

# Recent Advances in the Chemistry of Homo- and Heterometallic Alkoxides of p-Block Metal(loid)s

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changed to heterobimetallic alkoxides<sup>3,4</sup>) has also developed during the same period.

A number of reviews have appeared on alkoxides of transition<sup>4,5</sup> and inner-transition<sup>6,7</sup> metals since the publication of the book *Metal Alkoxides* in 1978,<sup>1</sup> but with the exception of two articles on alkoxy derivatives of silicon<sup>8</sup> and tin,<sup>8,9</sup> no review has been published on the chemistry of homo- and heterometallic alkoxides of main group metal(loid)s.

The chemistry of metal alkoxides as a whole has seen an unprecedented spurt of activity<sup>3-21</sup> during the last decade, due to a number of reasons, e.g., (i) potential applications as precursors<sup>9-11,13-17</sup> for oxide-based ceramic materials arising from their facile hydrolyzability, which can be modulated<sup>16-21</sup> by chelating ligands like carboxylates,  $\beta$ -diketonates, and alkoxy ethoxides, (ii) possibilities of excitingly novel structures,<sup>4,22,23</sup> (iii) formation of oxoalkoxides either by hydrolysis<sup>24,25</sup> or by some side reactions,<sup>22</sup> (iv) the extraordinary stability of alkoxide bridges between dissimilar metals, which retain in many cases their configuration during volatilization and hydrolysis<sup>21,22</sup> resulting in ultrahomogeneous mixed-metal oxide ceramic materials,<sup>14-16</sup> and (v) marked catalytic activity of these species.<sup>4</sup>

Simple binary alkoxides of the general formulae  $[M(OR)_x]_n$  are known for most s-, p-, d-, and f-block elements. Heterometallic alkoxides are now known for a wide variety of metal(loid)s and some of these exhibit remarkable features. For example, aluminum with lanthanoids forms an extensive series of heterometallic isopropoxides of formulae  $L_n\{Al(O^iPr)_4\}_3^7$  and  $[Ln\{Al(O^iPr)_4\}_2(\mu-Cl)(^iPrOH)]_2$ ,<sup>7</sup> and analogous gallate and indate derivatives are also possible.

## 1. Introduction

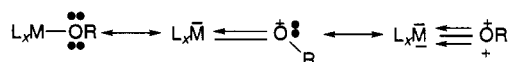
### 1.1. General

Beginning with alkyl orthosilicates and orthoborates in 1846,<sup>1</sup> the alkoxide chemistry of mostly main group (e.g., Be, Mg, Ca, Al, Ge, Se, Te, etc.) and only a few transition (e.g., Ti, Zr, Hf, and V) elements was investigated up to 1950, after which emphasis was shifted<sup>1</sup> to the transition metals during the next three decades. During last 15 years, however, the main group metal(loid)s have again received considerable attention. The chemistry of bimetallic alkoxides (termed initially as alkoxo salts,<sup>1</sup> followed by the term double alkoxides,<sup>2</sup> which has recently been

### 1.2. Structural Features

Alkoxide ligands have a remarkably flexible bridging tendency between similar as well as dissimilar metal atoms, adjusting themselves according to the extent of the ramification<sup>26-29</sup> of the alkyl groups and the atomic sizes of different metal atoms bridged (in  $\mu_2$  or  $\mu_3$  configurations) by them; these features give rise to a number of interesting structures as illustrated in Figure 1.

Another interesting feature of the alkoxo ligands is their ability to act as 3e or 5e donor ligands:





Professor Emeritus R. C. Mehrotra [M.Sc., D.Phil. (Allid.), Ph.D., D.Sc., (Lond.)] was born in Kanpur (U.P.), India. He served as lecturer at Allahabad University (1944–1954), Reader at Lucknow University (1954–1958), Professor and Head of the Department of Chemistry of Gorakhpur (1958–1962) and Rajasthan Universities (1962–1982), where he continues to be actively associated as Emeritus Professor. Since 1950 he has been working in the field of alkoxide chemistry and his research school has made notable contributions such as the aging phenomenon of aluminum alkoxides, applications of metal alkoxides as synthons for the synthesis of fascinating types of metal–organic derivatives (e.g., aluminum tricarboxylates and anhydrous tris( $\beta$ -diketonato)lanthanoids which can not be synthesized, so far, by any other route), and synthesis of stable heterometallic alkoxides. He is an inorganic chemist with interest in diversified areas such as Adsorption Indicators, Redox Titrmetry, Polymetaphosphates, and M–S derivatives (especially dialkyl thiophosphates) of a number of metals. He has authored/coauthored four books (e.g., *Metal alkoxides*, *Metal  $\beta$ -diketonates and allied derivatives*, *Metal carboxylates*, and *Organometallic chemistry*) and over 600 hundred research papers in these fields. He has received numerous honors and prizes in India and abroad, beginning with the prestigious Bhatnagar Award in 1965. In 1993 he was the first Indian to be elected to the fellowship of the Federation of Asian Chemical Societies. The contributions of his research school have been recognized by invitations to deliver plenary/key note/special lectures on different facets of alkoxide chemistry at dozens of international conferences/symposia/workshops dealing with coordination chemistry, organometallic chemistry, inorganic phosphorus chemistry, and more recently, sol–gel science and technology.

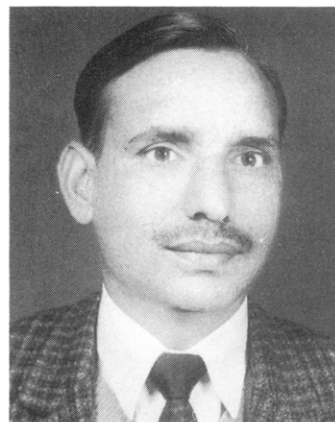
### 1.3. Scope and Organization of the Subject Matter

Of the “p”-block metal(oids) of groups 13 to 16, the main focus of this review is on homo- and heterometallic alkoxide chemistry of the elements marked with asterisk (\*), which appear to have received special attention during the last decade:

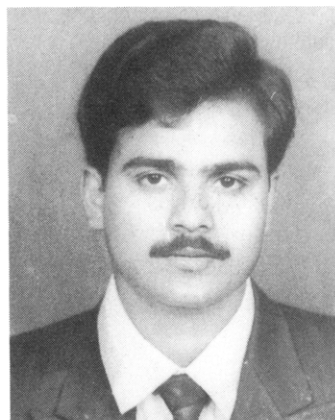
13	14	15	16	17
$s^2p^1$	$s^2p^2$	$s^2p^3$	$s^2p^4$	$s^2p^5$
B*	C	N	O	F
Al*	Si*	P	S	Cl
Ga*	Ge*	As*	Se	Br
In*	Sn*	Sb*	Te	I
Tl*	Pb*	Bi*	Po	At

## 2. Synthesis

Different methods of synthesis have been arranged in broad groups, allotting a code (A–G) to each of



Anirudh Singh, an Associate Professor of Chemistry at the University of Rajasthan, Jaipur, was born in a village (Bhojpur) of district Bahraich (U.P.), India, in 1938. He received the M.Sc. degree in Inorganic Chemistry from Lucknow University in 1965 and the Ph.D. degree (under the supervision of Professor R. C. Mehrotra) from the University of Rajasthan in 1972, where in 1971 he was appointed as Assistant Professor and became Associate Professor in 1987. He spent three years (1979–1982) as SERC postdoctoral fellow with Professor M. F. Lappert, FRS, at the University of Sussex (U.K.), working on synthetic, structural, and mechanistic studies in organometallic and inorganic chemistry and contributed richly in the areas of sterically hindered silylated cyclopentadienyls and aryloxides of d- and f-block metals. Dr. Singh has also been a visiting scientist (under the ALIS Programme, The British Council) at the University of Sussex for three months in 1987. His research interests have centered on the synthesis and reactivity and structural, magnetic, and electronic properties of metal(loid)–organic derivatives, with more emphasis since 1982 on homo- and heterometallic alkoxide/aryloxide/oximate/organometallic systems, having potentials as useful precursors for advanced ceramic materials. He is author and coauthor of over 90 research papers including approximately nine review articles. He has recently coauthored with Professor R. C. Mehrotra the widely known book entitled *Organometallic Chemistry: A Unified approach* (John Wiley, New York (Wiley Eastern, New Delhi), 1991).



Dr. Sanjeev Sogani was born in Jaipur in 1967. He received B.Sc. (1986), M.Sc. (1988), and Ph.D. (1992) degrees from the University of Rajasthan, Jaipur (India). His doctoral work entitled “Studies on Simple and Polymetallic Alkoxides of Some Group 2 and 12 Metals” was supervised by Professor Emeritus R. C. Mehrotra and Dr. A. Singh (Associate Professor) with whom he is presently working as a Research Associate. He has coauthored seven scientific papers. He is recipient of Indian Science Congress Association Young Scientist Award (1994). His current research interests are homo- and heterometallic alkoxides of s- and p-block metal(oid)s.

them, by which the method utilized for each specific derivative has been marked in subsections 2.1.1 and 2.2.1, incorporating the homo- and heterometallic alkoxides known so far.

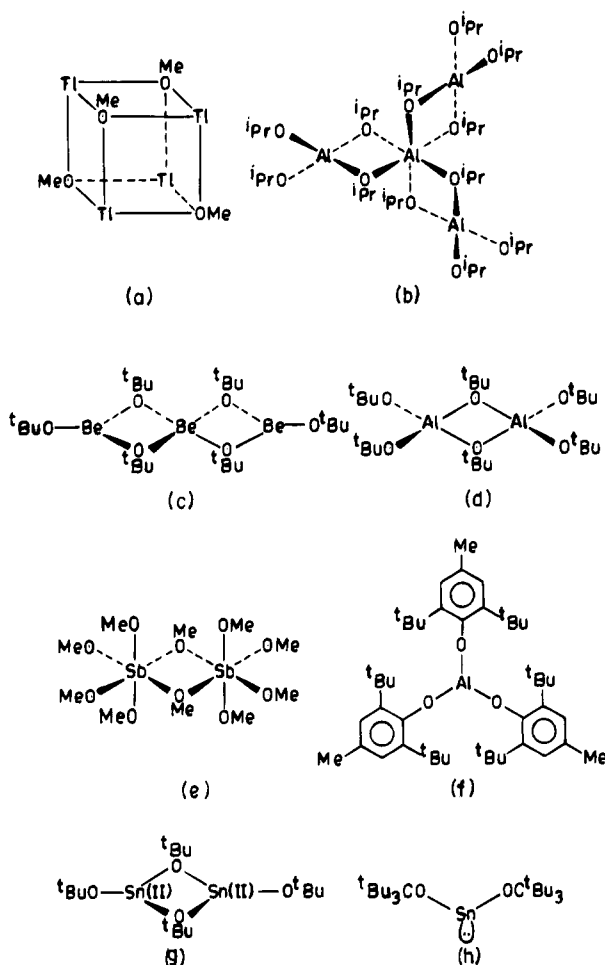
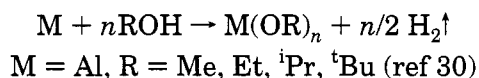


Figure 1.

## 2.1. Homometallic Alkoxides of Groups 13, 14, 15, and 16 (p-Block) Metal(loid)s

### 2.1.1. Synthetic Methods for Homometallic Alkoxides

**A. From the Metals.** A-1. *Reactions of the Bulk Metals with Alcohols.*

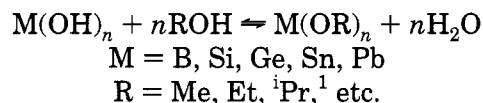
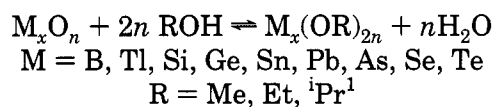


The facility of the reactions depends on both the nature of the elements and acidity of the alcohol. For less electropositive metal(loid)s, direct reaction between the bulk metal and alcohol is not observed. However, activation of metals like aluminum has been possible by addition of iodine or/and mercuric chloride. Similarly, the reduction of metal iodides in THF with potassium has been utilized for providing more reactive finely divided metal powders. In addition, methods A-2 and A-3 have also been utilized for the activation of less reactive metal(loid)s.

**A-2. Electrochemical Methods.** This method with increasing potential applicability was introduced in 1906 by Szilard for the synthesis of copper and lead methoxides and has so far been utilized for the synthesis<sup>31</sup> of alkoxides of Ga, Si, and Ge.

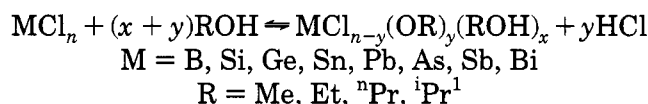
**A-3. Reaction of Metal Atom Vapors with Alcohols.** This method has been exploited so far for aryloxide derivatives<sup>32</sup> only. However, concerted efforts are continuing to extend the same for alkoxide derivatives also.

## B. From Metal Oxides or Hydroxides.

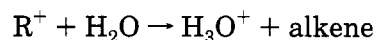
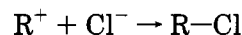
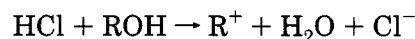


Metal(loid) oxides/hydroxides react with alcohols to form esters (alkoxides) and water. The liberated water has been generally removed azeotropically with a solvent like benzene. This method has been conveniently used for the synthesis of alkoxides of B, Tl, Si, Ge, Sn, Pb, As, Se, and Te. More recently, useful modifications<sup>33,34</sup> have been suggested for the removal of liberated water by the addition of a suitable dehydrating agent like  $CaH_2$  in the reaction mixture.<sup>34</sup> A few interesting examples of this method at suitable places are shown in Table 1.

**C. From Metal(loid) Chlorides.** C-1. *Reactions of Metal(loid) Chlorides with Alcohols.*

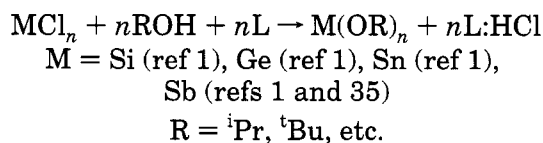


This method is suitable for the synthesis of alkoxides of less electropositive elements such as boron, silicon, and phosphorus, for which the reaction goes to completion ( $y = n$ ), and the corresponding alkoxides  $B(OR)_3$ ,  $Si(OR)_4$ , and  $P(OR)_3$  can be purified by distillation.<sup>1</sup> However, with other more electropositive metal(loid)s, the reaction does not go to completion and an equilibrium of the type shown above is set up. It is noteworthy to realize that the hydrogen chloride produced may enter into the following facile side reactions particularly with tertiary alcohols:



The water formed in the side reaction can be the cause of the hydrolysis and formation of oxoalkoxides.

**C-2. Reactions of Metal(loid) Chlorides in the Presence of a Base Such as Pyridine, Triethylamine, or Ammonia.**



Reactions of metal(loid) chlorides of more electropositive (compared to B and Si) metal(loid)s like Ge, Sn, Pb, etc., with alcohols can be pushed to completion by shifting the equilibrium to the right side by the addition of some proton acceptors (like  $C_5H_5N$  and  $NH_3$ ).

**Table 1. Homometallic Alkoxides of p-Block Metal(loid)s**

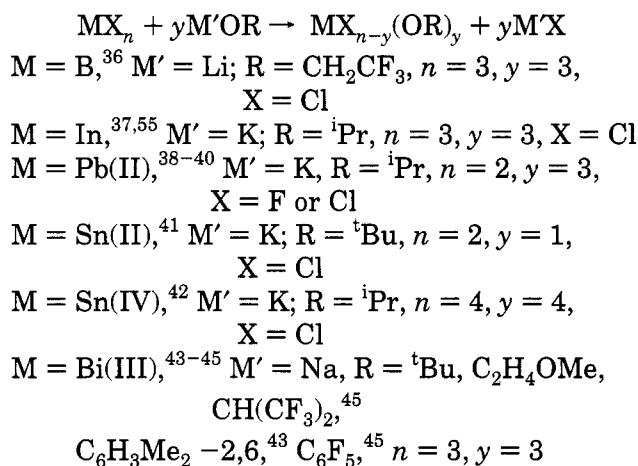
compound	method of preparation	characterization
Group 13: B, Al, Ga, Tl		
B(OR) <sub>3</sub>		
R = Me, Et, <sup>n</sup> Pr, <sup>i</sup> Pr, <sup>n</sup> Bu, <sup>1</sup> etc.	B-	IR, NMR, MW <sup>1</sup>
R = CH <sub>2</sub> CF <sub>3</sub> <sup>36</sup>	C-3	NMR ( <sup>1</sup> H, <sup>13</sup> C, <sup>11</sup> B) <sup>36</sup>
R = CH <sub>2</sub> CH=CHCH <sub>3</sub> <sup>a</sup>	E	IR, <sup>1</sup> HNMR <sup>a</sup>
R = C(CH <sub>3</sub> )CH=CH <sub>2</sub> <sup>b</sup>	B, E	IR, <sup>1</sup> HNMR <sup>b</sup>
R = CH <sub>2</sub> C(CH <sub>3</sub> )=CH <sub>2</sub> <sup>c</sup>	E	IR, <sup>1</sup> HNMR <sup>c</sup>
R = CH <sub>2</sub> CH <sub>2</sub> CH=CH <sub>2</sub> <sup>d</sup>	B	IR, MW <sup>d</sup>
ClB(OCH <sub>2</sub> CF <sub>3</sub> ) <sub>2</sub> <sup>36</sup>	PhB(OCH <sub>2</sub> CF <sub>3</sub> ) <sub>2</sub> + 1/2BCl <sub>3</sub>	NMR( <sup>1</sup> H, <sup>13</sup> C, <sup>11</sup> B) <sup>36</sup>
Al(OR) <sub>3</sub>		
R = Me, Et, <sup>i</sup> Pr, <sup>n</sup> Pr, <sup>n</sup> Bu, <sup>s</sup> Bu, <sup>t</sup> Bu, <sup>i</sup> Am <sup>1,30</sup>	A-1	IR, NMR ( <sup>1</sup> H, <sup>13</sup> C, <sup>27</sup> Al), MW, mass(R = <sup>i</sup> Pr) <sup>1,30</sup> X-ray (R = <sup>i</sup> Pr) <sup>26,27</sup>
R = <sup>t</sup> Bu <sup>28</sup>	D	X-ray
R = CH <sub>2</sub> CH=CHCH <sub>3</sub> <sup>a</sup>	E	IR, <sup>1</sup> HNMR <sup>a</sup>
R = C(CH <sub>3</sub> ) <sub>2</sub> CH=CH <sub>2</sub> <sup>b</sup>	E	IR, <sup>1</sup> HNMR <sup>b</sup>
R = CH <sub>2</sub> C(CH <sub>3</sub> )=CH <sub>2</sub> <sup>c</sup>	E	IR, <sup>1</sup> HNMR <sup>c</sup>
C <sub>6</sub> H <sub>11</sub> NH <sub>3</sub> <sup>+</sup> Al(O <sup>i</sup> Pr) <sub>4</sub> <sup>-e</sup>	Al(O <sup>i</sup> Pr) <sub>3</sub> + <sup>i</sup> PrOH + C <sub>6</sub> H <sub>11</sub> NH <sub>2</sub>	X-ray <sup>e</sup>
Ga(OR) <sub>3</sub>		
R = Me, Et, <sup>n</sup> Pr, <sup>i</sup> Pr, <sup>1,55</sup> etc.	C-3	IR, NMR ( <sup>1</sup> H) <sup>1,55</sup>
In(O <sup>i</sup> Pr) <sub>3</sub>	C-3	IR, NMR ( <sup>1</sup> H) <sup>1,55</sup>
In <sub>5</sub> O(O <sup>i</sup> Pr) <sub>13</sub> <sup>37</sup>	C-3	X-ray <sup>37</sup>
TlOR		
R = Et, Me	B	X-ray (R = Me) <sup>1</sup>
Group 14: Si, Ge, Sn, Pb		
Si(OR) <sub>4</sub>		
R = Me, Et, <sup>n</sup> Pr, <sup>i</sup> Pr, <sup>n</sup> Bu, <sup>s</sup> Bu, <sup>1</sup> etc.	B, C-1, C-3	IR, NMR ( <sup>1</sup> H, <sup>29</sup> Si) <sup>1</sup>
R = Me <sup>f</sup>	SiO <sub>2</sub> (s) + 2 MeOC(O)OMe(g)	
R = Et <sup>g</sup>	Ca <sub>3</sub> (SiO <sub>4</sub> )O + H <sup>+</sup> + EtOH	
2M <sup>+</sup> [(OC <sub>2</sub> H <sub>4</sub> O) <sub>2</sub> SiOC <sub>2</sub> H <sub>4</sub> OSi(OC <sub>2</sub> H <sub>4</sub> O) <sub>2</sub> ] <sup>2-h</sup>	SiO <sub>2</sub> /HOC <sub>2</sub> H <sub>4</sub> OH/MOH	<sup>29</sup> Si NMR <sup>h</sup>
M = Li, Na, K, Cs		
Ba <sup>2+</sup> [(OC <sub>2</sub> H <sub>4</sub> O) <sub>3</sub> Si] <sup>2-h</sup>	SiO <sub>2</sub> /HOC <sub>2</sub> H <sub>4</sub> OH/BaO	<sup>29</sup> Si NMR <sup>h</sup>
[K 18-Crown-6] <sup>+</sup> [Si(OR) <sub>5</sub> ] <sup>-90</sup>		
R = Me, Et, <sup>n</sup> Pr, <sup>i</sup> Pr, CH <sub>2</sub> CF <sub>3</sub> , etc.	F	<sup>29</sup> Si NMR <sup>90</sup>
K'[HSi(OR) <sub>4</sub> ]		
R = Me, Et, <sup>n</sup> Bu, <sup>i</sup> Pr <sup>90b</sup>	F	<sup>29</sup> Si NMR <sup>90b</sup>
Ge(OC <sup>t</sup> Bu) <sub>2</sub>	D	NMR ( <sup>1</sup> H, <sup>13</sup> C), X-ray <sup>47</sup>
Ge(OCH <sub>2</sub> CH=CHCH <sub>3</sub> ) <sub>4</sub> <sup>a</sup>	E	IR, <sup>1</sup> HNMR <sup>a</sup>
Ge(OCH <sub>2</sub> C(CH <sub>3</sub> )C=CH <sub>2</sub> ) <sub>4</sub> <sup>c</sup>	C-2, E	IR, <sup>1</sup> HNMR <sup>c</sup>
[Sn(O <sup>i</sup> Pr) <sub>4</sub> ] <sup>i</sup> PrOH] <sub>2</sub>	C-3	NMR ( <sup>1</sup> H, <sup>13</sup> C, <sup>119</sup> Sn), <sup>91</sup> X-ray <sup>42,91</sup>
Sn(O <sup>t</sup> Bu) <sub>4</sub>	D	X-ray <sup>91</sup>
Sn(O <sup>t</sup> Bu)Cl	C-3	X-ray <sup>41</sup>
Sn(O <sup>t</sup> Bu) <sub>2</sub>	D	NMR ( <sup>1</sup> H, <sup>119</sup> Sn) <sup>47</sup>
Pb(OR) <sub>2</sub>		
R = <sup>i</sup> Pr, <sup>t</sup> Bu, CMe <sub>2</sub> Et, CEt <sub>3</sub> , CH <sub>2</sub> CH <sub>2</sub> OMe, CHMeCH <sub>2</sub> NMe <sub>2</sub> <sup>48</sup>	D	X-ray (R = <sup>t</sup> Bu, CH <sub>2</sub> CH <sub>2</sub> OMe) <sup>48</sup>
R = C(CF <sub>3</sub> ) <sub>3</sub> <sup>i</sup>	Pb+2(CF <sub>3</sub> ) <sub>3</sub> CCOCl	
R = <sup>i</sup> Pr	C-3	IR, NMR <sup>38</sup>
Pb <sub>4</sub> O(O <sup>t</sup> Bu) <sub>39</sub>	D, Pb(OAc) <sub>2</sub> +NaOCMe <sub>3</sub>	IR, NMR <sup>39</sup>
Pb <sub>6</sub> O <sub>4</sub> (OR) <sub>4</sub>		
R = Et, <sup>i</sup> Pr <sup>40</sup>	C-3, D	IR, NMR, <sup>40</sup> X-ray (R = <sup>i</sup> Pr) <sup>102</sup>
Group 15: As, Sb, Bi		
As(OR) <sub>3</sub>		
R = Me, Et, <sup>n</sup> Pr, <sup>i</sup> Pr, <sup>1</sup> etc.	C-3	IR, NMR ( <sup>1</sup> H) <sup>1</sup>
As(OCH <sub>2</sub> CF <sub>3</sub> ) <sub>3</sub> <sup>f</sup>	As(OCH <sub>2</sub> CF <sub>3</sub> ) <sub>3</sub> + Cl <sub>2</sub> →	
	As(OCH <sub>2</sub> CF <sub>3</sub> ) <sub>3</sub> Cl <sub>2</sub> $\xrightarrow{+2CF_3CH_2OH}$	
Sb(OR) <sub>3</sub>		
R = Me, Et, <sup>n</sup> Pr, <sup>i</sup> Pr, <sup>1</sup> etc.	C-3	IR, NMR ( <sup>1</sup> H), <sup>1</sup> X-ray (R = Me) <sup>4</sup>
[Sb(OR) <sub>5</sub> L]		
R = Me, Et, <sup>i</sup> Pr, CH <sub>2</sub> CH <sub>2</sub> CHMe <sub>2</sub> ;	C-2	IR, NMR ( <sup>1</sup> H, <sup>13</sup> C), MW <sup>36</sup>
L = NH <sub>3</sub> , C <sub>5</sub> H <sub>5</sub> N <sup>36</sup>		
[Sb(OMe) <sub>5</sub> ] <sub>2</sub> <sup>1</sup>	Sb(C≡CMe) <sub>5</sub> + 5MeOH	X-ray <sup>1</sup>
Bi(OR) <sub>3</sub>		
R = <sup>t</sup> Bu, <sup>43,44</sup> CH <sub>2</sub> CH <sub>2</sub> OMe <sup>44</sup>	C-3	IR, NMR ( <sup>1</sup> H, <sup>13</sup> C), <sup>44</sup> X-ray (R = CH <sub>2</sub> CH <sub>2</sub> OMe) <sup>44</sup>
R = CMe <sub>2</sub> Et, CH <sub>2</sub> CH <sub>2</sub> OMe, CH <sub>2</sub> CH <sub>2</sub> NMe <sub>2</sub> , CHMeCH <sub>2</sub> NMe <sub>2</sub>	D	X-ray (R = CH <sub>2</sub> CH <sub>2</sub> OMe) <sup>49</sup>
R = C(CF <sub>3</sub> ) <sub>3</sub> <sup>i</sup>	Bi + 3(CF <sub>3</sub> ) <sub>3</sub> CCOCl	
[Bi(OSiPh <sub>3</sub> ) <sub>3</sub> (THF) <sub>3</sub> ] <sup>44</sup>	D	<sup>1</sup> R, NMR ( <sup>1</sup> H, <sup>29</sup> Si), X-ray <sup>44</sup>
[Bi(OCH(CF <sub>3</sub> ) <sub>2</sub> ) <sub>2</sub> (μ-OCH(CF <sub>3</sub> ) <sub>2</sub> )(THF)] <sub>2</sub> <sup>45</sup>	C-3	X-ray <sup>45</sup>

Table 1. (Continued)

compound	method of preparation	characterization
Group 16: Se, Te		
Se(OR) <sub>4</sub>		
R = Me, Et, <sup>i,m</sup> etc.	C-3, C-2	NMR ( <sup>1</sup> H, <sup>13</sup> C, <sup>77</sup> Se) <sup>m</sup>
R = CH <sub>2</sub> CF <sub>3</sub> <sup>m</sup>	C-2	NMR ( <sup>1</sup> H, <sup>13</sup> C, <sup>77</sup> Se, <sup>19</sup> F) <sup>m</sup>
Te(OR) <sub>4</sub>		
R = Me, Et, <sup>i,m</sup> Pr, <sup>i,m</sup> etc.	C-3	
R = CH <sub>2</sub> CF <sub>3</sub> <sup>m</sup>	C-2	NMR ( <sup>1</sup> H, <sup>13</sup> C, <sup>125</sup> Te, <sup>19</sup> F) <sup>m</sup>
R = C(CF <sub>3</sub> ) <sub>3</sub> <sup>j</sup>	Te + 4(CF <sub>3</sub> ) <sub>3</sub> CCOCl	
TeF <sub>3</sub> (OCH <sub>2</sub> CF <sub>3</sub> ) <sub>3</sub> <sup>n</sup>	C-1	NMR ( <sup>19</sup> F) <sup>n</sup>
TeF <sub>4</sub> (OCH <sub>2</sub> CF <sub>3</sub> ) <sub>2</sub> <sup>o</sup>	C-1	NMR ( <sup>19</sup> F) <sup>o</sup>

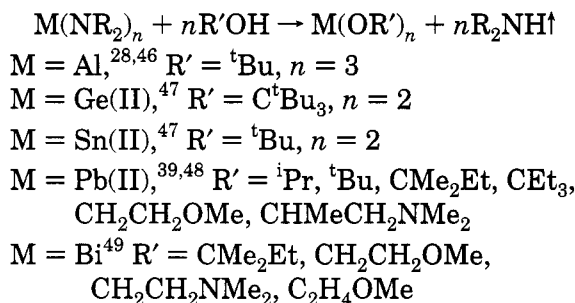
<sup>a</sup> Goel, S. C.; Mehrotra, R. C. *Z. Anorg. Allg. Chem.* **1978**, *440*, 281. <sup>b</sup> Goel, S. C.; Singh, V. K.; Mehrotra, R. C. *Z. Anorg. Allg. Chem.* **1978**, *447*, 253. <sup>c</sup> Goel, S. C.; Mehrotra, R. C. *Indian J. Chem.* **1981**, *20A*, 440. <sup>d</sup> Goel, S. C.; Mehrotra, R. C. *Indian J. Chem.* **1981**, *20A*, 1054. <sup>e</sup> Beagly, B.; Jones, K.; Parks, P.; Pritchard, R. G. *Synth. React. Inorg. Met.-Org. Chem.* **1988**, *18*, 465. <sup>f</sup> Suzuki, E.; Akiyama, M.; Ono, Y. *J. Chem. Soc., Chem. Commun.* **1992**, 136. <sup>g</sup> Goodwin, G. B.; Kenney, M. E. *Inorg. Chem.* **1990**, *29*, 1216. <sup>h</sup> Laine, R. M.; Blohowiak, K. Y.; Robinson, T. R.; Hoppe, M. L.; Nardi, P.; Kampf, J.; Uhm, J. *Nature* **1991**, *353*, 642. (See also Laine *et al.* *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 287.) <sup>i</sup> Canich, J. M.; Gard, G. L.; Shreeve, J. M. *Inorg. Chem.* **1984**, *23*, 441. <sup>j</sup> Denney, D. B.; Denney, D. Z.; Tseng, K. *Phosphorus Sulfur* **1985**, *22*, 33. <sup>k</sup> Ensinger, U.; Schwarz, W.; Schulz, S. K.; Schmidt, A. Z. *Anorg. Allg. Chem.* **1987**, *544*, 181. <sup>l</sup> Temple, N.; Schwarz, W. Z. *Anorg. Allg. Chem.* **1981**, *474*, 157. <sup>m</sup> Denney, D. B.; Denney, D. Z.; Hammond, P. J.; Hsu, Y. F. *J. Am. Chem. Soc.* **1981**, *103*, 2340. <sup>n</sup> Fraser, G. W.; Meikle, G. D. *J. Chem. Soc., Dalton Trans.* **1977**, 1985. <sup>o</sup> Frazer, G. W.; Meikle, G. D. *J. Chem. Soc., Perkin Trans.* **1975**, 312.

C-3. Reactions of Metal Halides (generally chlorides) with Alkali Metal Alkoxides.



These simple metathesis reactions appear to be more facile due to the precipitation of insoluble alkali metal halides from the reaction mixture.

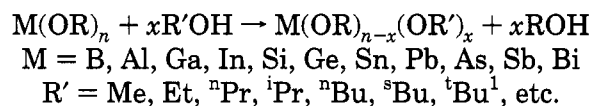
#### D. From Metal Dialkylamides.



This reaction goes to completion even with more branched alcohols, for example,<sup>24</sup> preparation of Al(O<sup>t</sup>Bu)<sub>3</sub> in high yield. It may be interesting to extend the method to the synthesis of sterically more hindered tris-alkoxides, e.g., Al(O<sup>t</sup>Am)<sub>3</sub>, for which earlier attempts by the method A-1 or by alcohol interchange reaction (E) of aluminum ethoxide or isopropoxide by the excess of tertiary amyl alcohol were not success-

ful,<sup>30</sup> since it would be interesting to see if these are monomeric like Al(OAr)<sub>3</sub> (Ar = C<sub>6</sub>H<sub>2</sub>Me-4-<sup>t</sup>Bu-2,6).<sup>29</sup>

#### E. Alcohol Interchange Reactions.



The procedure has been widely utilized for the synthesis of both homo- and heteroleptic alkoxides of a large number of metal(loid)s. In general, the facility of interchange of alkoxo groups by alcoholysis is sterically controlled and follows the order: tertiary < secondary < primary. Reactions with tertiary alcohols generally does not proceed to completion (x ≠ n). However, it is possible in some cases to shift the equilibrium more toward the right side, by fractionating out of the more volatile alcohol azeotropically (e.g., with benzene).

In view of the high electronegativity of oxygen (3.5), the metal(loid)-oxygen bonds in p-block metal(loid) alkoxides are expected to possess significant ionic character. However, most of the alkoxides of p-block elements are volatile and soluble in organic solvents, indicating the sufficiently covalent nature of metal(loid)-alkoxo bonds. This apparent decrease in the ionicity of M<sup>δ+</sup>-O<sup>δ-</sup> bond may be rationalized in terms of the electron releasing (+I) effect of the alkyl substituents on oxygen, the presence of oxygen p to metal(loid) pπ bonding for group 13 elements such as boron and aluminum or oxygen p to metal(loid) dπ bonding for group 14, 15, or 16 elements, and the formation of oligomeric species through alkoxide bridges (see Figure 1), which plays a key role in modulating the physical and spectroscopic characteristics of the alkoxide.

Investigations in metal(loid) alkoxide chemistry tend to indicate that oligomerization of alkoxide complexes [M(OR)<sub>n</sub>]<sub>k</sub> depends on a number of factors such as (i) the electrophilic nature of the metal(loid) center, more electron deficient metal centers favor the formation of highly oligomerized species; (ii) the size of the metal(loid) atom, larger metal atoms tend to attain higher coordination number through inter-

molecular association involving alkoxo bridging; (iii) the steric demand of the alkoxide groups, more sterically hindered alkoxo ligands would favor the formation of less associated species; and (iv) the electron-withdrawing or -donating nature of the substituents on the oxygen atom, electron-withdrawing substituents such as F or CF<sub>3</sub> on the carbon atom attached to the alkoxide oxygen, or the phenoxide moiety would reduce the electron density on the oxygen atom, rendering it less prone to the formation of alkoxo<sup>50,51</sup> or aryloxo bridging.<sup>52</sup> The associative tendency of an alkoxo ligand can also be reduced by replacing carbon in M—O—C system by boron or silicon atom. This apparent decrease in the tendency of oligomerization in M—O—B or M—O—Si bonded species may be rationalized in terms of deficiency of electron density on the oxygen atom due to the formation of pπ—pπ or pπ—dπ bonding respectively in M—O<sup>+</sup> ⇌ B<sup>-</sup> or M—O<sup>+</sup> ⇌ Si<sup>-</sup> type derivatives.<sup>53</sup>

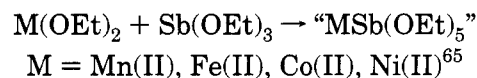
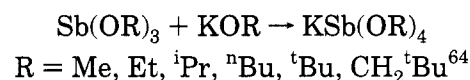
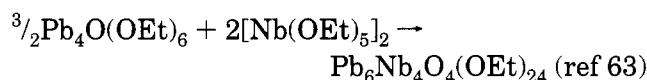
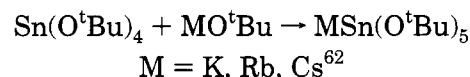
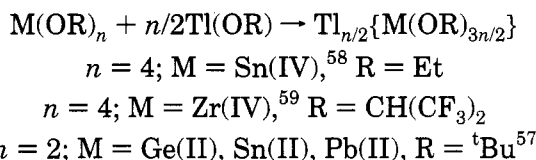
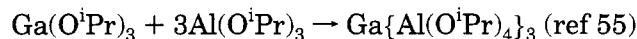
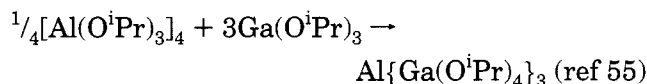
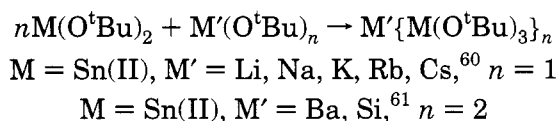
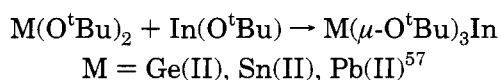
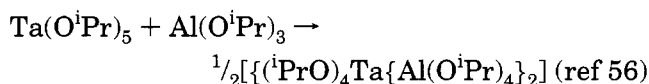
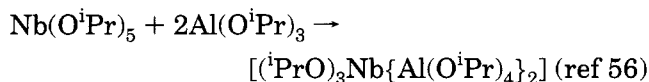
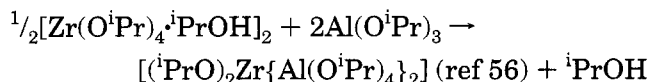
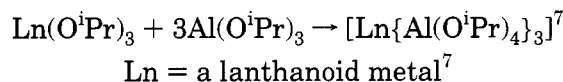
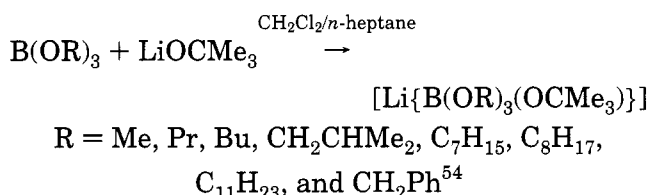
Alkoxides of the p-block elements are moisture-sensitive colorless solids, liquids, or highly viscous materials that are soluble in common organic solvents. The subvalent metal(loid) alkoxides tend to be generally more sensitive to air and moisture.

## 2.2. Heterometallic Alkoxides

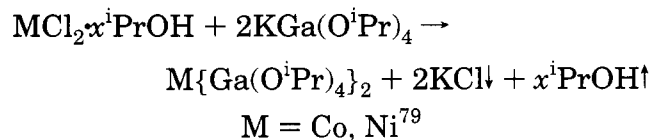
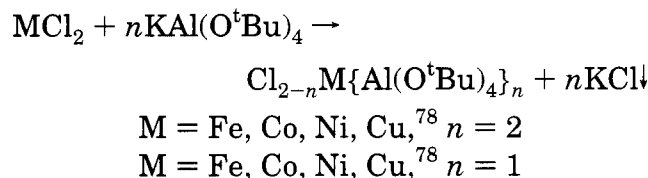
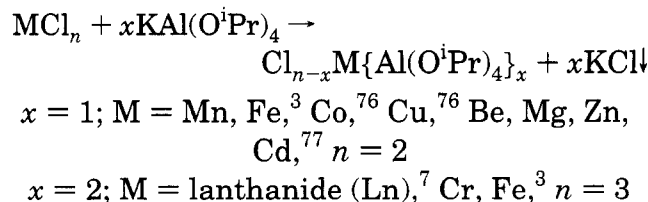
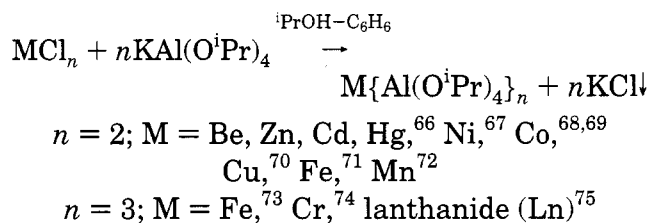
Methods used for the preparation of heterometallic alkoxides (Table 2) of p-block metal(loid)s are based on the following two types of reactions: (a) Lewis acid–base interactions, and (b) salt-elimination or metathesis reactions.

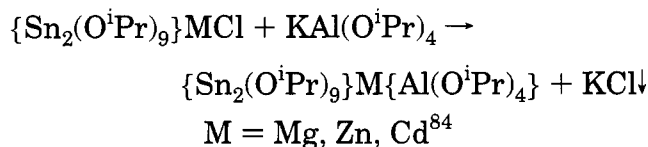
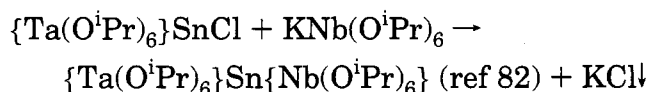
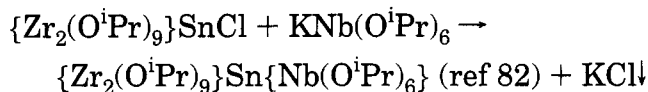
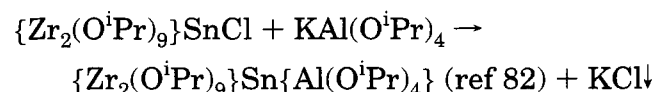
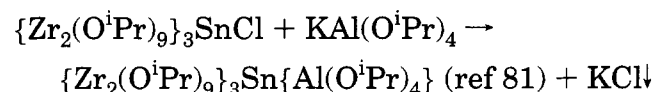
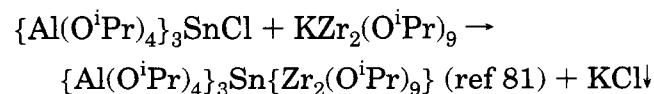
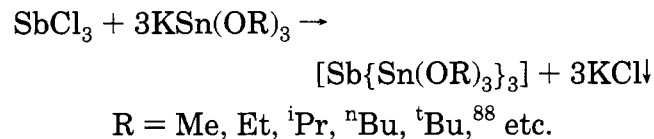
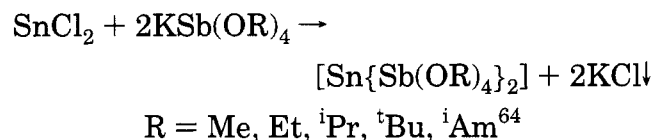
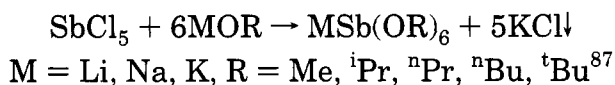
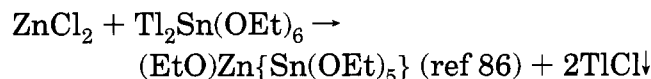
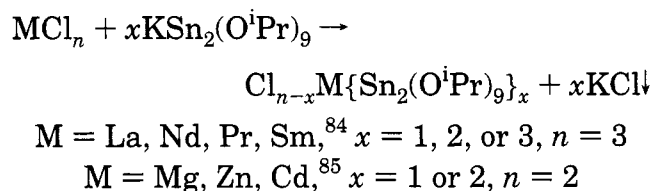
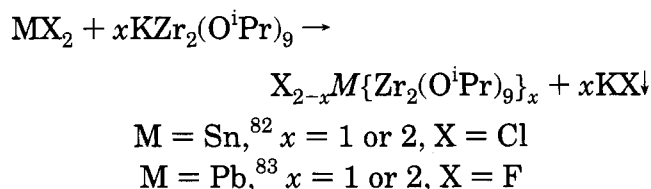
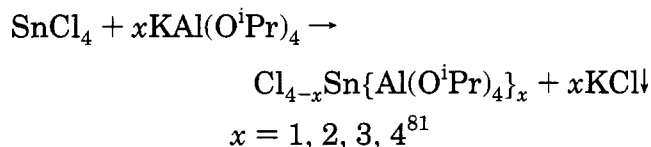
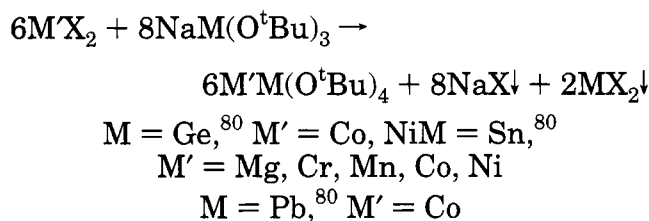
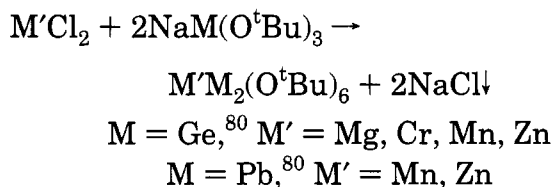
### 2.2.1. Preparative Routes to Heterometallic Alkoxides

#### F. Reaction between Two Different Metal Alkoxides (Lewis Acid–Base Reactions).



#### G. Substitution of an Anionic Ligand (Generally Chloride), by an Appropriate Alkoxo or Alkoxometallate Ligand (Salt-Elimination or Metathesis Reaction).





### 3. Physical Properties

#### 3.1. General Features

##### 3.1.1. Group 13: B, Al, Ga, In, Tl

With  $ns^2np^1$  valence shell electronic configuration, group 13 elements are expected to form compounds in +3 and +1 oxidation states. The first three elements are predominantly trivalent and only in the case of the last one, univalent state is fairly stable due to inert 's' pair effect. A stable indium(I) aryl-oxide has been recently prepared and X-ray crystallographically<sup>89</sup> characterized.

The monomeric tricoordinate alkoxides of the type  $M(OR)_3$  are coordinatively unsaturated and behave as Lewis acids; these therefore, accept a pair of electrons if sterically favorable either from neutral donor molecules or anions (e.g.,  $^-OR$ ) or by intermolecular association to give tetrahedral or both tetrahedral and octahedral species. For example, boron triisopropoxide,  $B(O^iPr)_3$ , is monomeric,<sup>1</sup> with a tricoordinate trigonal planar arrangement; the aluminum triisopropoxide,  $Al(O^iPr)_3$ , is dimeric in the vapor state and shows trimeric nature as a freshly distilled liquid;<sup>30</sup> it exhibits an interesting aging phenomenon and slowly crystallizes as a tetrameric solid.<sup>26,27</sup>

All these elements form interesting types of heterometallic alkoxides (cf. sections 2.2.1 and 4.2.1); some of these, particularly those involving monovalent indium and thallium, exhibit differing Lewis basicity of  $In^I/Tl^I$  compared with  $Sn^{II}$  in molecular  $In^I-Sn^{II}$  and  $Tl^I-Sn^{II}$  alkoxides (cf. section 4.2.1).

##### 3.1.2. Group 14: Si, Ge, Sn, Pb

The outer electronic configuration of carbon is  $2s^2-2p^2$  and those of Si, Ge, Sn, and Pb are  $ns^2np^2nd^0$ ; their vacant d orbitals can be used to expand the coordination states, e.g., in  $Si(O^iPr)_5$ <sup>90</sup> and  $Sn(OEt)_6$ <sup>2-85</sup> or to allow back-bonding. The 3p orbitals of silicon are too high in energy to give adequate  $\pi$  overlap with 2p orbitals, as a result of which derivatives such as  $\rangle Si=C \langle$  are very unstable, and stable compounds with silicon-oxygen double bonds are unknown. Out of the two possible oxidation states (+4 and +2), tetravalency is predominant in silicon and germanium alkoxides. The stability of compounds with oxidation state +2 increases with increasing atomic number of the elements.

All the tetraalkoxides of Si and Ge are monomeric,<sup>1</sup> but those of Sn are associated except in the cases of

**Table 2. Heterometallic Alkoxides Containing p-Block Metal(loid)s**

compound	method of preparation	characterization
Group 13: B, Al, Ga, In, Tl		
Li[B(OR) <sub>3</sub> (O <sup>t</sup> Bu)] R = Me, Pr, Bu, CH <sub>2</sub> CHMe <sub>2</sub> , CH <sub>2</sub> Ph, C <sub>7</sub> H <sub>15</sub> , C <sub>8</sub> H <sub>17</sub> , C <sub>11</sub> H <sub>23</sub> <sup>54</sup>	F	IR, NMR ( <sup>1</sup> H, <sup>11</sup> B) <sup>54</sup>
M{Al(O <sup>i</sup> Pr) <sub>4</sub> } <sub>n</sub> M = Be, Zn, Cd, <sup>66</sup> Ni, <sup>67</sup> Co, <sup>68,69</sup> Cu, <sup>70</sup> Fe, <sup>71</sup> Mn, <sup>72</sup> n = 2 M = Fe, <sup>73</sup> Cr, <sup>74</sup> Ln(III) (Ln = lanthanide); n = 3 Ln{Al <sub>3</sub> (O <sup>i</sup> Pr) <sub>11</sub> } (Ln = Sm(II), Yb(II)) <sup>72a</sup>	G	M = Be, Zn, Cd, <sup>66</sup> IR, NMR ( <sup>1</sup> H, <sup>13</sup> C), <sup>66</sup> MW; M = Ni, <sup>67</sup> Co, <sup>68,69</sup> Cu, <sup>70</sup> Fe, <sup>71</sup> Mn(II), <sup>72</sup> IR, UV-vis, MW M = Ni, <sup>67</sup> Co, <sup>68,69</sup> Cu, <sup>70</sup> Fe, <sup>71</sup> Mn(II), <sup>72</sup> IR, UV-vis, MW IR, mass, NMR ( <sup>1</sup> H, <sup>171</sup> Yb) <sup>72a</sup>
Cl <sub>n-x</sub> M{Al(O <sup>i</sup> Pr) <sub>4</sub> } <sub>x</sub> x = 1; M = Mn, Fe, <sup>3</sup> Co, <sup>76</sup> Cu, <sup>76</sup> Be, Mg, Zn, Cd; <sup>77</sup> n = 2  x = 2 or 1; M = Ln (lanthanide), <sup>7,105</sup> Cr, Fe(III); <sup>3</sup> n = 3	G	M = Be, Mg, Zn, Cd(II), <sup>77</sup> IR, NMR ( <sup>1</sup> H, <sup>27</sup> Al), <sup>66</sup> MW; <sup>77</sup> M = Co(II), <sup>76</sup> Cu(II), <sup>76</sup> Cr(III), Fe(III), <sup>3</sup> IR, UV-vis, MW X-ray (Ln = Pr) <sup>105</sup>
Cl <sub>2-x</sub> M{Al(O <sup>t</sup> Bu) <sub>4</sub> } <sub>x</sub> M = Fe, Co, Ni, Cu(II); <sup>78</sup> x = 1 or 2	G	IR, UV-vis, MW
M{OAl(O <sup>i</sup> Pr) <sub>2</sub> } <sub>2</sub> M = Cr, Mn, Fe, Co, Zn, Mo <sup>117</sup> M = Mg, Ca, Ba, Pb <sup>118</sup>	2Al(O <sup>i</sup> Pr) <sub>3</sub> + M(OAc) <sub>2</sub>	M = Zn, Mo ( <sup>1</sup> H, <sup>13</sup> C), mass (M = Fe), MW <sup>117</sup> NMR ( <sup>1</sup> H, <sup>13</sup> C) MW <sup>118</sup>
Al{Ga(O <sup>i</sup> Pr) <sub>4</sub> } <sub>3</sub> <sup>55</sup>	F	IR, NMR ( <sup>1</sup> H, <sup>13</sup> C), MW <sup>55</sup>
Ga{Al(O <sup>i</sup> Pr) <sub>4</sub> } <sub>3</sub> <sup>55</sup>	F	IR, NMR ( <sup>1</sup> H, <sup>13</sup> C), MW <sup>55</sup>
Ni{Ga(O <sup>i</sup> Pr) <sub>4</sub> } <sub>2</sub> <sup>79</sup>	G	IR, UV-vis, MW <sup>79</sup>
In{Ga(O <sup>i</sup> Pr) <sub>4</sub> } <sub>3</sub> <sup>55</sup>	G	IR, NMR ( <sup>1</sup> H, <sup>13</sup> C) <sup>55</sup>
In(O <sup>t</sup> Bu) <sub>3</sub> M M = Ge(II), Sn(II), Pb(II) <sup>57</sup>	F	IR, NMR ( <sup>1</sup> H, <sup>13</sup> C, <sup>119</sup> Sn), X-ray (M = Sn) <sup>57</sup>
Tl <sub>2</sub> Sn(OEt) <sub>6</sub>	F	IR, NMR ( <sup>1</sup> H, <sup>13</sup> C, <sup>119</sup> Sn), X-ray <sup>58</sup>
Tl(O <sup>t</sup> Bu) <sub>3</sub> M M = Ge(II), Sn(II), Pb(II) <sup>57</sup>	F	NMR ( <sup>1</sup> H, <sup>13</sup> C, <sup>119</sup> Sn) <sup>57</sup>
Tl <sub>2</sub> Zr(OCH <sub>2</sub> CF <sub>3</sub> ) <sub>6</sub>	F	NMR ( <sup>19</sup> F, <sup>205</sup> Tl), X-ray <sup>59</sup>
Group 14: Si, Ge, Sn, Pb		
MSn(O <sup>t</sup> Bu) <sub>3</sub> M = Li, Na, K, Rb, Cs <sup>60</sup>	F	NMR ( <sup>1</sup> H, <sup>119</sup> Sn), X-ray (M = K) <sup>60</sup>
MSn(O <sup>t</sup> Bu) <sub>5</sub> M = K, Rb, Cs <sup>61</sup>	F	NMR ( <sup>1</sup> H), X-ray (M = K) <sup>62</sup>
MSn <sub>2</sub> (O <sup>t</sup> Bu) <sub>6</sub> M = Ba, Sr	F	NMR ( <sup>1</sup> H, <sup>119</sup> Sn), X-ray (M = Sr) <sup>61</sup>
MM <sub>2</sub> (O <sup>t</sup> Bu) <sub>6</sub> M = Ge, M' = Mg, Cr, Mn, Zn <sup>80</sup> M = Pb, M' = Mn, Zn <sup>74</sup>	G	NMR, mass, X-ray (M = Ge, M' = Mn) <sup>80</sup>
M'M(O <sup>t</sup> Bu) <sub>4</sub> M' = Ge, M = Co, Ni <sup>80</sup>  M' = Sn, M = Mg, Cr, Mn, Co, Ni <sup>80</sup> M' = Pb, M = Co <sup>80</sup>	G	NMR, X-ray (M' = Ge, M = Co; M' = Sn, M = Mg, Cr, Mn, Co, Ni) <sup>80</sup>
ClSn{M(O <sup>i</sup> Pr) <sub>n</sub> } M = Al(III), n = 4; M = Nb(V), n = 6 <sup>82</sup>	G	IR, NMR ( <sup>1</sup> H, <sup>13</sup> C, <sup>119</sup> Sn), MW <sup>82</sup>
(RO)Sn{M(O <sup>i</sup> Pr) <sub>n</sub> } R = <sup>i</sup> Pr, <sup>t</sup> Bu; M = Al(III), n = 4; M = Nb(V), n = 6 <sup>82</sup>	G	IR, NMR ( <sup>1</sup> H, <sup>13</sup> C, <sup>119</sup> Sn), MW <sup>82</sup>
ClSn{Zr <sub>2</sub> (O <sup>i</sup> Pr) <sub>9</sub> } <sup>82</sup>	G	IR, NMR ( <sup>1</sup> H, <sup>13</sup> C, <sup>119</sup> Sn), MW <sup>82</sup>
(RO)Sn{Zr <sub>2</sub> (O <sup>i</sup> Pr) <sub>9</sub> } R = <sup>i</sup> Pr, <sup>t</sup> Bu <sup>82</sup>	G	IR, NMR ( <sup>1</sup> H, <sup>13</sup> C, <sup>119</sup> Sn), MW <sup>82</sup>
Cl <sub>4-x</sub> Sn{Al(O <sup>i</sup> Pr) <sub>4</sub> } <sub>x</sub> x = 1-4 <sup>81</sup>	G	IR, NMR ( <sup>1</sup> H, <sup>13</sup> C, <sup>119</sup> Sn, <sup>27</sup> Al), MW <sup>81</sup>
Cl <sub>n-x</sub> M{Sn <sub>2</sub> (O <sup>i</sup> Pr) <sub>9</sub> } <sub>x</sub> M = Mg, Zn, Cd, x = 1 or 2, n = 2 <sup>85</sup> M = La, Nd, Pr, Sm, x = 1, 2, or 3, n = 3 <sup>84</sup>	G	IR, NMR ( <sup>1</sup> H, <sup>13</sup> C, <sup>119</sup> Sn), MW <sup>84,85</sup>
Sn{Zr <sub>2</sub> (O <sup>i</sup> Pr) <sub>9</sub> }Cl <sub>2</sub> <sup>85c</sup>	SnCl <sub>2</sub> + 4Zr(O <sup>i</sup> Pr) <sub>4</sub>	IR, NMR ( <sup>1</sup> H, <sup>13</sup> C, <sup>119</sup> Sn), MW <sup>85c</sup>
ClSn{Zr <sub>2</sub> (O <sup>i</sup> Pr) <sub>9</sub> }Cl <sub>2</sub> <sup>85c</sup>	SnCl <sub>2</sub> + 2Zr(O <sup>i</sup> Pr) <sub>4</sub>	IR, NMR ( <sup>1</sup> H, <sup>13</sup> C, <sup>119</sup> Sn), MW <sup>85c</sup>
Sn{Al(O <sup>i</sup> Pr) <sub>3</sub> }Cl <sub>2</sub> <sup>85c</sup>	SnCl <sub>2</sub> + 2Al(O <sup>i</sup> Pr) <sub>3</sub>	IR, NMR ( <sup>1</sup> H, <sup>13</sup> C, <sup>119</sup> Sn, <sup>27</sup> Al), MW <sup>85c</sup>
(EtO)Zn{Sn(OEt) <sub>5</sub> } <sup>86</sup>	G	
{Al(O <sup>i</sup> Pr) <sub>4</sub> } <sub>3</sub> Sn{Zr <sub>2</sub> (O <sup>i</sup> Pr) <sub>9</sub> } <sup>81</sup>	G	IR, NMR ( <sup>1</sup> H, <sup>13</sup> C, <sup>27</sup> Al, <sup>119</sup> Sn), MW <sup>81</sup>
{Zr <sub>2</sub> (O <sup>i</sup> Pr) <sub>9</sub> } <sub>3</sub> Sn{Al(O <sup>i</sup> Pr) <sub>4</sub> } <sup>81</sup>	G	IR, NMR ( <sup>1</sup> H, <sup>13</sup> C, <sup>27</sup> Al, <sup>119</sup> Sn), MW <sup>81</sup>
{Zr <sub>2</sub> (O <sup>i</sup> Pr) <sub>9</sub> } <sub>3</sub> Sn{Al(O <sup>i</sup> Pr) <sub>4</sub> } <sup>82</sup>	G	IR, NMR ( <sup>1</sup> H, <sup>13</sup> C, <sup>27</sup> Al, <sup>119</sup> Sn), MW <sup>82</sup>
{Nb(O <sup>i</sup> Pr) <sub>6</sub> } <sub>3</sub> Sn{Ta(O <sup>i</sup> Pr) <sub>6</sub> } <sup>82</sup>	G	IR, NMR ( <sup>1</sup> H, <sup>13</sup> C, <sup>119</sup> Sn), MW <sup>82</sup>
Cd <sub>4</sub> Sn <sub>4</sub> (O) <sub>2</sub> (OAc) <sub>10</sub> (OCH <sub>2</sub> <sup>t</sup> Bu) <sub>10</sub> <sup>108</sup>	Cd(OAc) <sub>2</sub> + Sn(OCH <sub>2</sub> <sup>t</sup> Bu) <sub>4</sub>	IR, NMR ( <sup>1</sup> H, <sup>13</sup> C), X-ray <sup>108</sup>
F <sub>2-n</sub> Pb{Al(O <sup>i</sup> Pr) <sub>4</sub> } <sub>n</sub> <sup>83</sup> n = 1 or 2	G	NMR ( <sup>1</sup> H, <sup>13</sup> C, <sup>27</sup> Al, <sup>207</sup> Pb) <sup>83</sup>
( <sup>i</sup> PrO)Pb{Al(O <sup>i</sup> Pr) <sub>4</sub> } <sup>83</sup>	G	NMR ( <sup>1</sup> H, <sup>13</sup> C, <sup>27</sup> Al, <sup>207</sup> Pb) <sup>83</sup>
{Al(O <sup>i</sup> Pr) <sub>4</sub> } <sub>4</sub> Pb{Zr <sub>2</sub> (O <sup>i</sup> Pr) <sub>9</sub> } <sup>83</sup>	G	NMR ( <sup>1</sup> H, <sup>13</sup> C, <sup>27</sup> Al, <sup>207</sup> Pb) <sup>83</sup>
Pb <sub>2</sub> Zn <sub>2</sub> (OAc) <sub>4</sub> (OCH <sub>2</sub> CH <sub>2</sub> OMe) <sub>4</sub>	Zn(OAc) <sub>2</sub> + 3Pb(OAc) <sub>2</sub> + MeOCH <sub>2</sub> CH <sub>2</sub> OH	X-ray <sup>109</sup>



Table 2. (Continued)

compound	method of preparation	characterization
	Group 14: Si, Ge, Sn, Pb	
Pb <sub>6</sub> Nb <sub>4</sub> O <sub>4</sub> (OEt) <sub>24</sub>	F	IR, NMR ( <sup>1</sup> H, <sup>13</sup> C, <sup>207</sup> Pb), X-ray <sup>63</sup>
Pb <sub>2</sub> Ti <sub>4</sub> (OAc) <sub>2</sub> (OEt) <sub>2</sub> (OEt) <sub>14</sub>	Pb <sub>4</sub> O(OAc) <sub>6</sub> ·H <sub>2</sub> O + Ti(OEt) <sub>4</sub>	X-ray <sup>10</sup>
PbZr <sub>3</sub> (O)(OAc) <sub>2</sub> (O <sup>i</sup> Pr) <sub>10</sub>	[Zr(O <sup>i</sup> Pr) <sub>4</sub> (HO <sup>i</sup> Pr) <sub>2</sub> ] + Pb(OAc) <sub>2</sub>	X-ray <sup>110</sup>
	Group 15: As, Sb, Bi	
KSb(OR) <sub>4</sub>		
R = Me, Et, <sup>i</sup> Pr, <sup>n</sup> Bu, <sup>t</sup> Bu <sup>64</sup>	F	IR, NMR ( <sup>1</sup> H, <sup>13</sup> C), MW <sup>64</sup>
Ni <sub>5</sub> Sb <sub>3</sub> (O) <sub>2</sub> (OEt) <sub>15</sub> (HOEt) <sub>4</sub>	G	X-ray <sup>111</sup>
M{Sb(OR) <sub>4</sub> } <sub>2</sub>		
M = Sn(II), <sup>64</sup> or Pb(II) <sup>88</sup>	G	IR, NMR ( <sup>1</sup> H, <sup>13</sup> C, <sup>119</sup> Sn), <sup>64</sup> MW <sup>64,88</sup>
R = Me, Et, <sup>i</sup> Pr, <sup>n</sup> Bu, <sup>t</sup> Bu, etc.		
Sb{Sn(OR) <sub>3</sub> } <sub>3</sub>		
R = Me, Et, <sup>i</sup> Pr, <sup>n</sup> Bu, <sup>t</sup> Bu, etc.	G	IR, NMR ( <sup>1</sup> H, <sup>13</sup> C, <sup>119</sup> Sn), MW <sup>88</sup>
"MSb(OEt) <sub>5</sub> "		
M = Mn, Fe, Co, Ni(II) <sup>65</sup>	F	IR, UV-vis <sup>65</sup>
MSb(OR) <sub>6</sub>		
M = Li, Na, K; R = Me, <sup>i</sup> Pr, <sup>n</sup> Pr, <sup>n</sup> Bu, <sup>t</sup> Bu, <sup>87</sup> etc.	G	IR, NMR ( <sup>1</sup> H, <sup>13</sup> C), MW <sup>87</sup>

monomeric tertiary alkoxides.<sup>91</sup> The subvalent alkoxides, M(OR)<sub>2</sub> (M = Ge, Sn, Pb), derived from less sterically hindered alcohols, ROH (R = Me or Et) are polymeric.<sup>1</sup> Monomeric alkoxy species of Ge(II), Sn(II), and Pb(II) are obtained<sup>47,48</sup> with sterically demanding ligands, e.g., OC<sub>6</sub>H<sub>2</sub>Me-4-<sup>t</sup>Bu<sub>2</sub>-2,6, whereas OC<sup>t</sup>Bu<sub>3</sub> has been shown to yield monomeric species with Ge(II) and Sn(II).

Homo- and heterometallic tertiary alkoxides of subvalent group 14 elements having lone pair of electrons on the central metal atoms form derivatives with transition metal carbonyls (cf. section 4.2.1).

### 3.1.3. Group 15: As, Sb, Bi

The valence shell electronic configuration *ns<sup>2</sup>np<sup>3</sup>* of As, Sb, and Bi presages<sup>1</sup> their main oxidation states of +3 and +5. The coordination numbers in their alkoxides derivatives are variable, with three being much more common, particularly in Sb<sup>1,35</sup> and Bi.<sup>44,49</sup> The discrete M(OR)<sub>3</sub> derivatives are pyramidal with bond angles greater than 90° due to a sterically active lone pair, which could also be expected to form complexes with both main group Lewis acids and transition metal derivatives. However, in contrast to group 13 and 14 elements, no such complexes appear to have been reported until now.

Although the main focus of this review article is on alkoxide derivatives, which are generally associated in nature and particularly in the case of bismuth,<sup>44,45</sup> mention should be made of one aryloxide derivative, Bi(OC<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>-2,6)<sub>3</sub>,<sup>43</sup> which is so far the only example of a tricoordinate Bi-O-C derivative characterized by X-ray crystallography.

### 3.1.4. Group 16: Se, Te

With their *ns<sup>2</sup>np<sup>4</sup>* outer electronic configurations, these elements form alkoxides<sup>1</sup> of the types Se(OR)<sub>4</sub>, SeO(OR)<sub>2</sub>, Te(OR)<sub>4</sub>, TeO(OR)<sub>2</sub>, and TeX<sub>2</sub>(OR)<sub>4</sub>.

The lone pair of electrons in the valence shell of tetravalent Se and Te derivatives is sterically active and imposes a trigonal bipyramidal geometry on all M(OR)<sub>4</sub> species. It may be noted that in the solid state, additional alkoxy or other groups may weakly interact with Se or Te, giving higher coordination numbers. Similar to group 14 alkoxides, the Lewis

acid-base type complexes of Se and Te alkoxides have also not been reported so far.

## 3.2. Characterization and Identification

Although characterization and identification of homo- and heterometallic alkoxides can be achieved by a number of physicochemical techniques (such as IR, NMR, Mössbauer, X-ray crystallography, mass spectrometry, etc.), the X-ray crystallography provides more precise and definitive structural information.<sup>4-9</sup> Out of the above, a few illustrative applications of the techniques more widely employed for alkoxides of p-block elements will be discussed below.

### 3.2.1. IR Spectroscopic Studies

Infrared (IR) spectroscopy has become more useful for the confirmation of expected functionality than for detailed structural characterization. Thus, metal-ligand characteristic absorptions at ~1180  $\nu_{\text{OMe}}$ ; 1025, 1070  $\nu_{\text{OEt}}$ ; ~840, ~1125, ~1160  $\nu_{\text{O}^i\text{Pr}}$ ; ~805, ~760  $\nu_{\text{O}^t\text{Bu}}$  cm<sup>-1</sup> have generally been used to identify the presence of various alkoxy groups.<sup>1</sup> The metal-oxygen stretching frequencies generally appear in the range 500–700 cm<sup>-1</sup>, and in chloro derivatives additional metal-chlorine absorptions are observed<sup>92</sup> in the range 300–400 cm<sup>-1</sup>. These absorptions are usually strong, and thus the particular frequency and number of bands can be related to isomeric geometry and stereochemistry of these homo- and heterometallic systems. The absorptions due to  $\nu_{\text{CO}}$  generally lie in the ranges 1020–1080 (OMe), 940–1080 (O<sup>i</sup>Pr), and 1200–1230 (O<sup>t</sup>Bu). In all the alkoxide derivatives the absorption bands in the regions 1040–1190 and 940–1040 cm<sup>-1</sup> have been generally ascribed to terminal and bridging alkoxy groups respectively. Furthermore, isopropoxide derivatives exhibit strong doublets at about 1170, 1135 and 1375, 1365 cm<sup>-1</sup> due to *gem*-dimethyl groups.

### 3.2.2. Nuclear Magnetic Resonance Spectroscopy

In recent years the widespread availability of relatively inexpensive NMR equipment with Fourier transform capabilities has led to a great deal of NMR data aimed at exploring the potential of this tech-

nique for structural and stereochemical elucidation, not only by  $^1\text{H}$  and  $^{13}\text{C}$  NMR but also by the use of a few of the following NMR-active p-block nuclei:  $^{11}\text{B}^*$ ,  $^{27}\text{Al}^*$ ,  $^{115}\text{In}$ ,  $^{205}\text{Tl}^*$ ,  $^{29}\text{Si}^*$ ,  $^{73}\text{Ge}$ ,  $^{119}\text{Sn}^*$ ,  $^{207}\text{Pb}^*$ ,  $^{75}\text{As}$ ,  $^{121}\text{Sb}$ ,  $^{209}\text{Bi}$ ,  $^{77}\text{Se}$ ,  $^{125}\text{Te}$ ,  $^{17}\text{O}^*$ ,  $^{19}\text{F}^*$ , out of which those marked with asterisk have been already used as structural probes<sup>4,9,10,30,34,36,38,42,46-48,58,59,62,63,80-83</sup> for elucidating the coordination environment around them and the nature of the species present in solution as well as in solid state.  $^{29}\text{Si}$  and more recently  $^{17}\text{O}$  NMR spectroscopy<sup>93</sup> in particular have provided a rather useful tool to sort out the growth in the centers of hydrolysis of  $\text{Si}(\text{OEt})_4$  during the sol-gel process; these are of considerable interest in the identification of different types ( $\mu_2$ ,  $\mu_3$ ,  $\mu_4$ , etc.) of bridged oxygen atoms in oxide alkoxide derivatives.<sup>94</sup> The studies on hydrolysis reactions of  $\text{Si}(\text{OEt})_4$ <sup>93</sup> and  $\text{Ti}(\text{OEt})_4$ <sup>94</sup> by  $^{17}\text{O}$  NMR spectroscopy may be treated as a pacesetter for solution structural characterization of metal polyoxoalkoxides formed during the partial hydrolysis of p-block metal(loid) alkoxides.

A few selected illustrative examples of NMR applications for structural elucidation of alkoxides will be discussed below:

The dimeric aluminum *tert*-butoxide,  $\text{Al}_2(\text{O}^t\text{Bu})_6$ , displays<sup>26</sup> two types of  $^1\text{H}$  NMR signals in a 2:1 ratio, which is consistent with the structure 1d.

The  $^{27}\text{Al}$  NMR chemical shift,  $\delta$  54.0 ppm, is in the region characteristic of tetracoordinate aluminum.

Aluminum isopropoxide in the tetrameric form (Figure 1b)  $\text{Al}_4(\text{O}^i\text{Pr})_{12}$ , shows<sup>30</sup> three doublets for the *gem*-dimethyl protons in a 1:1:2 ratio, because the methyl groups in the bridging isopropoxo groups are nonequivalents. The tetramer of aluminum isopropoxide is described as the assembly of a nondistorted octahedral  $\text{AlO}_6$  unit and three distorted tetrahedral  $\text{AlO}_4$  units, as revealed by the presence of a sharp and a broad line in its  $^{27}\text{Al}$  NMR spectrum with an intensity ratio of 1:3.

The  $^1\text{H}$  NMR spectrum of  $\text{ZrAl}(\text{O}^i\text{Pr})_7$  exhibits<sup>55</sup> three doublets for *gem*-dimethyl protons in a ratio of 3:2:2, which is expected for  $(^i\text{PrO})_3\text{Zr}(\mu\text{-O}^i\text{Pr})_2\text{Al}(\text{O}^i\text{Pr})_2$ .

Although the  $^1\text{H}$  NMR spectrum of  $\text{Sn}(\text{O}^t\text{Bu})_2$  at room temperature shows a single peak due to *tert*-butyl protons, the variable-temperature  $^1\text{H}$  NMR spectroscopy and cryoscopic molecular weight determination showed dimeric nature in benzene. The dimeric  $[\text{Sn}(\text{O}^t\text{Bu})(\mu\text{-O}^t\text{Bu})_2]$  structure has been shown by the gas electron diffraction method<sup>47</sup> to persist in the gaseous phase also.

It may be noted that  $^1\text{H}$  NMR spectra sometimes offer less information, as they mainly display the pattern of the alkoxo ligand and therefore cannot distinguish between an alkoxo and oxoalkoxo derivatives. Characterization in such cases could be achieved by metal nuclei NMR. For example,  $^1\text{H}$  NMR spectra of  $[\text{Pb}(\text{O}^t\text{Bu})_2]_3$  and  $\text{Pb}_4\text{O}(\text{O}^t\text{Bu})_6$  were nearly identical,<sup>39,40</sup> but they showed different  $^{207}\text{Pb}$  NMR chemical shifts of  $\delta$  4152 and 5032, respectively.

### 3.2.3. Mass Spectrometry

Mass spectrometry can provide useful information on (i) the nuclearity of homo- and heterometallic

alkoxides and (ii) the composition of heterometallic alkoxides (provided they are volatile and stable with respect to disproportionation reactions in the vapor phase). It is interesting to note that fast-atom bombardment mass spectrometry (FABMS) may be of considerable utility in the future in the characterization of some nonvolatile higher molecular weight homo- and heterometallic alkoxides.<sup>4</sup> During the past one decade a number of mass spectral studies have been carried out on both homo- and heterometallic alkoxides of p-block elements such as (i)  $[\text{Al}(\text{O}^i\text{Pr})_3]_4$ ,<sup>1,30</sup> (ii)  $[\text{Al}(\text{OC}_6\text{H}_2^t\text{Bu}_2\text{-2,6-Me-4})_3]_3$ ,<sup>29</sup> (iii)  $[\text{Al}(\text{O}^i\text{Pr})(\text{OSiMe}_3)_2]_n$ ,<sup>27</sup> (iv)  $[\text{In}(\text{OC}_6\text{H}_2(\text{CF}_3)_3\text{-2,4,6})_2]_2$ ,<sup>89</sup> (v)  $\text{MGe}_2(\text{O}^t\text{Bu})_6$   $\text{M} = \text{Sr, Ba, Cd, Pb}$ ,<sup>41</sup> (vi)  $\text{CaSn}_2(\text{O}^t\text{Bu})_6$ , (vii)  $\text{GePb}_2(\text{O}^t\text{Bu})_6$ ,<sup>80</sup> (viii)  $\text{Mg}_2\text{Sn}_2(\text{O}^t\text{Bu})_8$ ,<sup>80</sup> (ix)  $(\text{O}^i\text{Pr})_x\text{M}(\mu\text{-O}^i\text{Pr})_2\text{Be}(\mu\text{-O}^i\text{Pr})_2\text{Al}(\text{O}^i\text{Pr})_2$ <sup>95</sup> ( $\text{M} = \text{Ti, x} = 3; \text{M} = \text{Nb, x} = 4$ ).

### 3.3. X-ray Crystallographic Studies

In spite of some limitations like extreme moisture sensitivity of alkoxides, single-crystal X-ray structures of a number of homo- and heterometallic alkoxides of p-block metal(loid)s have been reported in the past few years. They include (i)  $[\text{Al}(\text{O}^t\text{Bu})_3]_2$ ,<sup>28</sup> (ii)  $[\text{Al}(\text{O}^i\text{Pr})_3]_3$ ,<sup>26,27</sup> (iii)  $[\text{Al}_4(\text{O}^t\text{Bu})_{11}\text{OH}]$ ,<sup>96</sup> (iv)  $[\text{Al}_4(\text{O}^i\text{Pr})_7(\text{OH})\text{Cl}_4]$ ,<sup>98</sup> (v)  $\text{Al}_{10}\text{O}_4(\text{OEt})_{22}$ ,<sup>97</sup> (vi)  $[\text{Al}(\text{O}^i\text{Pr})_2(\text{acac})_3]_3$ ,<sup>99</sup> (vii)  $[\text{Al}(\text{O}^t\text{Bu})_3(\text{HNMe}_2)]_4$ ,<sup>46</sup> (viii)  $[\text{Al}_2(\text{NMe}_2)(\text{O}^t\text{Bu})_5]$ ,<sup>46</sup> (ix)  $[\text{In}_5\text{O}(\text{O}^i\text{Pr})_{13}]_3$ ,<sup>37</sup> (x)  $[\text{Ge}(\text{OC}^t\text{Bu})_3]_2$ ,<sup>47</sup> (xi)  $[\text{Sn}(\text{O}^i\text{Pr})_4(\text{HO}^i\text{Pr})_2]$ ,<sup>42,91</sup> (xii)  $[\text{Sn}(\text{O}^t\text{Bu})_4]_3$ ,<sup>91</sup> (xiii)  $[\text{Sn}_3\text{O}(\text{O}^t\text{Bu})_{10}2\text{HO}^t\text{Bu}]$ ,<sup>100</sup> (xiv)  $[\text{ClSn}(\mu\text{-OCMe}_3)_2\text{SnCl}]_4$ ,<sup>41</sup> (xv)  $[\text{Sn}\{\text{N}(\text{SiMe}_3)_2\}(\mu\text{-OCMe}_3)]_2$ ,<sup>101</sup> (xvi)  $[\text{Pb}(\text{OCH}_2\text{CH}_2\text{OMe})_2]_3$ ,<sup>48</sup> (xvii)  $[\text{Pb}(\text{O}^t\text{Bu})_2]_3$ ,<sup>48</sup> (xviii)  $\text{Pb}_6\text{O}_4(\text{O}^i\text{Pr})_4$ ,<sup>102</sup> (xix)  $\text{Pb}_4\text{O}(\text{OSiMe}_3)_6$ ,<sup>103</sup> (xx)  $[\text{Bi}(\text{OCH}_2\text{CH}_2\text{OMe})_3]_3$ ,<sup>49</sup> (xxi)  $[\text{Bi}\{\text{OSiPh}_3\}_3(\text{THF})_3]$ ,<sup>44b</sup> (xxii)  $[\text{Bi}\{\text{OCH}(\text{CF}_3)_2\}_3(\text{THF})_2]_2$ ,<sup>45</sup> (xxiii)  $\text{LiAl}(\text{OCEt}_3)_3\text{-Cl}$ ,<sup>104</sup> (xxiv)  $[\text{Pr}\{\text{Al}(\text{O}^i\text{Pr})_4\}_2(^i\text{PrOH})(\mu\text{-Cl})]_2$ ,<sup>105</sup> (xxv)  $\text{Mg}_2\text{Al}_3(\text{O}^i\text{Pr})_{13}$ ,<sup>106</sup> (xxvi)  $\text{In}(\text{O}^t\text{Bu})_3\text{Sn}$ ,<sup>57,107</sup> (xxvii)  $\text{Ti}_2\text{-Zr}(\text{OCH}(\text{CF}_3)_2)_6$ ,<sup>59</sup> (xxviii)  $[\text{Ti}_2\text{Sn}(\text{OEt})_6]_n$ ,<sup>58</sup> (xxix)  $[\text{KSr}(\text{O}^t\text{Bu})_3]_n$ ,<sup>60</sup> (xxx)  $[\text{KSr}(\text{O}^t\text{Bu})_5]_n$ ,<sup>62</sup> (xxxi)  $\text{SrSn}_2(\text{O}^t\text{Bu})_6$ ,<sup>61</sup> (xxxii)  $\text{Cd}_4\text{Sn}_4(\mu_4\text{-O})_2(\text{OAc})_{10}(\text{OCH}_2^t\text{Bu})_{10}$ ,<sup>108</sup> (xxxiii)  $\text{Pb}_6\text{Nb}_4\text{O}_4(\text{OEt})_{24}$ ,<sup>63</sup> (xxxiv)  $\text{Pb}_2\text{Zn}_2(\text{OAc})_4(\text{OCH}_2\text{-CH}_2\text{OMe})_4$ ,<sup>109</sup> (xxxv)  $\text{PbZr}_3(\mu_4\text{-O})(\mu\text{-OAc})_2(\text{O}^i\text{Pr})_{10}$ ,<sup>110</sup> (xxxvi)  $\text{Co}_2\text{Ge}_2(\text{OCMe}_3)_8$ ,<sup>80</sup> (xxxvii)  $\text{M}_2\text{Sn}_2(\text{OCMe}_3)_8$  ( $\text{M} = \text{Mg, Cr, Mn, Co, Ni}$ ),<sup>80</sup> and (xxxviii)  $\text{Ni}_5\text{Sb}_3\text{O}_2(\text{OEt})_{10}(\text{HOEt})_4$ .<sup>111</sup>

In the following pages, a brief description of molecular structures and their ORTEP drawing of some of the above derivatives will be discussed and selected crystallographic data for some derivatives are collected in Table 3.

The ORTEP drawing (Figure 2) of the  $\text{Al}_2(\text{O}^t\text{Bu})_6$  molecule show pseudotetrahedral coordination around each Al atom, with the smallest O—Al—O angle being  $81^\circ$  associated with the bridging OR ligands. The central  $\text{Al}_2(\mu\text{-O})_2$  moiety is planar. The Al—O—C groups associated with terminal  $\text{O}^t\text{Bu}$  ligands lie in a plane perpendicular to the  $\text{Al}_2(\mu\text{-O})_2$  moiety. The Al—O bridging distance are 0.15 Å longer than the terminal Al—O bond distances.

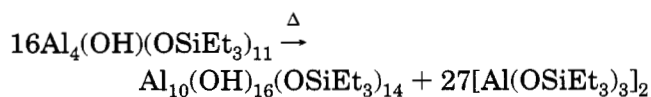
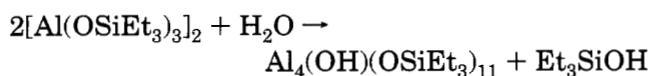
The ORTEP drawing (Figure 3) of the  $[\text{Al}(\text{O}^i\text{Pr})_3]_4$  molecule shows a central octahedral Al atom coordinated to three bidentate tetrahedral  $\{\text{Al}(\text{O}^i\text{Pr})_4\}^-$  groups. The planar  $\text{Al}(\mu_2\text{-O})_2\text{Al}$  rings have wider ( $\sim 132^\circ$ ) angles at O to increase the nonbonded Al—Al

**Table 3. Selected Crystallographic Data for Some Typical Homo- and Heterometallic Alkoxides of p-Block Metal(loid)s**

complex	space group	symmetry	crystal data
[Al(O <sup>i</sup> Pr) <sub>3</sub> ] <sub>4</sub> <sup>26,27</sup>	<i>P4<sub>1</sub>2<sub>1</sub>2<sub>1</sub></i>	tetragonal	$a = b = 12.317(3)$ , $c = 31.724(8)$ Å; $Z = 4$ ; $R = 0.0491$ , $R_w = 0.0457$
[Al(O <sup>i</sup> Bu) <sub>3</sub> ] <sub>2</sub> <sup>28</sup>	<i>P1</i>	triclinic	$a = 9.946$ , $b = 9.755$ , $c = 16.332$ Å; $\alpha = 88.89$ , $\beta = 73.81$ , $\gamma = 88.89^\circ$ ; $Z = 2$ ; $R = 0.0552$ , $R_w = 0.0578$
In <sub>5</sub> O(O <sup>i</sup> Pr) <sub>13</sub> <sup>37</sup>	<i>P2<sub>1</sub>/n</i>	monoclinic	$a = 12.665(2)$ , $b = 21.305(2)$ , $c = 20.910(6)$ Å; $\beta = 90.70(2)^\circ$ ; $Z = 4$ ; $R = 0.057$
[Ge(OC <sup>i</sup> Bu) <sub>3</sub> ] <sub>2</sub> <sup>47</sup>	<i>Pa3</i>	cubic	$a = 14.015(6)$ Å; $Z = 4$ ; $R = 0.11$
[ClSn(O <sup>i</sup> Bu) <sub>2</sub> THF] <sub>4</sub> <sup>41</sup>	<i>C2/c</i>	monoclinic	$a = 17.700(2)$ , $b = 11.370(1)$ , $c = 11.197(1)$ Å; $\beta = 122.33(1)^\circ$ ; $Z = 4$ ; $R = 0.024$ , $R_w = 0.032$
[Sn(O <sup>i</sup> Pr) <sub>4</sub> HO <sup>i</sup> Pr] <sub>2</sub> <sup>42,91</sup>	<i>P2<sub>1</sub>/c</i>	monoclinic	$a = 11.742(5)$ , $b = 14.285(3)$ , $c = 12.341(3)$ Å; $\beta = 95.37(1)^\circ$ ; $Z = 4$ ; $R = 0.048$ , $R_w = 0.048$
[Sn(O <sup>i</sup> Bu) <sub>4</sub> ] <sub>9</sub> <sup>91</sup>	<i>C2/c</i>	monoclinic	$Z = 4$ ; $R = 0.025$
Sn <sub>3</sub> O(O <sup>i</sup> Bu) <sub>10</sub> ·2 <sup>i</sup> BuOH <sup>100</sup>	<i>P1</i>	triclinic	$a = 13.635(7)$ , $b = 14.627(10)$ , $c = 16.377(2)$ Å; $\alpha = 95.40(5)$ , $\beta = 96.79(4)$ , $\gamma = 102.15(5)^\circ$ ; $Z = 2$
[Pb(O <sup>i</sup> Bu) <sub>2</sub> ] <sub>3</sub> <sup>48</sup>	<i>R3</i>	trigonal	$a = b = 10.174(2)$ , $c = 29.491(9)$ Å; $\gamma = 120^\circ$ ; $Z = 3$ ; $R = 0.054$ , $R_w = 0.0592$
[Pb(OCH <sub>2</sub> CH <sub>2</sub> OMe) <sub>2</sub> ] <sub>4</sub> <sup>48</sup>	<i>C2/c</i>	monoclinic	$a = 11.411(8)$ , $b = 14.64(6)$ , $c = 6.278$ Å; $\beta = 108.34^\circ$ ; $Z = 4$ ; $R = 0.0258$ , $R_w = 0.0320$
[Bi(OCH <sub>2</sub> CH <sub>2</sub> OMe) <sub>3</sub> ] <sub>4</sub> <sup>49</sup>	<i>P1</i>	triclinic	$a = 10.849(8)$ , $b = 12.041(9)$ , $c = 13.11(1)$ Å; $\alpha = 66.57(6)$ , $\beta = 73.54(6)$ , $\gamma = 66.71(5)^\circ$
[LiAl(OCeEt <sub>3</sub> ) <sub>3</sub> Cl(THF) <sub>2</sub> ] <sub>10</sub> <sup>44</sup>	<i>P2<sub>1</sub>/c</i>	monoclinic	$a = 16.49(3)$ , $b = 10.65(1)$ , $c = 20.05(3)$ Å; $\beta = 106.97(11)^\circ$ ; $Z = 4$ ; $R = 0.055$ , $R_w = 0.063$
[Pr{Al(O <sup>i</sup> Pr) <sub>4</sub> } <sub>2</sub> ( <sup>i</sup> PrOH)(μ-Cl) <sub>2</sub> ] <sub>10</sub> <sup>55</sup>	<i>C2/c</i>	monoclinic	$a = 25.181(6)$ , $b = 16.937(3)$ , $c = 19.376(3)$ Å; $\beta = 91.60(2)^\circ$ ; $Z = 4$
Mg <sub>2</sub> Al <sub>3</sub> (O <sup>i</sup> Pr) <sub>13</sub> <sup>106</sup>	<i>P2<sub>1</sub>/c</i>	monoclinic	$a = 15.927(4)$ , $b = 18.239(7)$ , $c = 19.914(7)$ Å; $\beta = 91.34(2)^\circ$ ; $Z = 4$ ; $R = 0.096$
[In(O <sup>i</sup> Bu) <sub>3</sub> Sn] <sub>5</sub> <sup>57</sup>	<i>P2<sub>1</sub>/n</i>	monoclinic	$Z = 4$ ; $R = 0.062$
[Tl <sub>2</sub> Sn(OEt) <sub>6</sub> ] <sub>n</sub> <sup>58</sup>	<i>C2</i>	monoclinic	$a = 6.487(3)$ , $b = 16.831(9)$ , $c = 9.293(5)$ Å; $\beta = 101.88(4)^\circ$ ; $Z = 2$ ; $R = 0.084$ , $R_w = 0.091$
[Tl <sub>2</sub> Zr(OCH(CF <sub>3</sub> ) <sub>2</sub> ) <sub>6</sub> ] <sub>5</sub> <sup>59</sup>	<i>C2/c</i>	monoclinic	$a = 19.879(2)$ , $b = 10.182(1)$ , $c = 20.456(1)$ Å; $\beta = 122.97(0)^\circ$ ; $Z = 4$ ; $R = 0.0481$ , $R_w = 0.0497$
[KSn(O <sup>i</sup> Bu) <sub>3</sub> ] <sub>6</sub> <sup>60</sup>	<i>P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub></i>	orthorhombic	$a = 25.149(11)$ , $b = 29.658(13)$ , $c = 32.558(2)$ Å; $Z = 32$ ; $R = 0.061$ , $R_w = 0.065$
SrSn <sub>2</sub> (O <sup>i</sup> Bu) <sub>6</sub> <sup>61</sup>	<i>R3</i>	trigonal	$a = 10.17(1)$ , $c = 29.86(2)$ Å; $Z = 3$ ; $R = 0.033$
KSn(O <sup>i</sup> Bu) <sub>5</sub> <sup>62</sup>	<i>Fddd</i>	orthorhombic	$a = 25.149(22)$ , $b = 29.658(26)$ , $c = 32.558(43)$ Å; $Z = 32$ ; $R = 0.061$ , $R_w = 0.065$
MnGe <sub>2</sub> (O <sup>i</sup> Bu) <sub>8</sub> <sup>80</sup>	<i>Pnma</i>	orthorhombic	$a = 19.624(9)$ , $b = 16.950(8)$ , $c = 9.910(6)$ Å; $Z = 4$ ; $R = 0.054$ , $R_w = 0.063$
Co <sub>2</sub> Ge <sub>2</sub> (O <sup>i</sup> Bu) <sub>8</sub> <sup>80</sup>	<i>P2<sub>1</sub>/n</i>	monoclinic	$a = 10.054(7)$ , $b = 14.794(8)$ , $c = 14.999(8)$ Å; $\beta = 97.06(7)^\circ$ ; $Z = 2$ ; $R = 0.069$ , $R_w = 0.064$
Sn <sub>2</sub> Mg <sub>2</sub> (O <sup>i</sup> Bu) <sub>8</sub> <sup>80</sup>	<i>P2<sub>1</sub>/n</i>	monoclinic	$a = 10.100(7)$ , $b = 14.951(8)$ , $c = 15.009(9)$ Å; $\beta = 97.30(6)^\circ$ ; $Z = 2$ ; $R = 0.037$ , $R_w = 0.041$
Cr <sub>2</sub> Sn <sub>2</sub> (O <sup>i</sup> Bu) <sub>8</sub> <sup>80</sup>	<i>P2<sub>1</sub>/c</i>	monoclinic	$a = 13.645(9)$ , $b = 10.411(8)$ , $c = 15.729(9)$ Å; $\beta = 103.27(8)^\circ$ ; $Z = 2$ ; $R = 0.056$ , $R_w = 0.068$
Mn <sub>2</sub> Sn <sub>2</sub> (O <sup>i</sup> Bu) <sub>8</sub> <sup>80</sup>	<i>P2<sub>1</sub>/c</i>	monoclinic	$a = 10.072(5)$ , $b = 15.149(8)$ , $c = 15.082(8)$ Å; $\beta = 97.11(4)^\circ$ ; $Z = 2$ ; $R = 0.073$ , $R_w = 0.077$
Co <sub>2</sub> Sn <sub>2</sub> (O <sup>i</sup> Bu) <sub>8</sub> <sup>80</sup>	<i>P2<sub>1</sub>/n</i>	monoclinic	$a = 10.032(7)$ , $b = 15.052(9)$ , $c = 14.978(9)$ Å; $\beta = 97.08(7)^\circ$ ; $Z = 2$ ; $R = 0.054$ , $R_w = 0.069$
Ni <sub>2</sub> Sn <sub>2</sub> (O <sup>i</sup> Bu) <sub>8</sub> <sup>80</sup>	<i>P2<sub>1</sub>/n</i>	monoclinic	$a = 9.959(7)$ , $b = 15.083(9)$ , $c = 14.920(9)$ Å; $\beta = 96.96(7)^\circ$ ; $Z = 2$ ; $R = 0.055$ , $R_w = 0.059$
Cd <sub>4</sub> Sn <sub>4</sub> (O) <sub>2</sub> (OAc) <sub>10</sub> (OCH <sub>2</sub> <sup>i</sup> Bu) <sub>10</sub> <sup>108</sup>	<i>C2/c</i>	monoclinic	$a = 25.316(15)$ , $b = 15.076(7)$ , $c = 28.221(10)$ Å; $\beta = 98.1(4)^\circ$ ; $Z = 4$ ; $R = 0.070$ , $R_w = 0.089$
Pb <sub>6</sub> Nb <sub>4</sub> O <sub>4</sub> (OEt) <sub>24</sub> <sup>63</sup>	<i>P2<sub>1</sub>/n</i>	monoclinic	$a = 15.444(5)$ , $b = 23.403(5)$ , $c = 23.572(8)$ Å; $\beta = 92.630(3)^\circ$ ; $Z = 4$ ; $R = 0.0740$ , $R_w = 0.0889$ .

distance, while the terminal O<sup>i</sup>Pr groups show the shortest, 1.70 Å, Al—O distances in the molecule; they are nevertheless strongly bent (~140°) at O.

Recently hydrolytically stable alumonxane Al<sub>10</sub>(OH)<sub>16</sub>(OSiEt<sub>3</sub>)<sub>14</sub>, synthesized according to the following equations, has been characterized by X-ray crystallographic study<sup>112</sup> (Figure 4).



Although a number of aryloxide derivatives of aluminum have been characterized by single-crystal

X-ray crystallographic study,<sup>113,114,115</sup> these may generally be considered to be out of place in this article which is mainly dealing with the alkoxide derivatives. However, a typical aryloxide derivative has been represented as a unique tricoordinate species<sup>29</sup> (Figure 1f).

Recently a pentaindium oxo alkoxide derivative with a central pentacoordinated oxygen In<sub>5</sub>O(O<sup>i</sup>Pr)<sub>13</sub> has been characterized by X-ray crystallographic study (Figure 5), in which an O-centered square pyramid of indium atoms is bridged by four μ<sub>2</sub>-isopropoxo groups around the equator and for μ<sub>3</sub>-isopropoxo groups on the triangular faces of the pyramid; the oxoisopropoxide molecule exhibits approximate C<sub>4v</sub> symmetry and the coordination envi-

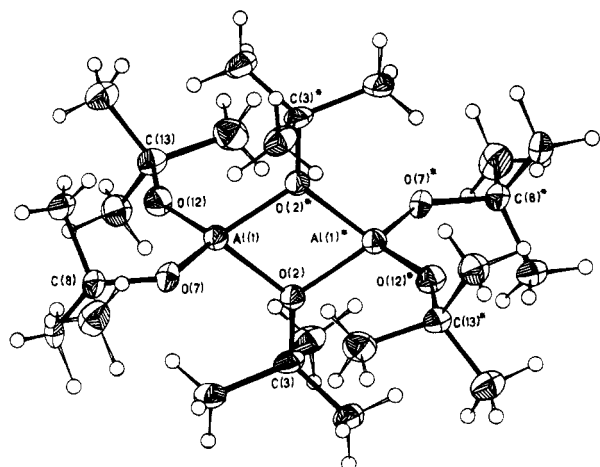


Figure 2. An ORTEP drawing of  $\text{Al}_2(\text{O}^t\text{Bu})_6$ .<sup>28</sup>

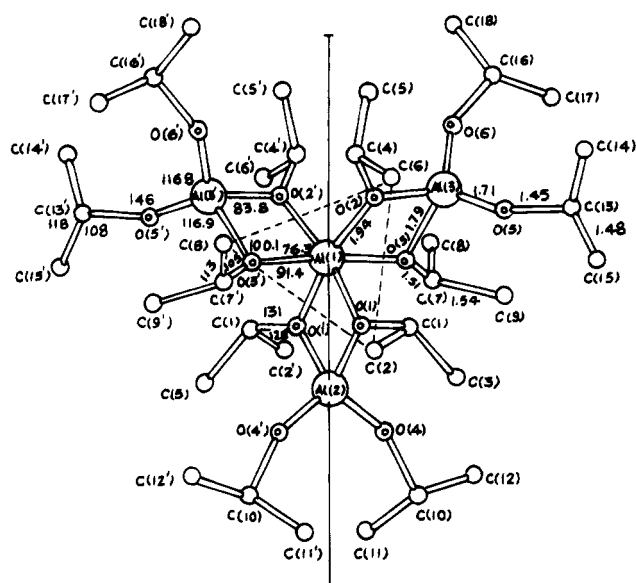


Figure 3. An ORTEP drawing of  $\text{Al}_4(\text{O}^i\text{Pr})_{12}$ .<sup>26,27</sup>

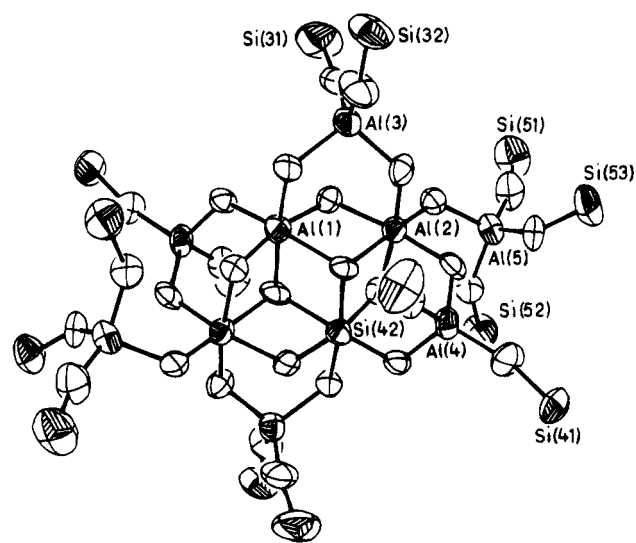


Figure 4. An ORTEP drawing of  $\text{Al}_{10}(\text{OH})_{16}(\text{OSiEt}_3)_{14}$ .<sup>112</sup>

ronment about each indium is highly distorted octahedral.

It appears that no reports have been published on the crystallographic studies of Ge(IV) simple alkoxide derivatives, but a Ge(II) alkoxide  $[\text{Ge}(\text{OC}^t\text{Bu}_3)_2]$  has

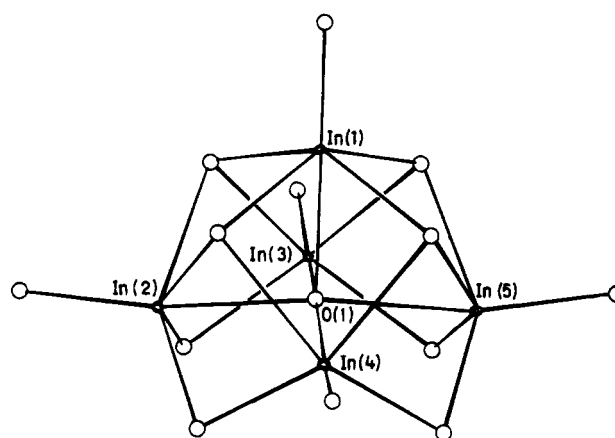


Figure 5. Structure of the  $\text{In}_5\text{O}_{14}$  unit in  $\text{In}_3(\text{O}^i\text{Pr})_{13}$ .<sup>37</sup>

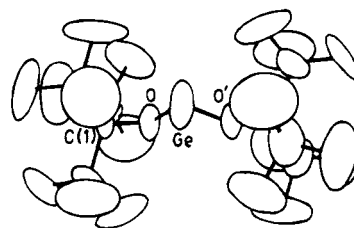


Figure 6. An ORTEP drawing of  $[\text{Ge}(\text{OC}^t\text{Bu}_3)_2]$ .<sup>47</sup>

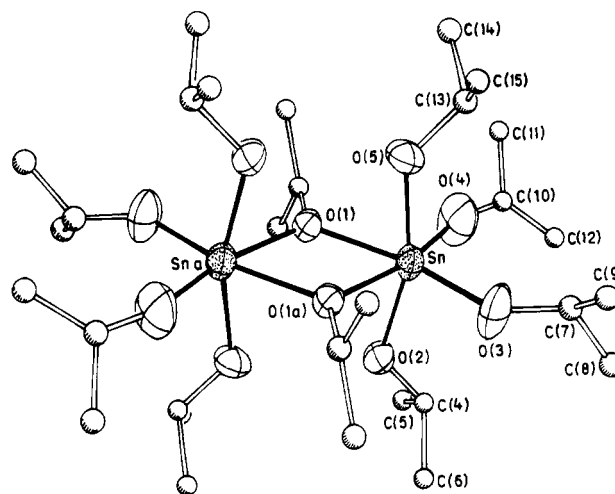


Figure 7. An ORTEP drawing of  $[\text{Sn}(\text{O}^i\text{Pr})_4(\text{HO}^i\text{Pr})]_2$ .<sup>42,91</sup>

been characterized by an X-ray crystallographic study (Figure 6) which indicates V-shaped monomer (cf. Figure 1h), with an exceptionally small O—Ge—O angle of  $85.9(4)^\circ$  and with coordination number two at the Ge(II) center.

Recently the crystal structure of  $[\text{Sn}(\text{O}^i\text{Pr})_4(\text{HO}^i\text{Pr})]_2$  has been determined by Hampden-Smith *et al.*<sup>91</sup> and Reuter *et al.*<sup>42</sup> It consists of discrete, dimeric molecules (Figure 7) in which the two Sn atoms are bridged by two  $^i\text{PrO}^-$  groups. The distorted octahedral coordination sphere for each Sn atom is completed by one solvent molecule. The distorted geometry of the molecule is due to the presence of asymmetric hydrogen bonding between axially coordinated alcohol ligands and an isopropoxide ligand.

The structure of  $[\text{Sn}(\text{O}^t\text{Bu})_4]$  has also been determined recently by a single-crystal X-ray diffraction study. The  $\text{Sn}(\text{O}^t\text{Bu})_4$  (Figure 8) is monomeric in the solid state with a distorted tetrahedral Sn-coordination environment.

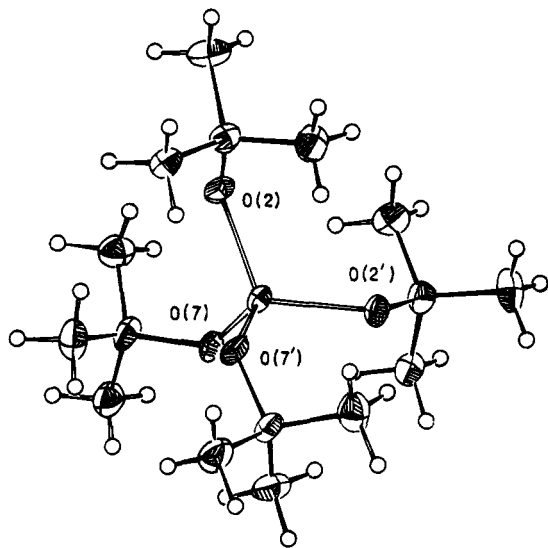


Figure 8. An ORTEP drawing of  $\text{Sn}(\text{O}^t\text{Bu})_4$ .<sup>91</sup>

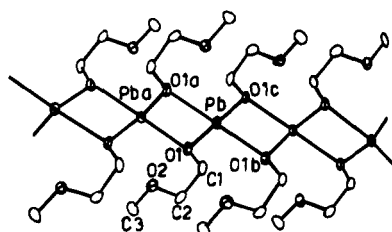


Figure 9. View of a segment from the chain form of  $[\text{Pb}(\text{OCH}_2\text{CH}_2\text{OMe})_2]_\infty$ .<sup>48</sup>

Two lead(II) alkoxides,  $[\text{Pb}(\text{OCH}_2\text{CH}_2\text{OMe})_2]_\infty$ <sup>48</sup> and  $[\text{Pb}(\text{O}^t\text{Bu})_2]_3$ <sup>48</sup> have been recently characterized by X-ray crystallography. The  $[\text{Pb}(\mu, \eta^1\text{OCH}_2\text{CH}_2\text{OMe})_2]_\infty$  has been shown (Figure 9) to have a polymeric one-dimensional chain structure. All alkoxide ligands in the chain are crystallographically equivalent and bridge two, tetracoordinate lead atoms. No terminal ligand is present. The potential bidentate alkoxide ligands do not chelate through either oxygen; instead they adopt dangling conformations. The sawhorse configuration about lead, conforms to a trigonal bipyramid having a stereochemically active lone pair in an equatorial position. The trigonal bipyramid is significantly distorted. Both the  $\text{O}_{\text{ap}}-\text{Pb}-\text{O}_{\text{ap}}$  and  $\text{O}_{\text{eq}}-\text{Pb}-\text{O}_{\text{eq}}$  angles,  $151.7(2)$  and  $89.5(2)^\circ$ , respectively, are compressed below ideal values, confirming the equatorial lone pair.

The trimeric structure of  $[\text{Pb}(\text{O}^t\text{Bu})_2]_3$  is shown in the Figure 10. The trimer consists of two tricoordinate terminal lead atoms, a central hexacoordinate lead atom and six bridging alkoxide ligands.  $\text{Pb}-\text{O}$  distances involving central Pb atom are  $2.55(1)$  Å (av), and the terminal  $\text{Pb}-\text{O}$  distance is  $2.17(2)$  Å. These values suggest that  $\text{Pb}-\text{O}$  bonds involving central the Pb (CN 6) atom are dative and those involving terminal Pb (CN 3) atoms are covalent in nature. The overall geometry around the central Pb atom is a trigonally distorted octahedral with a stereochemically inactive lone pair.

The similar structural unit is also present in heterobimetallic tertiary butoxides with the difference that the central lead atom is replaced by strontium (Figure 16) and manganese (Figure 20)

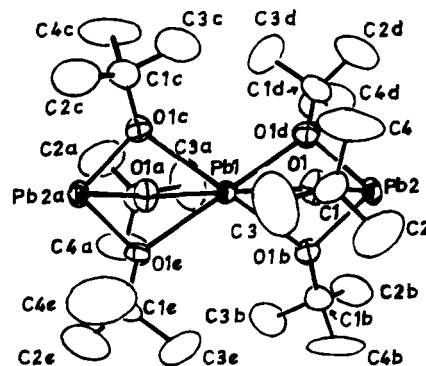


Figure 10. Crystal structure of  $[\text{Pb}(\mu\text{-O}^t\text{Bu})_2]_3$ .<sup>48</sup>

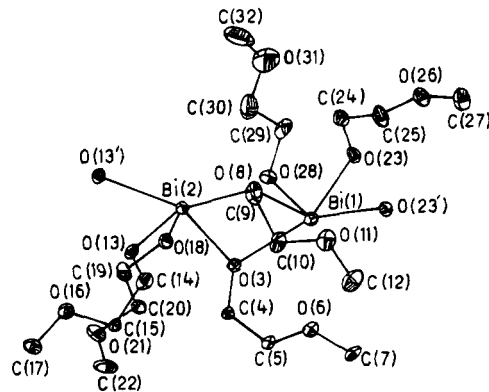


Figure 11. An ORTEP view of the asymmetric  $[\text{Bi}_2(\text{OC}_2\text{H}_4\text{OMe})_6]$ <sup>44,49</sup> subunit.

atoms respectively and the outer lead atoms by tin and germanium, respectively.

In the same year 1990, Hubert-Pfalzgraf *et al.*<sup>44</sup> and Buhro *et al.*<sup>49</sup> reported the X-ray crystal structure of the same polymeric  $[\text{Bi}(\mu\text{-}\eta^1(\text{OCH}_2\text{CH}_2\text{OMe})_2(\eta^1\text{-OCH}_2\text{CH}_2\text{OMe}))]_\infty$  compound prepared by two different methods. This highly soluble compound appears to be a one-dimensional polymer based on dinuclear asymmetric  $\text{Bi}_2(\mu_2\text{-OC}_2\text{H}_4\text{OMe})_4(\text{OC}_2\text{H}_4\text{OMe})_2$  units in the solid. At first approximation, all bismuth atoms are pentacoordinated, with bismuth alkoxo bond lengths ranging from  $2.071(6)$  to  $2.673(6)$  Å. The lone pair is stereochemically active and appears to be directed opposite to the apical alkoxo group. The overall structure can thus be viewed as a polymerization of  $\text{MX}_3$  units to a chain of  $\text{MX}_5$  pyramids *trans* fused at a basal edge (Figure 11).

A single-crystal X-ray diffraction study of  $\text{Tl}_2\text{Sn}(\text{OEt})_6$  revealed<sup>58</sup> that it exists as a one-dimensional polymer in the solid state containing tin(IV) atoms octahedrally coordinated by ethoxide ligands and distorted trigonal bipyramid thallium(I) atoms with the lone pair occupying the vacant equatorial coordination site. There are two types of ethoxide ligands; one triply bridging and another containing double bridging (Figure 12).

The X-ray diffraction determination of the structure of  $\text{Tl}_2\text{Zr}(\text{OCH}(\text{CF}_3)_2)_6$  (Figure 13) reveals<sup>59</sup> a  $\text{Tl}(\mu\text{-OR})_3\text{Zr}(\mu\text{-OR})_3\text{Tl}$  connectivity, based on a distorted octahedral  $\text{Zr}(\text{OR})_6^{2-}$  substructure with thallium ions occupying opposite triangular  $\text{ZrO}_3$  faces. The molecule is rigorously centrosymmetric, and thus the  $\text{Tl}/\text{Zr}/\text{Tl}$  unit is linear. The alkoxide oxygen coordination environment about thallium is completed by

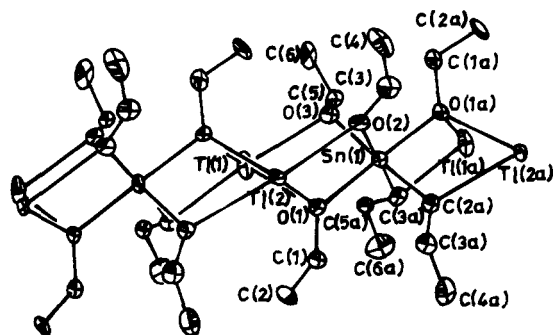


Figure 12. An ORTEP drawing of  $[\text{Tl}_2\text{Sn}(\text{OEt})_6]_n$ .<sup>58</sup>

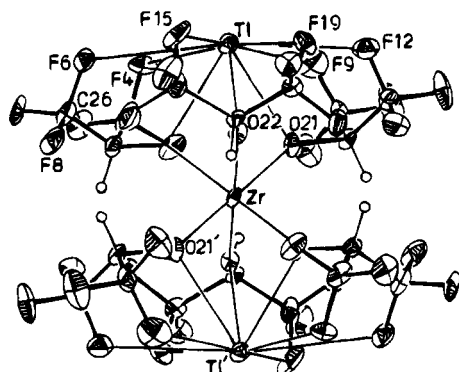


Figure 13. An ORTEP drawing of  $\text{Tl}_2\text{Zr}(\text{OCH}(\text{CF}_3)_2)_6$ .<sup>59</sup>

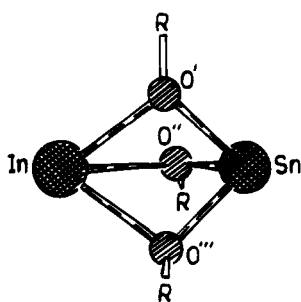


Figure 14. Structure of  $\text{Sn}(\text{O}^t\text{Bu})_3\text{In}$ .<sup>57</sup>

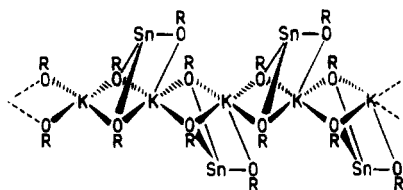


Figure 15. Structure of  $[\text{KSn}(\text{O}^t\text{Bu})_3]_n$ .<sup>57</sup>

a planar array of six Tl/F contacts (one from each  $\text{CF}_3$  group).

Crystal structure of  $\text{Sn}(\text{O}^t\text{Bu})_3\text{In}$ , a monomeric trigonal bipyramidal cage molecule is given in Figure 14.

X-ray structure of  $\text{MSn}(\text{O}^t\text{Bu})_3$  ( $\text{M} = \text{Li}, \text{Na}$ ) shows<sup>60</sup> that the metal atoms Li and Na in molecules are tetracoordinated and the tin atoms are tricoordinated. The polycyclic unit  $\text{Sn}_2\text{O}_6\text{M}_2$  is composed of two seco-norcubane analogous subunits that share a common face. The similar alkoxides of heavy alkali metal like K (and the isomorphous Rb and Cs) show polymeric arrangements of trigonal bipyramidal cages  $\text{Sn}(\text{O}^t\text{Bu})_3\text{M}$  (Figure 15), in which the alkali metal atom is coordinated by five oxygens and forms the link between the cages. The larger radius and accessibility of d orbitals may favor larger coordination numbers for K, Rb, and Cs.

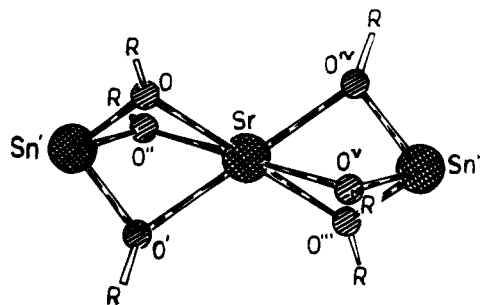


Figure 16. Structure of  $\text{SrSn}_2(\text{O}^t\text{Bu})_6$ .<sup>61</sup>

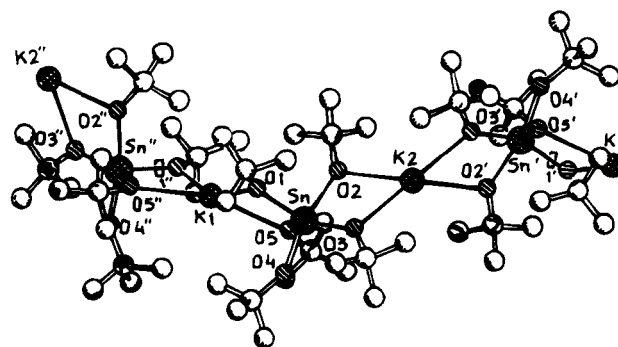


Figure 17. Crystal structure of  $[\text{KSn}(\text{O}^t\text{Bu})_5]_n$ .<sup>62</sup>

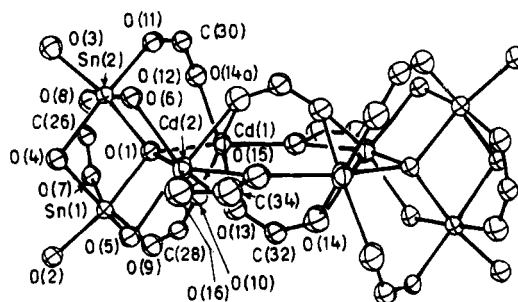


Figure 18. Molecular structure of  $[\text{Cd}_4\text{Sn}_4(\mu_4\text{-O})_2(\text{OAc})_{10}(\text{OCH}_2^t\text{Bu})_{10}]$ .<sup>108</sup>

Crystal structure of  $\text{SrSn}_2(\text{O}^t\text{Bu})_6$  (Figure 16) consists<sup>61</sup> of two trigonal bipyramids connected via a common apex with retention of the 3-fold axis. This apical position, which at the same time is a center of inversion, is occupied by the Sr atom, which is situated in a distorted octahedral environment ( $\text{O}-\text{Sr}-\text{O}$   $90 \pm 24.4(1)^\circ$ ). The Sn atoms are trigonal bipyramidally coordinated ( $\text{O}-\text{Sn}-\text{O}$   $82.3(1)^\circ$ ). The average Sn—O and Sr—O distances are 2.078(3) and 2.523(3) Å respectively.

The X-ray structure of  $\text{KSn}(\text{O}^t\text{Bu})_5 \cdot 0.5\text{C}_7\text{H}_8$  (Figure 17) shows<sup>62</sup> it to be coordinated as a helical polymer with the tin atom in the center of a trigonal bipyramid of *tert*-butoxide groups interlinked by two structurally different potassium atoms.

The molecular unit of  $\text{Cd}_4\text{Sn}_4(\mu_4\text{-O})_2(\text{OAc})_{10}(\text{OCH}_2^t\text{Bu})_{10}$  (Figure 18) includes an eight-membered,  $\text{Cd}_4\text{O}_4$  planar ring with cadmium ions bridged by acetates and further linked in pairs by  $\mu_4$ -oxo, acetate, and neopentoxide bridges to two tin(IV) atoms which in turn are bridged by neopentoxide and acetate groups:<sup>108</sup>  $\text{Sn}-\text{O}(\text{b})_{\text{av}} = 2.0967(17)$  Å;  $\text{Sn}-\text{O}(\text{t}) = 1.963(19)$  Å,  $\text{Cd}-\text{O}(\text{av}) = 2.299(12)$  Å,  $\text{Sn}-\text{O}-\text{Sn}(\text{av}) = 100.5(7)^\circ$ ,  $\text{Sn}-\text{O}-\text{Cd}(\text{av}) = 110.0(7)^\circ$ ;  $\text{Cd}-\text{O}-\text{Cd} = 114.5(7)^\circ$ .

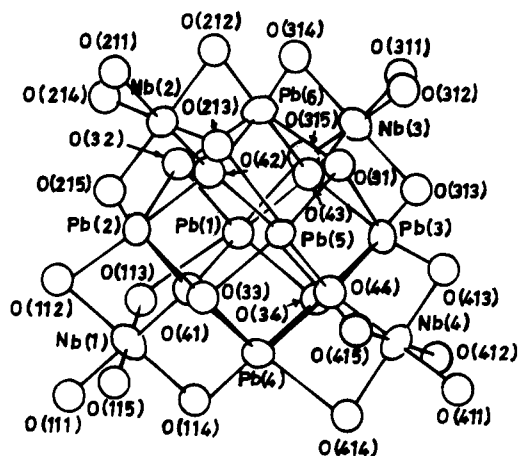


Figure 19. An ORTEP view of  $\text{Pb}_6\text{Nb}_4\text{O}_4(\text{OEt})_{24}$ .<sup>63</sup>

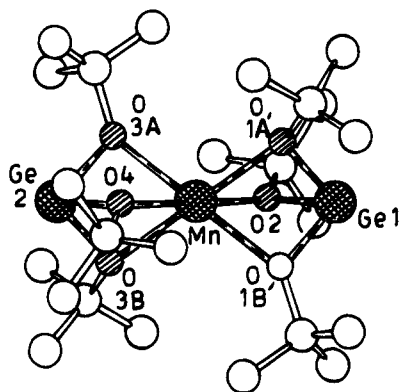


Figure 20. An ORTEP drawing of  $\text{MnGe}_2(\text{O}^t\text{Bu})_6$ .<sup>80</sup>

The molecular structure of the decanuclear species  $\text{Pb}_6\text{Nb}_4\text{O}_4(\text{OEt})_{24}$  (Figure 19) includes an octahedral  $\text{Pb}_6$  framework. Four of the faces of this octahedron are capped by an  $\mu_4$ -oxo ligand, connected to a  $\text{Nb}(\text{OEt})_5$  moiety and to three lead atoms.<sup>63</sup> The remaining faces of the lead octahedron are capped by  $\mu_3$ -ethoxo groups. The  $\text{Pb}-\text{O}$  distances follow the pattern  $\text{Pb}-\mu_4\text{-O} < \text{Pb}-\mu_3\text{-OR} < \text{Pb}-\mu_2\text{-OR}$  with the values ranging from 2.28(8) to 3.1(1) Å.

In the crystal structure of  $\text{MnGe}_2(\text{O}^t\text{Bu})_6$  (Figure 20), the Mn atom occupies the center of an elongated  $\text{O}_6$  octahedron with the Ge(II) atoms displaying pyramidal coordination by three oxygen atoms. The central molecular cage can be described as two  $\text{MnO}_3\text{-Ge}$  trigonal bipyramids sharing the common central Mn atom and being wrapped by *tert*-butyl groups linked to the oxygen atoms.

X-ray structures of the compounds  $[\text{MM}'(\text{O}^t\text{Bu})_4]_2$ <sup>80</sup> ( $\text{M}' = \text{Ge}$ ,  $\text{M} = \text{Co}$ ;  $\text{M}' = \text{Sn}$ ,  $\text{M} = \text{Mg}$ ,  $\text{Cr}$ ,  $\text{Mn}$ ,  $\text{Ni}$ ) show similar features; the central  $\text{M}_2(\text{O}^t\text{Bu})_2$  four-membered ring is spirocyclically connected to two  $\text{M}(\text{O}^t\text{Bu})_2\text{M}'$  rings through the common metal atoms M, along with the coordination of an exocyclic *tert*-butoxy group to the terminal  $\text{M}'$  atoms. The metal atoms M are quasi-tetrahedrally coordinated while the Ge and Sn atoms are in pyramidal 3-fold oxygen atom environments. The molecule  $\text{Co}_2\text{Ge}_2(\text{O}^t\text{Bu})_8$ <sup>80</sup> (Figure 21) displays a  $\text{Ge}\cdots\text{Co}\cdots\text{Co}\cdots\text{Ge}'$  one-dimensional arrangement.<sup>80</sup>

Derivatives  $\text{M}'_2\text{M}_2(\text{O}^t\text{Bu})_8$ <sup>80</sup> ( $\text{M} = \text{M}' = \text{Co}$ ,  $\text{Ge}$ ;  $\text{Co}$ ,  $\text{Sn}$ ) with a stereochemically active lone pair on metal atom  $\text{M}'$  form adducts of the type  $\text{M}'_2\text{M}_2(\text{O}^t\text{Bu})_8\cdot 2\text{Fe}(\text{CO})_4$ , which in the case of  $\text{M}' = \text{Sn}$  has been X-ray

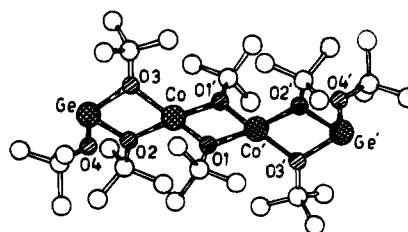


Figure 21. Molecular structure of  $\text{Co}_2\text{Ge}_2(\text{O}^t\text{Bu})_8$ .<sup>80</sup>

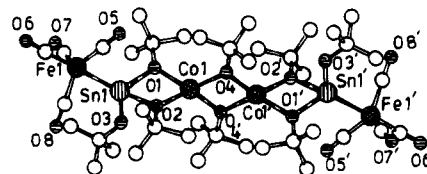


Figure 22. Molecular structure of  $\text{Co}_2\text{Sn}_2(\text{O}^t\text{Bu})_8\cdot 2\text{Fe}(\text{CO})_4$ .<sup>80</sup>

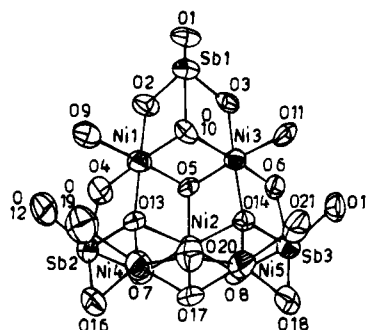


Figure 23. An ORTEP drawing of  $\text{Ni}_5\text{Sb}_3\text{O}_2(\text{OEt})_{15}\cdot(\text{HOEt})_4$ .<sup>111</sup>

crystallographically characterized (Figure 22).

The derivative  $\text{Ni}_5\text{Sb}_3\text{O}_2(\text{OEt})_{15}(\text{HOEt})_9$ <sup>111</sup> has been characterized by single-crystal diffraction study. The packing of the wedge-shaped molecules in  $\text{Ni}_5\text{Sb}_3\text{O}_2(\text{OEt})_{15}(\text{HOEt})_4$  can be considered as bcc. One of the Sb atom is tetracoordinated by the oxygen atoms, while the other two are pentacoordinated. The Sb atoms are all trivalent, and the stereoactive lone pairs complete the coordinations. The coordination around the Sb atoms is a distorted trigonal bipyramid (Figure 23) and octahedron respectively. Three of the five Ni atoms are almost octahedrally coordinated by O atoms, and remaining two Ni atoms, pentacoordinated in the shape of a distorted square pyramid.

## 4. Chemical Properties

### 4.1. Homometallic Alkoxides

The high electronegativity of oxygen makes metal-alkoxy bond(s) polarize in the direction  $\text{M}^{\delta+}-\text{O}^{\delta-}-\text{C}$  and as a consequence metal alkoxides exhibit both Lewis acid and base properties (cf. section 2.2) depending upon the nature of the metal and the reactant. The Lewis base properties are further enhanced due to the presence of a lone pair of electrons as in alkoxides of the types  $\text{M}(\text{OR})$  ( $\text{M} = \text{In}$ ,  $\text{Tl}$ ),  $\text{M}(\text{OR})_2$  ( $\text{M} = \text{Ge}$ ,  $\text{Sn}$ , or  $\text{Pb}$ ),  $\text{M}(\text{OR})_3$  ( $\text{M} = \text{As}$ ,  $\text{Sb}$ , or  $\text{Bi}$ ), and  $\text{M}(\text{OR})_4$  ( $\text{M} = \text{Se}$  or  $\text{Te}$ ). The facile reactivity of metal-alkoxy bonds with hydroxy compounds<sup>1</sup> (e.g., alcohols, silanols, glycols, carboxylic acids,  $\beta$ -diketones, Schiff bases, alkanolamines,

thiols, etc.) including water renders metal alkoxides as unique synthons for a variety of metalloorganic derivatives<sup>1,4-11,14-21</sup> most of which have not been prepared by any other convenient route.

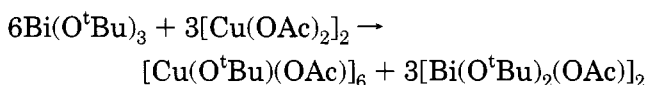
In fact the water susceptibility of metal alkoxides and modulation of their chemical reactivity by the use of chelating ligands like carboxylates,  $\beta$ -diketonates, and alkoxyethoxides, makes them attractive precursors for the synthesis of mixed-metal oxide ceramic materials by the sol-gel technique.<sup>9-11,13-18</sup>

Metal alkoxides also react exothermally with acyl halides and acetic anhydride with the replacement of alkoxide groups by halide (generally Cl or Br) or acetate groups, yielding<sup>1</sup> products of the types,  $M(OR)_{n-x}(X)_x$ , where X = Cl, Br or OAc:

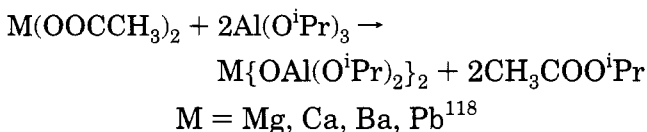


Incidentally these chloride alkoxides can be used as precursors for the synthesis of heterobimetallic alkoxides by reacting these with alkali alkoxometalates like  $M\{Al(OR)_4\}$  or  $M\{Ta(OR)_6\}$  (M = Li, Na or K).

The exchange of ligands between two different homoleptic derivatives has been utilized in the preparation of a mixed alkoxide acetate of bismuth and copper recently:<sup>116</sup>



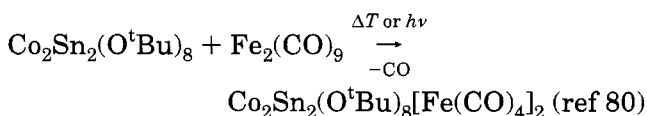
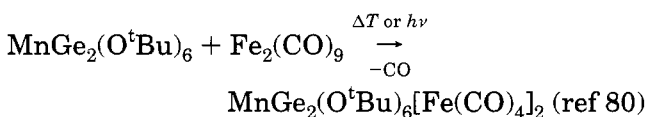
The reaction between metal alkoxides and carboxylates generally consists in ester elimination with the formation of heterometal oxide alkoxides.<sup>117,118</sup>



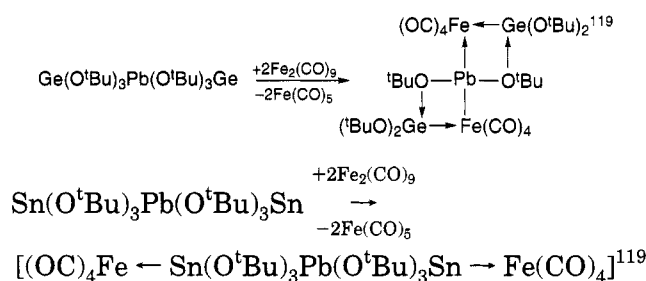
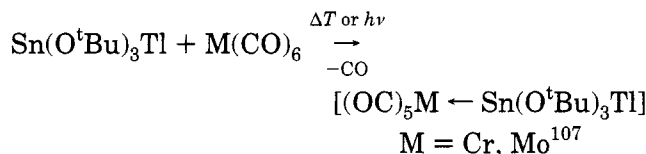
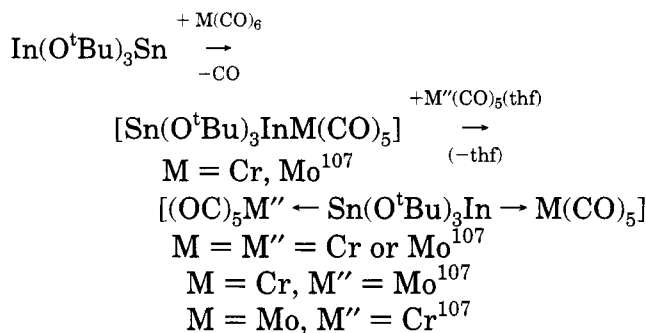
## 4.2. Heterometallic Alkoxides

As expected these derivatives exhibit properties similar to those of constituent homometallic alkoxides. Some typical reactions are illustrated below.

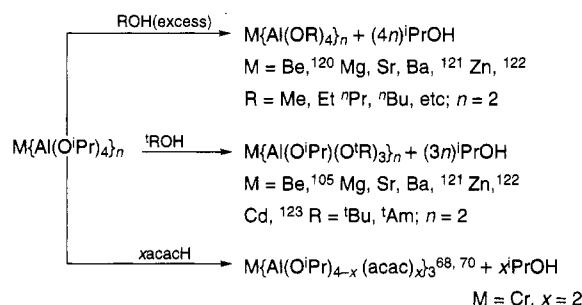
### 4.2.1. Reactions with Metal Carbonyls



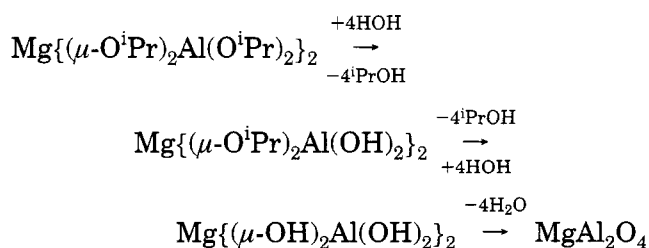
Comparative stereochemical reactivity of the electrons lone pair on heterometallic alkoxides of sub-valent group 13 and 14 elements may be illustrated by the following equations:



### 4.2.2. Ligand Exchange Reactions



The facile hydrolyzability of heterometal alkoxides with retention of their structural features (particularly in the initial stages) makes them highly attractive precursors for homogeneous mixed-metal oxides.<sup>124,125</sup>



In view of the difficulty in handling homoleptic alkoxides due to their strong susceptibility of hydrolysis even by atmospheric moisture, heterometal oxide alkoxides could provide more attractive precursors for ceramic materials. Such possibilities have led to a detailed investigation<sup>118</sup> on the mechanism of methanolysis and hydrolysis reactions. Results on methanolysis and hydrolysis reactions of the Ca<sup>126</sup> and Mg<sup>127</sup> derivatives have been published recently. Besides hydrolysis reaction the reactions with other



protic reagents like acetic acid,  $\beta$ -diketones and glycols, etc., have shown that only three of the four isopropoxy groups of  $\text{CaO}_2\text{Al}_2(\text{O}^i\text{Pr})_4$  are replaceable, suggesting an interesting tetrameric structure.<sup>128</sup>

## 5. Conclusions

The preceding account of the chemistry of homo- and heterometal alkoxides of p-block elements reflects an active resurgence brought about by the key role played by metals like bismuth and lead in novel superconducting materials<sup>129</sup> and successful crystal structure elucidation. Although most of these structures depict unique features which may be related in general to the size of the central metal atoms and the steric requirements of the alkoxy ligands, convincing correlations would be feasible only with the availability of such data for a much larger number of species in which the variation is limited to one of the controlling parameters only.

The attractive potentialities of the metal alkoxides as precursors for ceramic materials by the sol-gel process<sup>8-11,14-17,21</sup> has led to extensive work on the search of suitable chelating ligands like alkoxy-alkanols<sup>44,48,49</sup> or alkoxometalates.<sup>1-7,12</sup> The chelation of a central metal by different alkoxometalates has yielded a variety of heterometal alkoxide systems,<sup>1-7</sup> opening up the possibilities of single-source precursors. Although extensive studies have centered around the hydrolysis and condensation reactions of alkyl orthosilicates,<sup>10</sup> similar studies on other homo- and even more so on heterometal species are just being initiated and could be expected to grow rapidly, elucidating the chemistry and nature of intermediate species. The formation of anion pentaalkoxy silicates,<sup>90</sup>  $\text{Si}(\text{OR})_5^-$ , and  $\text{R}'_n\text{Si}(\text{OR})_{5-n}$  derivatives offers strong support for previous suggestions of the existence of species of this type as intermediates in silicon reaction mechanisms, e.g. in the sol-gel process. The isolation of  $[\text{K } 18\text{-crown-6}]^+[\text{PhSi}(\text{OCH}_2\text{CF}_3)_4]^-$ <sup>90a</sup> as a crystalline solid indicates the high stability associated with some members of this class.

The isolation and characterization of a number of crystalline oxide alkoxide derivatives like  $\text{In}_5\text{O}(\text{O}^i\text{Pr})_{13}$ <sup>37</sup> without intervention of water has led to unique investigations like conversion of  $\text{Zn}(\text{OCEt}_3)_2$  to  $\text{ZnO}$  using acetone as a condensing agent.<sup>130</sup> Efforts in similar directions appear to be in progress in a number of laboratories,<sup>9,10,17,93</sup> in addition to sophisticated physicochemical studies<sup>93,94</sup> on hydrolysis and condensation reactions in general. In view of some very interesting chemistry which is currently emerging from the study of double Lewis basicity of species such as  $\text{Tl}(\text{O}^t\text{Bu})_3\text{Sn}$ ,  $\text{In}(\text{O}^t\text{Bu})_3\text{Sn}$ ,  $\text{M}(\text{O}^t\text{Bu})_3\text{Pb}(\text{O}^t\text{Bu})_3\text{M}$  [ $\text{M} = \text{Ge}$  or  $\text{Sn}(\text{II})$ ], it is reasonable to predict that heterobimetallic alkoxides containing electron-rich metal atoms of the typical combinations, groups 15/13, 15/14, should exhibit enormous potential in generating excitingly novel metal clusters supported by the p-block metal(loid) alkoxides systems.

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