ <sup>18</sup> ( $\text{Ar} = \text{C}_6\text{H}_3\text{Bu}_2$ -2,6). An interesting point to note about the structure of  $\text{Cd}(\text{OAr})_2(\text{thf})_2$  is its square planar geometry rather than the tetrahedral type as expected on the basis of VSEPR theory.

### 3 Heterobimetallic Alkoxides of Group 1,2, and 12 Metals

One of the most interesting aspects of heterobimetallic alkoxides is the extraordinary stability (compared with associated mono-

metallic species, *e.g.*, that of  $\text{Ln}\{\text{Al}(\text{OPr}^i)_4\}_3$  versus  $\text{Al}\{\text{Al}(\text{OPr}^i)_4\}_3$  as exhibited by volatilization in an unchanged form, which tends to indicate a greater stability of  $\text{M}(\mu\text{-OR})_2\text{M}'$  bridges between dissimilar metals.

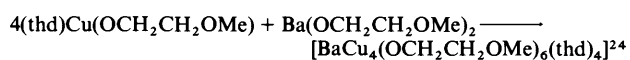
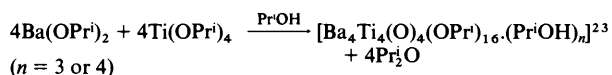
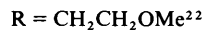
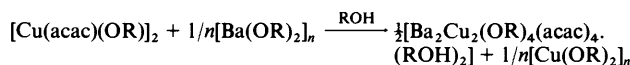
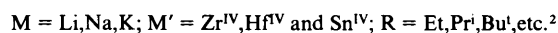
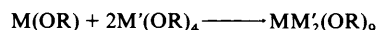
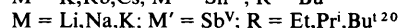
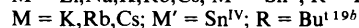
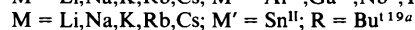
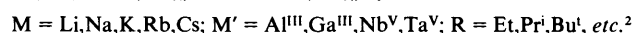
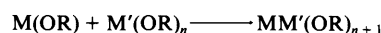
Furthermore, the synthesis of heterobimetallic alkoxides has provided a facile route for obtaining soluble, volatile, and generally monomeric species of group 2 and 12 metals of which homo-metallic alkoxides are generally polymeric, insoluble, and non-volatile. A brief account of the synthesis and characterization of heterobimetallic alkoxides of group 1,2, and 12 metals is presented in the following sections.

#### 3.1 Synthesis

Heterobimetallic alkoxides of group 1,2, and 12 metals have been mainly synthesized according to the following methods.

##### 3.1.1 Reactions between Component Alkoxides or their Derivatives

A large number of bimetallic alkoxides of alkali and alkaline earth metals have been synthesized by the Lewis acid–base interaction of simple alkoxides of these metals with alkoxides of less electropositive elements as illustrated by some typical examples:

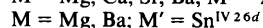
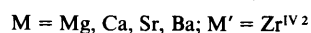
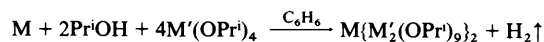
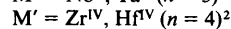
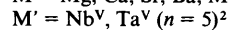
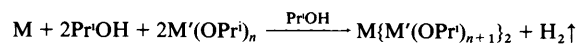


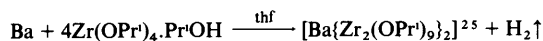
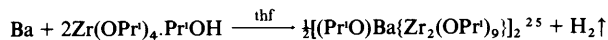
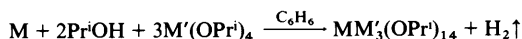
(where thd = 2,2,6,6-tetramethyl-3,5-heptanedionato)

Almost all of the above derivatives are soluble in common organic solvents in which they generally show monomeric behaviour.

##### 3.1.2 Reactions of Metals with Alcohols in the Presence of Appropriate Metal Alkoxides

Facile dissolution of alkaline earth metals in alcohols in the presence of alkoxides of less electropositive elements in requisite molar ratios has been shown to yield soluble monomeric volatile bimetallic alkoxides of group 2 metals:

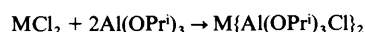
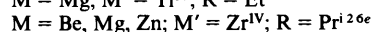
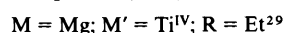
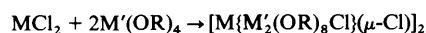
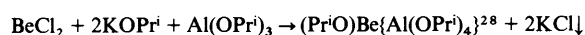
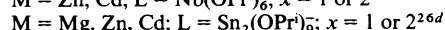
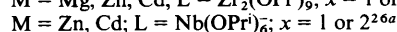
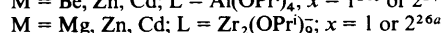
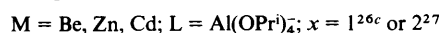
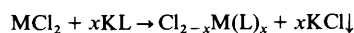




In the above reactions of alkaline earth metals with alcohols, the dissolution may be facilitated by the solubility of the final bimetallic alkoxides or the greater acidity of species like  $H\{Al(OPr^i)_4\}$  or  $H\{Zr_2(OPr^i)_9\}$  formed *in situ* in the solution.

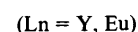
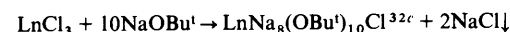
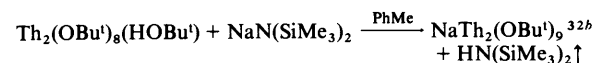
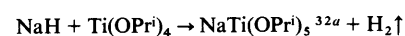
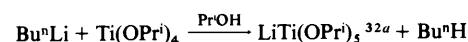
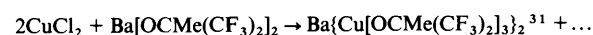
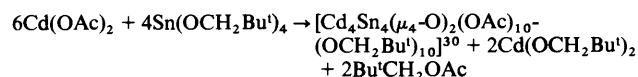
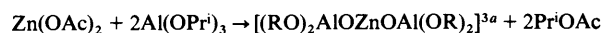
### 3.1.3 Reactions of Metal Chlorides with Metal Alkoxides

This method which has proved<sup>3a,3b</sup> to be applicable for a large number of bimetallic alkoxides of other metals (later transition) has also been utilized effectively in the authors' laboratories for the synthesis of bimetallic alkoxides of group 12 (Zn, Cd) as well as for Be and Mg metals:



### 3.1.4 Miscellaneous Methods

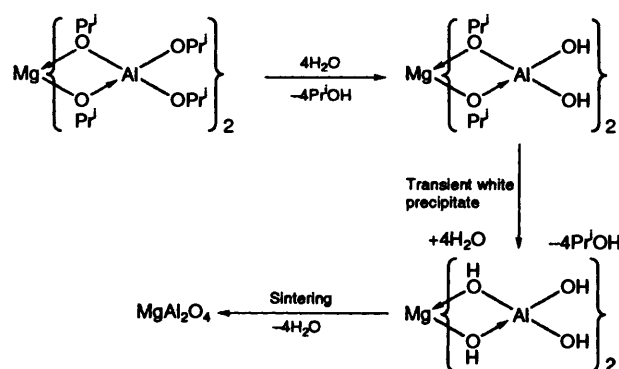
In addition to methods described above (*cf.*, Sections 3.1.1, 3.1.2, and 3.1.3) some other methods have also been employed, which are for brevity illustrated only in the form of the following equations:



## 3.2 Chemical Properties

The most characteristic property of facile reactivity of metal alkoxy bonds towards water (and other hydroxyl reagents) is being widely used for the preparation of oxide-based ceramic materials by the *sol-gel* process. For example, the spinel  $MgAl_2O_4$  has been prepared<sup>33</sup> by the hydrolysis of the bimetallic alkoxide  $Mg\{Al(OPr^i)_4\}_2$  following the plausible mechanism indicated in Scheme 1.

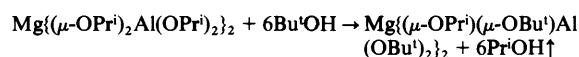
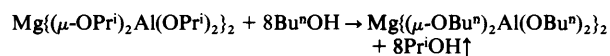
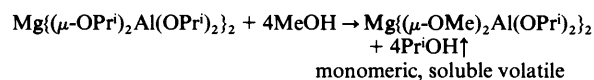
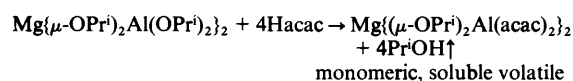
The retention of the original frame-work has been demonstrated by <sup>27</sup>Al NMR and other physico-chemical properties. Similar conclusions have been reached for the formation of



Scheme 1

oxide heterometal alkoxides in the initial hydrolysis of  $BaTi(OCH_2CH_2OMe)_6$ ,  $[LiTi(OPr^i)_5]_2$ , and  $[Ba\{Zr_2(OPr^i)_9\}_2]$ , which have been shown by X-ray structure analysis to give oxo-alkoxides of composition  $Ba_4Ti_{13}O_{18}(OCH_2CH_2OMe)_{24}$ ,<sup>34</sup>  $[LiTi(O)(OPr^i)_3]_4$ ,<sup>35</sup> and  $[BaZr_4(OH)(OPr^i)_{17}]$ <sup>35</sup> respectively.

Reactions with other protic reagents (*e.g.* alcohols) and acetylacetone have also been shown to follow a similar pattern.<sup>3a</sup>



In the last reaction, it appears that all the isopropoxy groups are not replaced by the *t*-butoxy group because of steric factors.

## 3.3 Physical Properties

Similar to the parent homo-metal species, the hetero-bimetallic alkoxides are highly reactive species. By contrast, heterometallic alkoxides are comparatively more soluble in common organic solvents, monomeric and generally volatile. These features are exploited in the preparation of mixed oxides by *sol-gel* or MOCVD techniques.<sup>1</sup>

### 3.3.1 Spectroscopic Studies

Characterization of heterobimetallic alkoxides has generally been carried out by physico-chemical techniques such as infrared, nuclear magnetic resonance, and mass spectrometry, and in a few cases by X-ray diffraction studies, in addition to the newer techniques like EXAFS, XANES.

In the following pages the application of various physico-chemical methods in the structural elucidation of heterometal alkoxides of group 1,2, and 12 metals will be briefly described.

#### 3.3.1.1 Infrared Spectroscopy

Infrared spectroscopy has often proved of considerable utility in the identification of alkoxy groups<sup>2,3a,3b,26-28</sup> and their presence in the bridging and terminal positions along with the appearance of absorptions in the region  $800-400\text{ cm}^{-1}$  characteristic of metal oxygen stretching frequencies.

### 3.3.1.2 Nuclear Magnetic Resonance Spectroscopy

Structural features of the following have been elucidated by the distinctive appearance of the terminal and bridging alkoxy group signals in their  $^1\text{H}$  NMR spectra:  $\text{Be}\{\text{Al}(\text{OPr}^i)_4\}_2$ ,<sup>27</sup>  $\text{Zn}\{\text{Al}(\text{OPr}^i)(\text{OBU}^t)_3\}_2$ ,<sup>27</sup>  $\text{Ba}\{\text{Zr}_2(\text{OPr}^i)_9\}_2$ ,<sup>25</sup> (at  $-60^\circ\text{C}$ ),  $[(\text{Pr}^i\text{O})\text{Ba}\{\text{Zr}_2(\text{OPr}^i)_9\}_2]$ ,<sup>25</sup> and  $\text{K}\{\text{Zr}_2(\text{OPr}^i)_9\}$ ,<sup>3b</sup> (in  $\text{C}_6\text{D}_6$ ).

However, fast exchange of alkoxy groups, even at lower temperatures, limits the utility of this simple technique.

Although it would appear that  $^{13}\text{C}$  NMR of Ca in the alkoxide group should be more diagnostic for terminal,  $\mu_2$  or  $\mu_3$  groups, in view of the greater chemical shift dispersion in  $^{13}\text{C}$  NMR (compared with  $^1\text{H}$  NMR), no convincing observations have been accumulated in this direction. Since the usefulness of  $^{17}\text{O}$  NMR spectroscopy<sup>3f</sup> as a structural probe has been demonstrated previously in different systems, the technique may prove of considerable assistance in diagnosing terminal  $\mu_2$ - and  $\mu_3$ -alkoxide groups, but such studies are still lacking.

Further, solid state NMR (MAS) would be more promising and could complement X-ray diffraction studies and serve as an alternative source of solid state structural elucidation, particularly in cases where suitable crystals cannot be obtained.

### 3.3.1.3 Mass Spectrometry

This technique can give valuable information on the composition of volatile and stable heterometallic alkoxides, in the vapour phase. Thus, for more complete characterization and their optimum use in MOCVD techniques, mass spectroscopy allows a first rough selection of such precursors. The technique has been used to establish the heterometallic character of species of the type:  $[(\text{Pr}^i\text{O})_3\text{Ti}(\mu\text{-OPr}^i)_2\text{Be}(\mu\text{-OPr}^i)_2\text{Al}(\text{OPr}^i)_2]$ ,<sup>36</sup>  $[(\text{Pr}^i\text{O})_4\text{Nb}(\mu\text{-OPr}^i)_2\text{Be}(\mu\text{-OPr}^i)_2\text{Al}(\text{OPr}^i)_2]$ ,<sup>36</sup> and  $\text{NaCu}(\text{OCMe}_3)_3$ .<sup>4</sup>

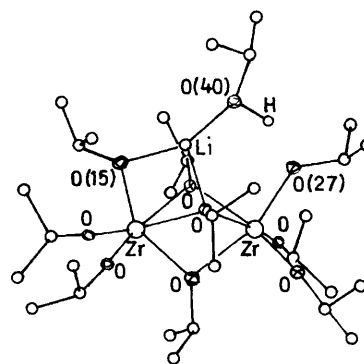
## 3.4 X-Ray Crystallographic Studies

Although X-ray crystallography is a more precise and definitive technique for structural elucidation its application in the study of metal alkoxides has been (as stated earlier) in general frustrated by the following factors:<sup>1b,3b</sup> (i) difficulties in crystallization due to high solubility in common organic solvents, (ii) crystallographically unsuitable crystals, (iii) disorder phenomena, (iv) twinning problems, and (v) extreme moisture sensitivity. In spite of these limitations, single crystal X-ray structures of a number of heterometallic alkoxides of groups 1, 2, and 12 metals such as: (i)  $[\text{Li}\{\text{Zr}_2(\text{OPr}^i)_9\}\cdot\text{Pr}^i\text{OH}]$ ,<sup>37</sup> (ii)  $[\text{LiNb}(\text{OCH}_2\text{CH}_3)_6]$ ,<sup>38</sup> (iii)  $[\text{LiTi}(\text{OPr}^i)_5]$ ,<sup>32</sup> (iv)  $\text{Na}_2[\text{Cu}(\text{OCH}(\text{CF}_3)_2)_4]$ ,<sup>4</sup> (v)  $\text{NaTh}_2(\text{OBU}^t)_9$ ,<sup>32b</sup> (vi)  $\text{Na}_8\text{Ln}(\text{OBU}^t)_{10}\text{X}^{32c}$  (Ln = Y, Eu; X = Cl, OH), (vii)  $[\text{KSn}(\text{OBU}^t)_5]_\infty$ ,<sup>19b</sup> (viii)  $[\text{KSn}(\text{OBU}^t)_3]_\infty$ ,<sup>19a</sup> (ix)  $[\text{LiTi}(\text{OPr}^i)_3]_4$ ,<sup>35</sup> (x)  $[\text{Ba}_2\text{Cu}_2(\text{OC}_2\text{H}_4\text{OME})_4(\text{acac})_4(\text{MeOC}_2\text{H}_4\text{OH})_2]$ ,<sup>22</sup> (xi)  $\text{Ba}\{\text{Cu}[\text{OCMe}(\text{CF}_3)_2]_3\}_2$ ,<sup>31</sup> (xii)  $[\text{Ba}_4\text{Ti}_3(\text{O})_{18}(\text{OCH}_2\text{CH}_2\text{OME})_{24}]$ ,<sup>34</sup> (xiii)  $[\text{Ba}_4\text{Ti}_4(\text{O})_4(\text{OPr}^i)_{16}(\text{Pr}^i\text{OH})_n]^{23}$  ( $n = 4$  or  $3$ ), (xiv)  $[\text{BaZr}_2(\text{OPr}^i)_{10}]_2$ ,<sup>25</sup> (xv)  $\text{Ba}\{\text{Zr}_2(\text{OPr}^i)_9\}_2$ ,<sup>25</sup> (xvi)  $[\text{BaCu}_4\{\text{OC}(\text{R})\text{C}(\text{H})\text{C}(\text{R})\text{O}\}_4(\text{OR}')_2(\text{HOR}')_4]$ ,<sup>24</sup> ( $\text{R} = \text{C}(\text{CH}_3)_3$ ,  $\text{R}' = \text{CH}_2\text{CH}_2\text{OCH}_3$ ), (xvii)  $[\text{BaZr}_4(\text{OH})[\text{OPr}^i]_{17}]$ ,<sup>35</sup> (xviii)  $[\text{Ti}_2(\text{OC}_2\text{H}_5)_8\text{Cl}]_2\text{Mg}(\mu\text{-Cl})_2\text{Mg}]$ ,<sup>29</sup> (xix)  $\text{Mg}_2\text{Al}_3(\text{OPr}^i)_{13}$ ,<sup>3d</sup> (xx)  $[\text{SrSn}_2(\text{OBU}^t)_6]$ ,<sup>19c</sup> (xxi)  $[\text{Cd}_4\text{Sn}_4(\text{O})_2(\text{OAc})_{10}(\text{OCH}_2\text{CMe}_3)_{10}]$ ,<sup>30</sup> (xxii)  $[\{\text{Cd}[\text{Zr}_2(\text{OPr}^i)_9]-(\mu\text{-Cl})_2\}]$ ,<sup>26b</sup> (xxiii)  $[\text{Sr}_2\text{Ti}(\text{OPr}^i)_8(\text{Pr}^i\text{OH})_5]$ ,<sup>21</sup> have been characterized recently.

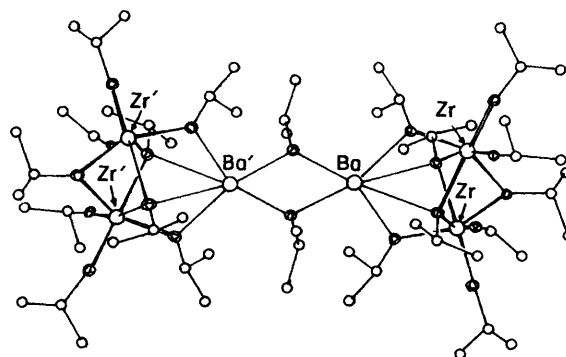
The molecular structures (Figures 10—18) of some of the more important derivatives listed above are discussed in the following sections.

### 3.4.1 Molecular Structure of $[\text{Li}\{\text{Zr}_2(\text{OPr}^i)_9\}\cdot\text{Pr}^i\text{OH}]$ <sup>37</sup>

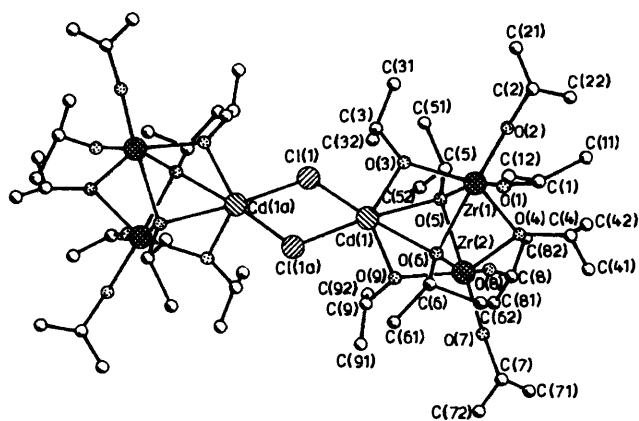
Hydrocarbon-soluble  $\text{Li}\{\text{Zr}_2(\text{OPr}^i)_9\}\cdot\text{Pr}^i\text{OH}$  has a solid state structure (Figure 10) in which the small lithium atom interacts with a  $(\text{Pr}^i\text{O})_3\text{Zr}(\mu_2\text{-OPr}^i)_3\text{Zr}(\text{OPr}^i)_3$  sub-structure via two  $(\mu_2\text{-OPr}^i)$  bridging groups and one terminal  $(\text{OPr}^i)$  group. The fourth coordination site on Li is occupied by  $\text{Pr}^i\text{OH}$ , which also forms hydrogen bonds to oxygen of a terminal alkoxide on Zr.



**Figure 10** ORTEP drawing of  $[\text{Li}\{\text{Zr}_2(\text{OPr}^i)_9\}\cdot\text{Pr}^i\text{OH}]$ .<sup>37</sup> Selected bond lengths (Å): Zr—O, 1.923(3)—1.945(3); Zr—( $\mu_2$ -O) 2.143(3)—2.226(3); Zr—( $\mu_3$ -O) 2.229(3)—2.287(3); Li—O 1.88; Li—O (PrOH) 1.840(8); Li—( $\mu_3$ -O) 2.027(8), 2.066(9).



**Figure 11** ORTEP drawing of  $[\text{BaZr}_2(\text{OPr}^i)_{10}]_2$ .<sup>25,37</sup> Selected bond lengths Zr—O, 1.924(7)—2.252(6); Zr—O, 1.931; Zr—( $\mu$ -OBa) 2.055 Å; Zr—( $\mu_2$ -O—Zr) 2.199 Å; Zr—( $\mu_3$ -O) 2.239 Å; Ba—O 2.551(7)—2.895(6); Ba—(OBa) 2.572 Å; Ba—( $\mu$ -OZr) 2.748 Å; Ba—( $\mu_3$ -O) 2.884 Å.



**Figure 12** ORTEP drawing of  $[\{\text{Cd}\{\text{Zr}_2(\text{OPr}^i)_9\}\cdot(\mu\text{-Cl})_2\}]$ .

### 3.4.2 Molecular Structure of $[\text{BaZr}_2(\text{OPr}^i)_{10}]_2$ .<sup>25,37</sup>

The solid state structure of dimer  $[(\text{Pr}^i\text{O})\text{Ba}\{\text{Zr}_2(\text{OPr}^i)_9\}]_2$  (Figure 11) shows two triangular  $\text{BaZr}_2(\mu_3\text{-OR})_2(\mu_2\text{-OR})_3(\text{OR})_4$  units linked together by two isopropoxides bridging the barium centre, or alternatively exists as a  $\text{Ba}_2(\mu\text{-OR})_2^+$  unit in which each Ba—unlike the smaller Li (Figure 10)—is sequestered by four alkoxides arms of a face-shared bioctahedral  $\text{Zr}_2(\text{OPr}^i)_9$  unit. Ba in this structure is six-coordinated, but far from octahedral, and forms bonds nearly as short to oxygen bound to one zirconium 2.71 and 2.79(1) Å as to oxygen bound to two zirconiums 2.87 and 2.90(1) Å; this also evident in the *trans* O—Ba—O angles, which range from 114.55 to 167.63°.

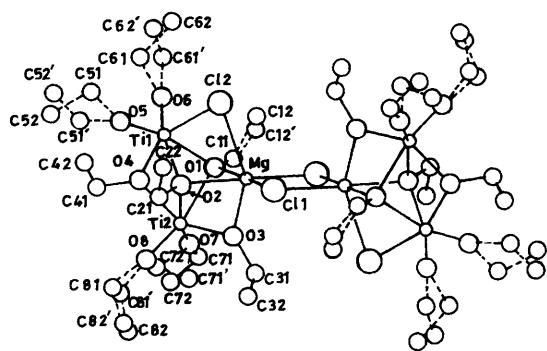


Figure 13 ORTEP drawing of  $[\text{Ti}_2(\text{OC}_2\text{H}_5)_8\text{Cl}]_2\text{Mg}(\mu\text{-Cl})_2\text{Mg}$ .<sup>29</sup>

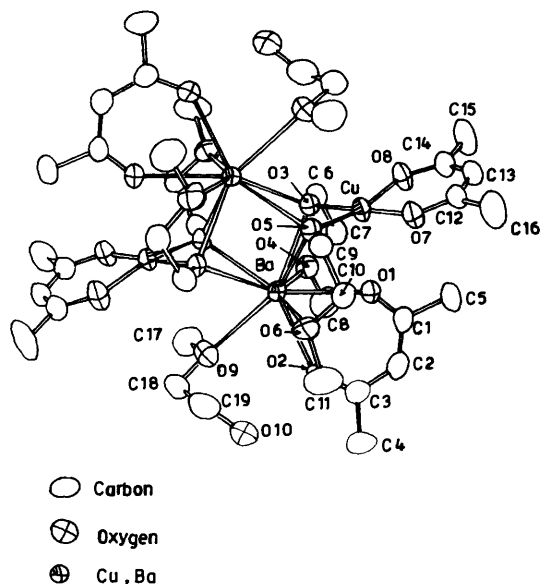


Figure 14 ORTEP drawing of  $\text{Ba}_2\text{Cu}_2(\mu_3\text{-OC}_2\text{H}_4\text{OMe})_4(\text{acac})_4(\text{MeOC}_2\text{H}_4\text{OH})_2$ .<sup>22</sup>

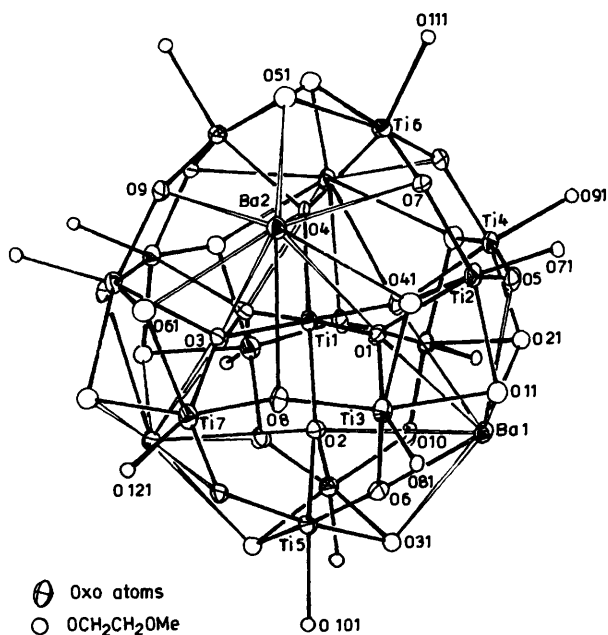


Figure 15 Molecular structure of  $\text{Ba}_4\text{Ti}_{13}(\mu_3\text{-O})_{12}(\mu_5\text{-O})_6(\mu\text{-}\eta^1\text{-OCH}_2\text{CH}_2\text{OCH}_3)_{12}(\mu_1, \mu_3\text{-}\eta^2\text{-OCH}_2\text{CH}_2\text{OCH}_3)_{12}$ .<sup>34</sup>

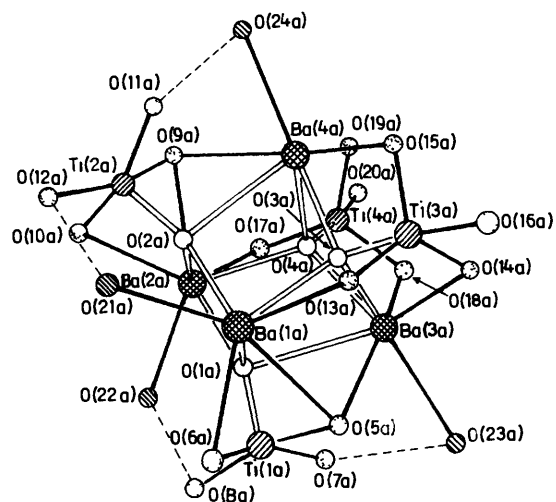


Figure 16 Molecular structures of  $[\text{Ba}_4\text{Ti}_4(\mu_4\text{-O})_4(\mu_3\text{-OR})_2(\mu\text{-OR})_8(\text{OR})_6(\text{ROH})_4]$  (A) and  $[\text{Ba}_4\text{Ti}_4(\mu_4\text{-O})_4(\mu_3\text{-OR})_2(\mu\text{-OR})_9(\text{OR})_3(\text{ROH})_3]$  (B).<sup>23</sup>

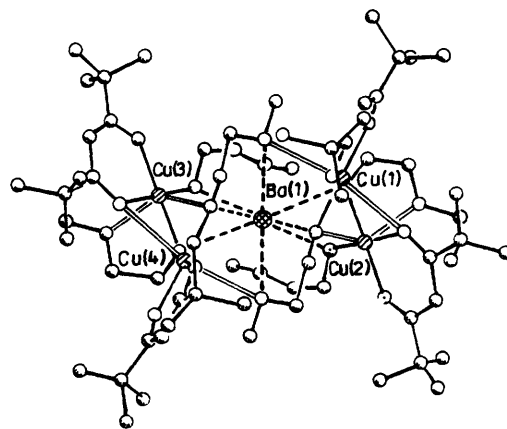
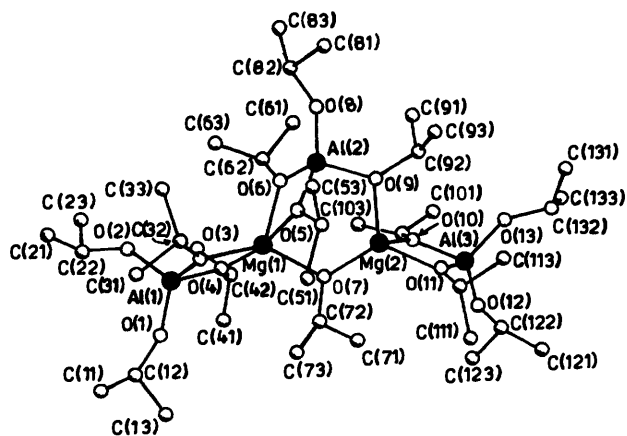


Figure 17 Molecular structure of  $[\text{BaCu}_4(\text{thd})_4(\text{OCH}_2\text{CH}_2\text{OMe})_6]^{2+}$  (thd = 2,2,6,6-tetramethyl-3,5-heptanedionato).





**Figure 18** Molecular structure of  $\text{Mg}_2\text{Al}_3(\text{OPr})_{13.3d}$ . Average bond lengths (Å): Al–O(terminal) 1.65(1), Al–O (bridging) 1.77(1). The Mg–O bonds show greater variation: Mg(1)–O(3) 2.005(8), Mg(1)–O(4) 2.077(8), Mg(1)–O(5) 2.136(9), Mg(1)–O(6) 2.019(8), Mg(1)–O(7) 1.99(8), Mg(2)–O(7) 1.910(8), Mg(2)–O(9) 1.989(8), Mg(2)–O(10) 1.949(9), Mg(2)–O(11) 1.980(9).

### 3.4.3 Molecular Structure of $\{[\text{Cd}[\text{Zr}_2(\text{OPr})_9(\mu\text{-Cl})]_2\}^{26b}$

The solid state structure of dimeric derivative  $\{[\text{Cd}[\text{Zr}_2(\text{OPr})_9(\mu\text{-Cl})]_2\}$  (Figure 12) is composed of two triangular  $\text{CdZr}_2(\mu_3\text{-OPr})_2(\mu\text{-OPr})_3(\text{OPr})_4$  units linked by two chloride bridges. In each of these units cadmium interacts (similarly to Ba, Figure 11) with a face-shared bioctahedral  $\text{Zr}_2(\text{OPr})_9$  moiety *via* two terminal and two bridging OPr groups of the  $\text{Zr}_2(\text{OPr})_9$  unit. Although the Cd is six-coordinated there are substantial departures from ideal octahedral geometry around the atom, tending towards a bicapped tetrahedral arrangement. The average of the Cd–Cl bond lengths 2.556(2) Å is significantly less than the sum of the ionic radii (2.780 Å) and shows that these bonds are essentially covalent. This Cd–Cl distance is considerably shorter than is found in octahedrally coordinated cadmium complexes. Thus the Cd–Cl bond length observed in the complex is consistent with highly distorted octahedral geometry.

### 3.4.4 Molecular Structure $\{[\text{Ti}_2(\text{OC}_2\text{H}_5)_8\text{Cl}]_2\text{Mg}(\mu\text{-Cl})_2\text{Mg}\}^{29}$

This molecule is a centrosymmetric dimer (Figure 13). The two symmetric parts of the molecules consist of three distorted face-shared octahedral arrangements around the magnesium and the two titanium atoms surrounded by the terminal ethyl groups. One of the titanium atoms is hexacoordinated by one chlorine and five oxygen atoms, the other by six oxygens. The magnesium is surrounded by three oxygen and three chlorine atoms. The titanium–oxygen distances vary considerably depending upon the number of metal atoms coordinated to the oxygen: for oxygen bonded to three metal atoms the mean Ti–O distance is 2.135(4) Å; for oxygen bonded to two metal atoms, 1.974(3) Å; for the other five oxygens bonded to one metal atom, 1.761(5) Å. The Ti–Cl (bridged with Mg) distance [2.458(2) Å] was in the range found for TiCl (bridge) complexes. A very surprisingly long Mg–Cl (bridged by Ti) distance [2.673(2) Å] suggests a very weak link probably due to the strong distortion of the octahedral arrangement. The pseudo-octahedral geometry in the molecule is also confirmed by bond angles around the hexa-coordinated Ti(1), Ti(2), and Mg atoms, which deviate from the theoretical value by up to 21°.

### 3.4.5 Molecular Structure of $\text{Ba}_2\text{Cu}_2(\mu_3\text{-OC}_2\text{H}_4\text{OMe})_4(\text{acac})_4(\text{MeOC}_2\text{H}_4\text{OH})_2$

In the molecule  $\text{Ba}_2\text{Cu}_2(\mu_3\text{-OC}_2\text{H}_4\text{OMe})_4(\text{acac})_4(\text{MeOC}_2\text{H}_4\text{OH})_2$  the metals are arranged in a rhomboid with triply bridging alkoxide oxygens above and below the two triangular planes

defined by two barium atoms and one copper atom. Each metal atom is bound to an acac ligand and the barium is further coordinated by the methoxy oxygen of the triply bridging alkoxide and a 2-methoxyethanol.

### 3.4.6 Molecular Structure of $\text{Ba}_4\text{Ti}_{13}(\mu_3\text{-O})_{12}(\mu_5\text{-O})_6(\mu\text{-}\eta^1\text{-OCH}_2\text{CH}_2\text{OCH}_3)_{12}(\mu_1,\mu_3\text{-}\eta^2\text{-OCH}_2\text{CH}_2\text{OCH}_3)_{12}$

X-Ray structural analysis of the above crystalline derivative revealed a tetrahedron of  $\text{BaO}_3$  units superimposed on a  $\text{TiO}_6$  ( $\text{TiO}_3$ )<sub>12</sub> core (Figure 15). Each barium atom interacts with twelve oxygen atoms, six from three chelating alkoxide ether ligands and six from oxo ligands. The unique central Ti atom is octahedrally coordinated to six trigonal-bipyramidal oxo ligands. External Ti atoms are coordinated to one internal ( $\mu_5$ ) and two bridging ( $\mu_3$ ) oxo ligands in addition to one terminal ( $\mu_1\text{-}\eta^1$ ) and two bridging ( $\mu_1,\mu_3\text{-}\eta^2$ ) alkoxide oxygen atoms.

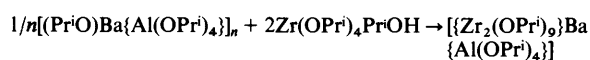
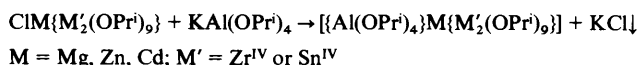
### 3.4.7 Crystal Structure of $\text{BaTiO}(\text{OPr})_4 \cdot 7/8\text{Pr}^{\text{IV}}\text{OH}^{23}$

An X-ray structural study of this complex shows that it contains two different kinds of molecules:  $[\text{Ba}_4\text{Ti}_4\text{O}_4(\text{OR})_{16}(\text{ROH})_4]$  (A) and  $[\text{Ba}_4\text{Ti}_4\text{O}_4(\text{OR})_{16}(\text{ROH})_3]$  (B), which differ mainly in the number of solvating alcohol molecules in the crystal: 4 and 3 for complexes A and B respectively (Figure 16). Both the complexes have the same metal–oxygen core: a distorted cube with alternating Ba and O (oxo groups) atoms in its vertices. Each oxo atom is bonded to one of the Ti atoms which are also linked to the  $\text{Ba}_4\text{O}_4$  core by the bridging alkoxide groups Ti–OR–Ba.

## 4 Heterotrimetallic Alkoxides

In spite of the extraordinary stability exhibited by bimetallic alkoxides, only few attempts have been made so far to synthesize tri- and tetra-metallic species, in view of the generally observed instability of such heterometallic species in the absence of metal–metal bonds and auxiliary ligands like CO.

In fact the stability of the first trimetallic species of Be characterized (in 1985)<sup>36</sup> was initially ascribed to the smallness of the central Be atom. However, the work has been since extended to the synthesis and characterization of a large number of tri-/tetra-metallic species of some other elements<sup>3a,3b</sup> also; a few of these, belonging to group 2 and 12 metals,<sup>26d,26e</sup> are described below:



## 5 Metal Alkoxides as Precursors for Oxide-Ceramic Materials

It is now well established that preparation of ceramics *via* the *sol-gel* route can be described by three stages: (1) gel synthesis, (2) drying, and (3) ceramic conversion. Gel synthesis can be achieved either by (i) destabilization of colloidal solutions, or (ii) controlled hydrolysis of solutions of suitable metal salts/derivatives in alcohols followed by polycondensation of the sol thus obtained (Figure 19).

This technique has been applied not only to the preparation of single component oxide glasses, *e.g.*  $\text{SiO}_2$ , but also more recently to the preparation of multicomponent oxide glasses and ceramic materials (in different forms, *e.g.* bulk, powder, wire, coating *etc.*). Metal ethoxide, -isopropoxide, and -butoxide complexes have received considerable interest as precursors. The reactions involved in the process of making metal oxide ceramics from homo- and hetero-metallic alkoxides *via* the *sol-gel* process may be represented as follows:

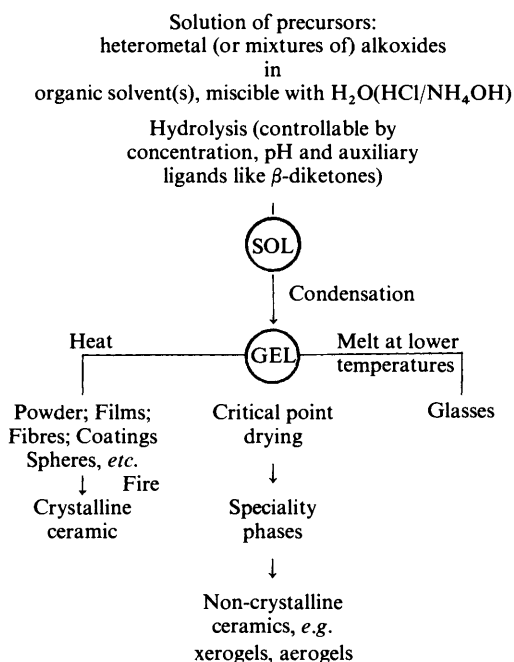
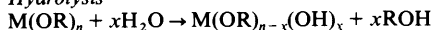
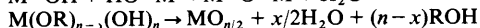
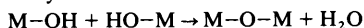


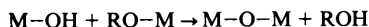
Figure 19

*Hydrolysis**Condensation*

## (a) Dehydration



## (b) Dealcoholation



If a multicomponent alkoxide solution or single alkoxide and a soluble inorganic salt<sup>3c</sup> are mixed in solution, hetero-metallic oxides may form according to the above reactions – except that the reactions now occur between two different metal ion species.

Such reactions occur simultaneously in most cases, but the real attraction of the alkoxide route is the possibility of controlling the rate of formation of M-O-M or M-O-M' networks by chemical means (e.g. addition of auxiliary bidentate ligands such as alkoxyalkanols, aminoalkanols,  $\beta$ -diketones, and carboxylic acids).

The mechanisms and rates of these reactions are greatly influenced by several factors, including water/alkoxide ratio, dilution of reacting species in the carrier solvents, pH, temperature, auxiliary ligand, and electrolyte. Furthermore, depending on the varying conditions of the reactions, either linear polymers or more cross-linked clusters can form. The main advantages of the sol-gel technique are: (1) much lower sintering temperatures than those required in the conventional procedure of fusing the metal oxides, and (2) the possibility of obtaining the final material in the desired (bulk, powder, wire, and coating) forms by slight variations of the concentrations of solution and conditions of gellification as well as of sintering.

In this rapidly developing technique, metal alkoxides are proving to be attractive precursors owing to their facile hydrolyzability which can be generally modified/controlled by replacement of some of the alkoxy groups on the metals with less hydrolysable ligands, e.g.  $\beta$ -diketonates and chelating alcohols.

To explain the ultrahomogeneity of the final ceramic material obtained by the sol-gel process using a number of alkoxides of different metals, Dislich had conjectured (1971) that in addition to the obvious advantage of more intimate physical mixing of metal alkoxides at the molecular level in solution, new chemical bonds might be getting formed amongst different alkoxides.

This unnoticed conjecture of Dislich has been virtually confirmed by the facile formation and isolation of a wide variety of heterometal alkoxide species and, sometimes, oxide-alkoxide species, from mixtures of constituent alkoxides in solution.

In view of the above, it could well be expected that the use of presynthesized heterometal alkoxides as precursors would offer advantages over the randomly formed heterometal alkoxide species in solution. This expectation has been confirmed in the preparation of (i) crystalline lithium niobate (a well-known ferroelectric and piezoelectric material with a high curie temperature) fibres and potassium niobate discs<sup>39</sup> from the corresponding alkali hexaethoxyniobate Li/KNb(OEt)<sub>6</sub>; (ii) crystalline films LiNb<sub>x</sub>Ta<sub>1-x</sub>O<sub>3</sub> (0 < x ≤ 1)<sup>40</sup> from a mixture of LiNb(OEt)<sub>6</sub> and LiTa(OEt)<sub>6</sub>; (iii) the YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> thin films or bulk powders from Ba<sub>2</sub>Cu<sub>2</sub>(OR)<sub>4</sub>(acac)<sub>4</sub>(HOR)<sub>2</sub> (R = CH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>),<sup>24</sup> (iv) relaxor-based dielectrics and piezoelectrics from Pb<sub>2</sub>Zn<sub>2</sub>(C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>)<sub>4</sub>(C<sub>3</sub>H<sub>7</sub>O<sub>2</sub>)<sub>4</sub>,<sup>41</sup> (v) high frequency ceramic capacitors from an oxo-alkoxide complex Ba<sub>4</sub>Ti<sub>13</sub>O<sub>18</sub>(OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>)<sub>24</sub>,<sup>34</sup> (vi) lead magnesium niobate {Pb(Mg<sub>1/3</sub>Nb<sub>2/3</sub>)O<sub>3</sub>}<sub>42</sub> as relaxor ferroelectrics from Mg{Nb(OEt)<sub>6</sub>}<sub>2</sub> and Pb(OAc)<sub>2</sub> in methoxyethanol, and (vii) lead zinc niobate {Pb(Zn<sub>1/3</sub>Nb<sub>2/3</sub>)O<sub>3</sub>}<sub>43</sub> based ceramics from Zn{Nb(OEt)<sub>6</sub>}<sub>2</sub> and Pb(OAc)<sub>2</sub> in methoxyethanol.

Following the advent of superconducting materials, concerted efforts have been directed as described above towards the preparation of soluble alkoxides of bivalent metals like alkaline earth metals and copper, etc. Most of the efforts have been so far centred around the use of chelating alcohols like alkoxyalkanols, followed by hydrolysing an alcoholic solution of Y(OR)<sub>3</sub>, Ba(OR)<sub>2</sub>, and Cu(OR)<sub>2</sub> in the molar ratio of 1:2:3, followed by sintering the gel in the presence of oxygen. Attempts are being made, with so far only marginal success, to presynthesize a hetero-metal alkoxide of overall composition corresponding to YBa<sub>2</sub>Cu<sub>3</sub>(OR)<sub>13</sub>, which could then be used as a single-source precursor.

## 6 Future Prospects and Need for Further Investigations

Although a considerable amount of empirical knowledge has been accumulated during the past decade on alkoxides of various elements including those of groups 1,2, and 12, yet precise physico-chemical data, particularly on bonding energies, are not yet available. These could throw fresh light on the observed higher stability of heterometallic derivatives involving alkoxy bridges between different metals, and could be of immense help in predicting the stability of different oxide-alkoxide derivatives which have been isolated and characterized by X-ray crystallography. This in turn should provide a better understanding of the unique stability of the heterometal species and could also lead towards fulfilling the dream of synthesizing 'single source precursors' of a composition corresponding to the targeted final ceramic material.

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