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Review

Novel heterometallic alkoxide coordination systems of polyols (glycols, di- and tri-ethanolamines) derived from the corresponding homometallic moieties

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Contents

Abstract

In view of the interesting structural features and suitability of heterometallic alkoxides (supported by chelating ligands) as precursors for oxide-ceramic materials, studies have been recently extended to novel types of heterometallic alkoxides derived from various polyols. These are generally obtained by the interactions of residual hydroxy groups in the homometallic derivatives with alkoxides of other metals.

In this review, the synthesis and characterization (including X-ray-based structures) of these novel heterometallic coordination systems with polyols (glycols, di- and tri-ethanolamines (teaH_3)), derived from the corresponding homometallic species, have been reviewed with a full list of compounds described till 2002.

Keywords: Heterometallic alkoxides; Polyolates; Glycolates; Diethanolaminates; Triethanolaminates

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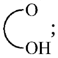
Abbreviations: acac, acetylacetonate; Bu, butyl; deaH_2, diethanolamine: $HN(CH_2CH_2OH)_2$; deaH, diethanolaminate(1-): $HN(CH_2CH_2O)(CH_2CH_2OH)$; dea, diethanolaminate(2-): $HN(CH_2CH_2O)_2{}^{2-}$; Et, ethyl; HOGOH (GH_2), a glycol; GH, glycolate(1-): OGOH/  ; G, glycolate(2-): OGO/  ; G^1, CH_2CH_2; G^2, CMe_2CMe_2; G^3, $CHMeCH_2CMe_2$; G^4, $CMe_2CH_2CH_2CMe_2$; *i*-Pr, isopropyl (CMe_2H); Oac, acetate; OEt, ethoxide; O-*i*-Pr, i-propoxide; O-*t*-Bu, *tert*-butoxide; Me, methyl; Ph, phenyl; PhMe, toluene; *t*-Bu, *tert*-butyl (CMe_3); teaH_3, $N(CH_2CH_2OH)_3$: tri-ethanolamine; teaH_2, $N(CH_2CH_2O)(CH_2CH_2OH)_2{}^{-}$; teaH, $N(CH_2CH_2O)_2(CH_2CH_2OH)^{2-}$; tea, $N(CH_2CH_2O)_3{}^{3-}$; THF, tetrahydrofuran

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1. Introduction and scope of the review

Heterometallic alkoxides are unique coordination systems stabilized merely by alkoxo-bridges between different metal atoms, similar to the type of bridges between atoms of the same metal in oligomeric homometal alkoxides. However, in spite of their unique stability as depicted by the volatility and non-conducting nature of the derivatives of even electropositive metals, e.g., $[KZr_2(O\text{-}i\text{-}Pr)_9]$ [1,2], $[Ln\{Al(O\text{-}i\text{-}Pr)_4\}_3]$ [3–5], $[KNb(O\text{-}i\text{-}Pr)_6]$ [6], and $[Ba\{Ta(O\text{-}i\text{-}Pr)_6\}_2]$ [7], scepticism persisted even about their identity, as they were termed [8] as 'mixed' metal alkoxides even as late as 1987. Emphasizing their covalent characteristics, Mehrotra et al. [9] had named them as 'double' alkoxides in 1972. The current name 'heterometallic alkoxides' has been finally assigned [10–12], based on their unequivocal characterization [10–12] as coordination compounds.

Such bi- and even ter- and tetra- heterometallic alkoxides of a large number of metals have been synthesized [13] generally by the reactions of metal halides with various alkali alkoxometallates. Plausible structures of these heterometal derivatives had been suggested mainly on the basis of colligative, chemical, and spectroscopic (e.g., NMR) studies. Many of these plausible structures have been later confirmed unequivocally by X-ray crystallographic studies during the past 10–15 years [14–17]. The chemistry of these conventional heterometallic alkoxides has also been extensively reviewed by us [13–18] as well as others [11,19–21].

An altogether novel class of heterometallic alkoxides has been described during the last few years, beginning with $[La(tea)_2\{Nb(O\text{-}i\text{-}Pr)_4\}_3]$ [22], involving polyol (e.g., tri- as well as di-ethanolamines and various glycols) derivatives. In spite of the growing literature, these novel types of heterometallic alkoxides have not been adequately reviewed except to a limited extent in a recent article [23], which deals mainly with the derivatives of functional alcohols of alkoxyalkanol type. The present review, therefore, focuses on this special class of heterometallic derivatives mainly. As the synthesis of the title compounds generally involves the reactions of homometallic complexes of polyols, with residual hydroxy groups, a brief account of these starting materials (precursors) is being briefly summarized in Section 2 before presenting in detail the chemistry of novel types of heterometallic derivatives synthesized from them.

2. Chemistry of relevant homometallic derivatives (used as starting materials)

The general synthetic routes so far employed for these derivatives are being described in the following pages. Although many of the homometallic complexes described herein may be associated species, yet for simplicity and convenience these are represented in the text and tables generally as mononuclear.

2.1. Metal glycolates

2.1.1. From metal alkoxides

Reactions of alkoxides of different metals (and metalloids) with a wide variety of glycols [13,17,24,25] afford products according to the general reaction shown in Eq. (1):

$$M(OR)_x + (y+z)HOGOH \xrightarrow[-(2y+z)ROH]{\text{benzene}} M(OR)_{x-2y-z}(OGO)_y(OGOH)_z \qquad (1)$$

where x is the valency of the metal, y and z are integers and their values are dependent on x: e.g., when $x = 2$: $y = 1$ and $z = 1$; when $x = 3$: $y = 1$ and $z = 0$ or 1; similarly, when $x = 4$: $y = 1(z = 0)$, $2(z = 0)$, $3(z = 1)$ and when $x = 5$ $(z = o)$, $2(z = 0$ or $1)$.

Using the above procedure, depending on the stoichiometric ratios of the reactants used, structurally [13,17] and synthetically interesting derivatives of alkaline earth metals [24–27], lanthanides [17,24], titanium [28–39], zirconium [31–39], uranium [40], oxovanadium [41], niobium [38,42–44], tantalum [45], iron [46], boron [47], aluminum [33,48], silicon [49,50], germanium [51], tin [52], antimony [53], selenium [54a], and tellurium [54b] have been prepared.

The above method has also been utilized by Crans et al. [55] for the synthesis of oxovanadium glycolates with *trans*-1,2-cyclohexanediol, (±)2,3-butanediol, 2*R*,3*R*-butanediol, and ethyleneglycol. These compounds contain two diols for each vanadium presumably in a dimeric arrangement.

In 1995, Plafzgraf et al. [56,57] have described the preparation of mixed ethyleneglycolate-isopropoxide derivatives via an interesting C–O bond cleavage reaction of 2-hydroxyethylmethylacrylate induced by oxophilic metal centers (Eq. (2)) such as Ti and Nb:

$$\begin{aligned} & M(O\text{-}i\text{-}Pr)_x + HOC_2H_4OC(O)CMe{=}CH_2 \\ & \xrightarrow[(-Pr\text{-}i\text{-}OH)]{} \frac{1}{n}[M(O\text{-}i\text{-}Pr)_{x-2}(OC_2H_4O)]_n \\ & \quad + i\text{-}PrCO_2CMe{=}CH_2 \end{aligned} \qquad (2)$$

M: Ti ($x = 4$), $n = 5$; Nb ($x = 5$), $n = 4$.

The soluble derivatives of Ti (Fig. 1) and Nb (Fig. 2) display several interesting structural features such as five-, six, and seven-coordinated Ti centers as well as four types of ligating modes of ethyleneglycolate groups: μ,η2-chelating doubly bridging, two types of triply-bridging μ_3, η^2- and a μ_4, η^2-fly-over manner.

In the centrosymmetric tetranuclear niobium derivative $Nb_4(\mu,\eta^2\text{-}OC_2H_4O)_4(\mu\text{-}OC_2H_4O)(O\text{-}i\text{-}Pr)_{10}$ (Fig. 2); the ethyleneglycolate groups arrange themselves around six- and seven-coordinated Nb with the two central heptacoordinated Nb in a distorted bipyramidal pentagonal arrangements.

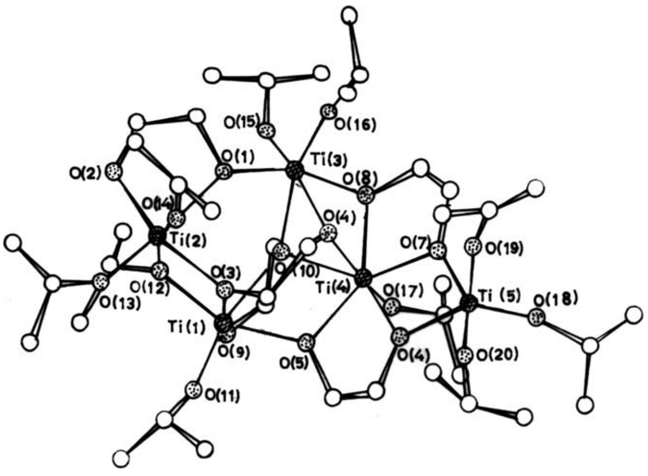


Fig. 1. Crystal structure of $[Ti(O\text{-}i\text{-}Pr)_2(OC_2H_4O)]_5$ (from Ref. [23]).

2.1.2. From metal amides

Interactions between three equivalents of pinacol and tungsten hexakis-(dimethylamide) (Eq. (3)) and ditungsten hexakis(dimethylamide) (Eq. (4)) in diethyl ether/*n*-hexane afford tungsten tris(pinacolate) and ditungsten tris(pinacolate) respectively, of which structure (Fig. 3) for tungsten tris(pinacolate) has been established by X-ray crystallographic studies [58,59]:

$$W(NMe_2)_6 + 3\,HOCMe_2CMe_2OH \longrightarrow W(\overline{OCMe_2CMe_2O})_3 + 6HNMe_2 \qquad (3)$$

$$(Me_2N)_3W \equiv W(NMe_2)_3 + 3HOCMe_2CMe_2OH \rightarrow W_2(OCMe_2CMe_2O)_3 + 6HNMe_2 \qquad (4)$$

The tungsten(VI) tris(pinacolate) has a distorted octahedral WO_6 moiety and a crystallographically imposed twofold axis of symmetry (Fig. 3). The preference for an octahedral geometry has been explained [58] on the basis of Opπ to Wdπ bonding.

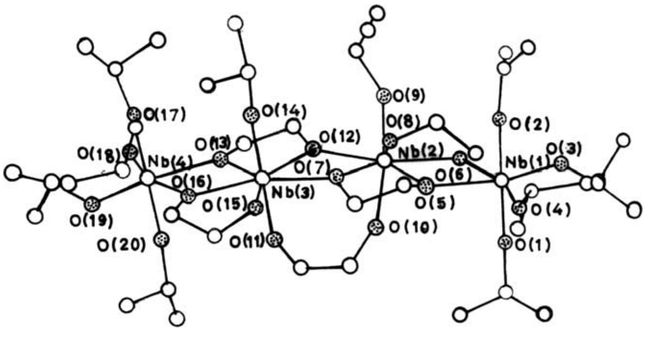


Fig. 2. Ball-and-stick drawing of the molecular structure of $Nb_4(\mu,\eta^2\text{-}OC_2H_4O)_4\ (\mu\text{-}OC_2H_4O)(O\text{-}i\text{-}Pr)_{10}$ (from Ref. [23]).

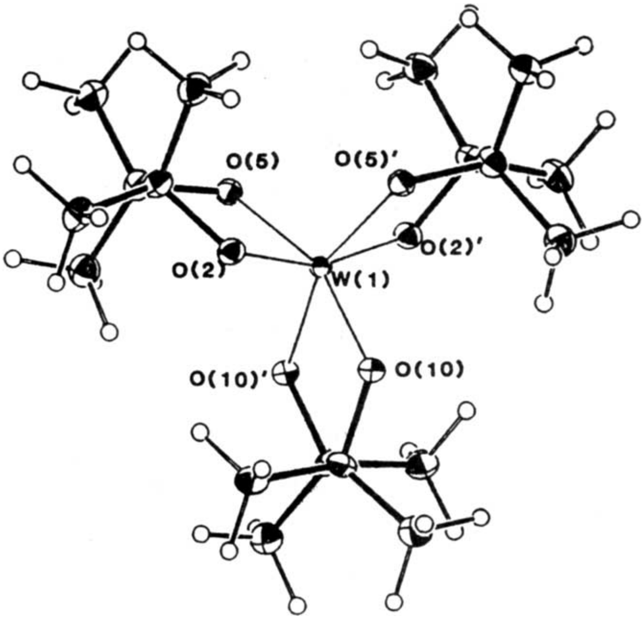
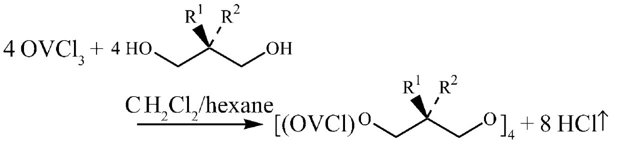


Fig. 3. ORTEP drawing of the $W(\overline{OCMe_2CMe_2O})_3$ molecule showing atom-numbering scheme (from Ref. [58]).

2.1.3. From metal halides

The reactions between oxovanadium trichloride and one equivalent of 1,3-propanediol, 2, 2-dimethyl-1,3-propanediol, 2-ethyl-2-methyl-1,3-propanediol, and 2-methyl-2-ethyl-2-propyl-1,3-propanediol in methylene chloride (Eq. (5)) afford air-stable orange powders [60], which have been characterized by multinuclear NMR spectroscopy:



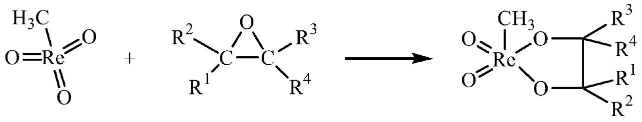
$$4\,OVCl_3 + 4\,HOCH_2CR^1R^2CH_2OH \xrightarrow{CH_2Cl_2/hexane} [(OVCl)OCH_2CR^1R^2CH_2O]_4 + 8\,HCl\uparrow \qquad (5)$$

where R^1, R^2: H, H; Me, Me; Me, Et; *n*-Pr.

Interestingly, a similar reaction with pinacol [61] produces the dimeric product $[OV(OCMe_2CMe_2O]_2$.

2.1.4. Miscellaneous methods

In addition to the above preparative routes, the following few glycolate derivatives under review have also been synthesized from metal oxides [62,63] and other starting materials [64] (cf. Eqs. (6)–(9)):



(6)

$$2BuSnO_{3/2} + HOGOH \xrightarrow{benzene} [BuSn(OGO)]_2O + H_2O\uparrow \qquad (7)$$

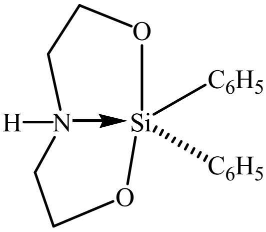
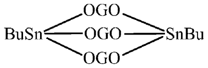


Fig. 4. The molecular structure of $(C_6H_5)_2Si[(OC_2H_4)_2NH]$ (from Ref. [65]).

$$2BuSnO_{3/2} + 3HOGOH \xrightarrow{benzene} (OGO)BuSnOGOSnBu(OGO) + 3H_2O$$

or



(8)

G: CH_2CH_2, $CHMeCH_2$, CHMeCHMe, CMe_2, CMe_2CMe_2, $CHMeCH_2CMe_2$, etc. [63,64].

$$Sb(OAc)_3 + HOCH_2CH_2OH \xrightarrow{benzene} 1/n[\overline{Sb(OC_2H_4O})(OAc)]_n + 2AcOH \quad [64] \qquad (9)$$

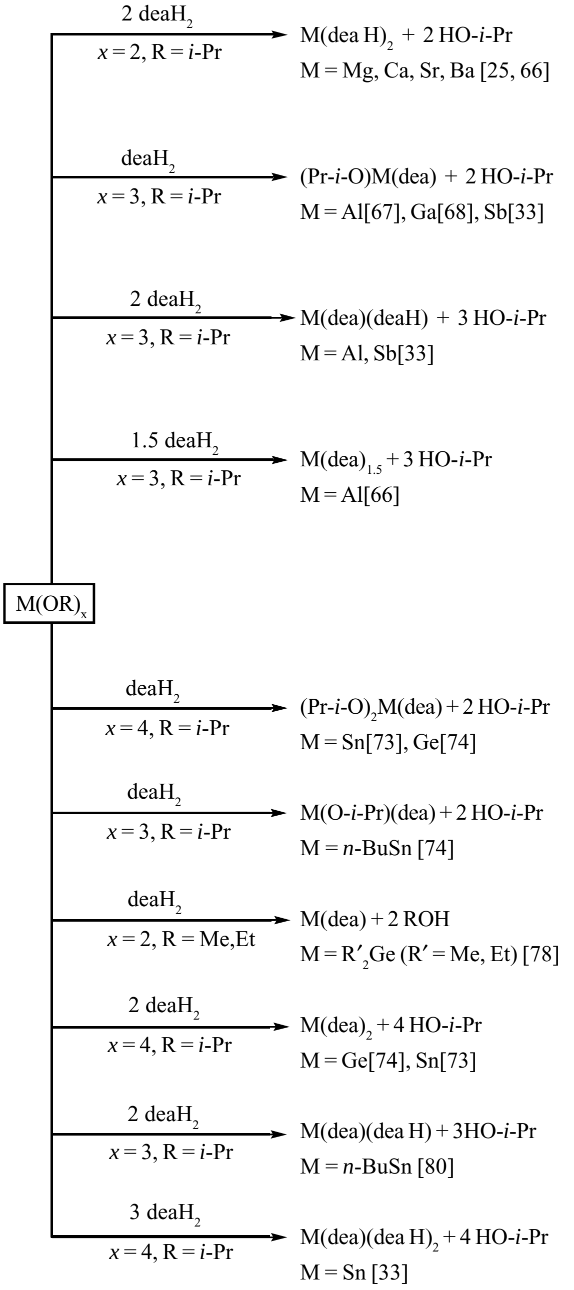
Furthermore, the reactions of metal and metalloid oxides such as TiO_2, Al_2O_3, SiO_2, GeO_2 with ethyleneglycol in basic media (alkali metal hydroxides) have led to the synthesis of interesting heterometallic anionic derivatives of these elements (see Section 3.2).

It is apparent from the foregoing account that alcoholysis (transesterification) reactions have been most widely employed for the synthesis of glycolates of different metals. The reactions of metal alkoxides with diols (pK_a lower than that of alcohols) are generally facile. The solubility of the resulting metal glycolates depends on the degree of substitution and on the extent of deprotonation of the diol concerned. The products obtained by complete deprotonation of glycols are generally soluble and of higher nuclearity, whereas partial deprotonation leaves residual hydroxy group(s) (IR: νOH ≈ 3400–3300 cm^{-1}; ^1H NMR (δ): 2.0–3.8) which are generally involved in intermolecular hydrogen bonding. Such homoleptic metal glycolates act as assembling templates for heterometal derivatives (cf. Section 3.2).

2.2. *Derivatives of diethanolamine*

The potentially tridentate chelating behavior of diethanolamine (abbreviated as $deaH_2$) was established by X-ray crystallographic studies on $(C_6H_5)_2Si(OCH_2CH_2)_2NH$ (Fig. 4) as early as 1974 [65].

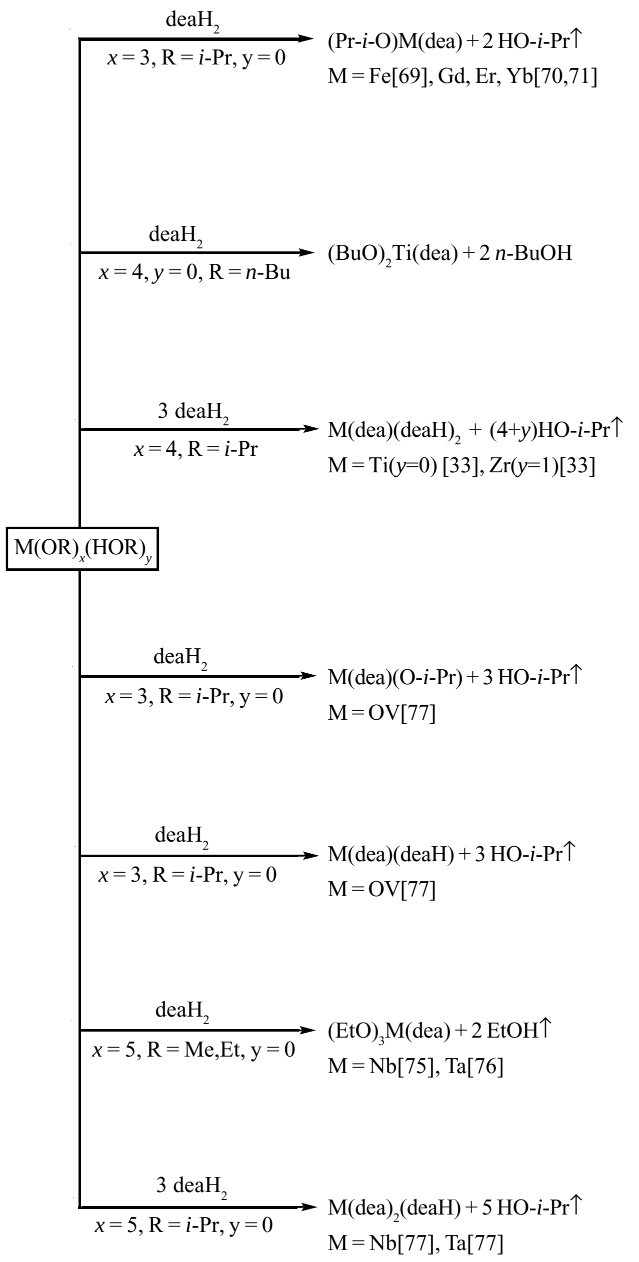
For better selectivity and even for topological control, constrained polyols such as di- and tri-ethanolamines ($teaH_3$) have been used as a source of hydroxyl groups and structure directing reagents. For example, reactions of main- (Scheme 1) and transition- (Scheme 2) group metal alkoxides with diethanolamine in benzene have mainly been investigated in our laboratories [25,33,66–80], yielding a wide variety of structurally interesting homometallic complexes depending on both the metal and stoichiometric ratios of the reactants (Schemes 1 and 2).



Scheme 1. Reactions of main group metal and organometal alkoxides with diethanolamine.

As expected, diethanolamine derivatives are less moisture-sensitive and oligomeric than the parent metal alkoxides.

It would be interesting to extend the methods employed so far to the synthesis of diethanolaminate derivatives of different metals, by using other starting materials such as metal amides and halides, etc., also as mentioned in Sections 2.1.2–2.1.4 for the glycolate derivatives.

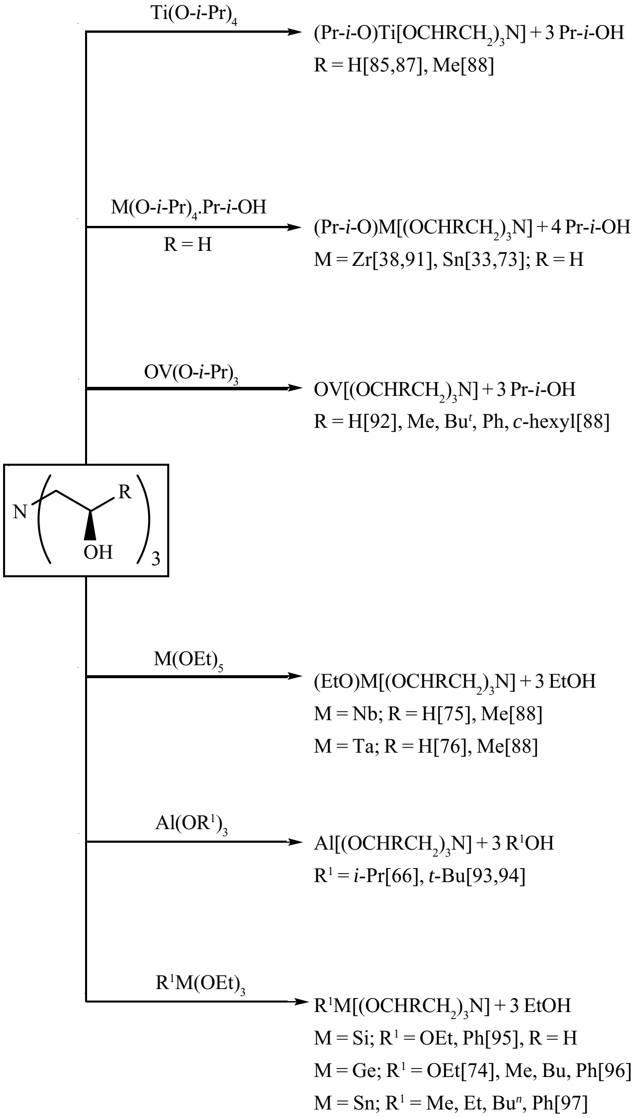


Scheme 2. Reactions of transition metal alkoxides with diethanolamine.

2.3. Derivatives of trialkanolamines

The tetradentate trialkanolamines have been shown to react with alkoxides of metals and metalloids (cf. Schemes 3 and 4) to produce thermally robust, less moisture-sensitive tricyclic ("atrane") derivatives which are monomeric (Fig. 5a and b), dimeric (Fig. 5c) and oligomeric (Fig. 5d) with interesting crystallographically established structures of the following types.

Metal complexes of tri-ethanolamines and its analogues can be prepared by a variety of routes [85–103]. Some typical reactions are illustrated in Scheme 3 (1:1 molar ratio) and 4 (2:1 molar ratio) as well as by Eqs. (10)–(17).



Scheme 3. Reactions in equimolar amounts of metal alkoxides and tri-alkanolamines.

Tri-ethanolamine complexes have also been prepared by a number of other methods, e.g., reactions represented by the Eqs. (10)–(17) [81,87,100–103]

$$\mathrm{NaClO_4} + \mathrm{teaH_3} \xrightarrow{\mathrm{THF}} \mathrm{Na(tea\,H_3)ClO_4} \tag{10}$$

$$2\mathrm{Ba(ClO_4)_2} + 4\mathrm{teaH_3} \xrightarrow{\mathrm{MeCN}} [\mathrm{Ba(teaH_3)_2(ClO_4)_2}]_2 \tag{11}$$

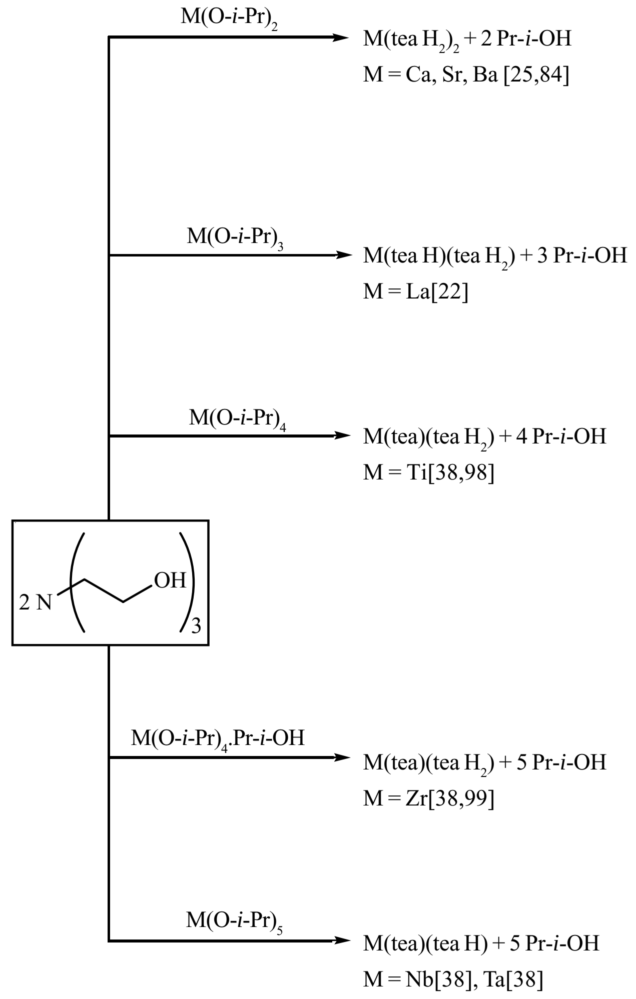
$$\mathrm{M} + 2\mathrm{teaH_3} \xrightarrow{\mathrm{PhMe/THF}} \mathrm{M(tea\,H_2)_2} + \mathrm{H_2} \tag{12}$$

M: Ca [84], Sr [84], Ba [83].

$$\mathrm{TiX_4} + 2\mathrm{teaH_3} \xrightarrow{\mathrm{CHCl_3\ or\ THF}} \mathrm{XTi(tea)} + 3\mathrm{HX} \tag{13}$$

X: Cl, NMe_2 [87].

$$n\mathrm{AlEt_3} + n\mathrm{teaH_3} \rightarrow [\mathrm{Al(tea)}]_n + 3n\mathrm{C_2H_6} \tag{14}$$



Scheme 4. Reactions in 1:2 molar amounts of metal alkoxides and tri-ethanolamine.

$$n\mathrm{Al(NMe_2)_3} + n\mathrm{teaH_3}[\mathrm{Al(tea)}]_n + 3n\mathrm{HNMe_2} \qquad (15)$$

$$4\mathrm{Al(CH_3)_3}+2\mathrm{teaH_3} \xrightarrow{n\text{-}\mathrm{C_6H_{14}}} [(\mathrm{tea})\mathrm{Al_2Me_3}]_2+6\mathrm{CH_4} \qquad (16)$$

$$\mathrm{SnCl_4} + 2\mathrm{teaH_3} \rightarrow \mathrm{Sn(teaH)_2} + 4\mathrm{HCl} \qquad (17)$$

Verkade [104] drew attention, in 1993, towards some structurally ‘unexpected’ derivatives of *atrane* type. In addition, some of these have also been reported to be biologically active [105] and are useful in a variety of synthetic and catalytic systems [88].

More recently, Holmes et al. [106] have introduced a new ligand tris(2-hydroxy-3,5-dimethylbenzyl)amine to obtain a new class of silatranes with tricyclic rings which are six-membered; this ligand, interestingly, offers the possibility of a wide variation in donor–acceptor interaction and molecular flexibility.

The above account reveals that the nature of the derivatives obtained depends as exemplified above on the type of (a) the metal and its valency and (b) the other inorganic or organic group(s) attached to it. For example, because of their low oxidation states, metals from groups 1 and 2 are unable to form structures of the type, depicted in Fig. 5a. Thus, barium forms the complex of configuration shown in Fig. 6C, in which Ba is octa-coordinated [83] by two $\mathrm{teaH_2}^-$ moieties in neutral monomeric units.

In conclusion, tri-ethanolamine and other closely related ligands possess a number of advantages that enhance the importance of the study of their metal complexes. For example: (i) tetradentate ligating mode of the ligand increases the possibility of preparing robust monomeric tricyclic (*atrane*) structures of the type $\mathrm{N(CH_2CH_2O)_3M{-}X}$, which are soluble and in many cases, volatile also at relatively low temperatures [104], (ii) tri-ethanolamine is commercially available and relatively inexpensive, and (iii) tris(2-hydroxy-3,5-dimethylbenzyl)amine is expected to offer wide variation in intramolecular coordination and molecular geometry.

3. Novel heterometallic alkoxide coordination systems

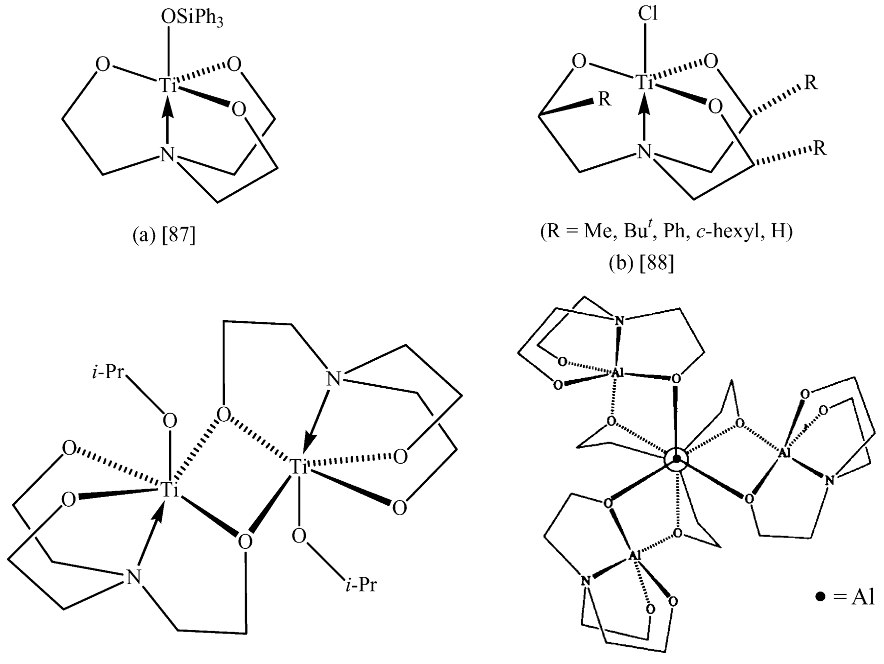
3.1. Introduction

The above brief account reflects many interesting features. For example, more flexible ethyleneglycolate moiety is uniquely versatile in terms of its coordination modes [23]: η^1, bridging; η^2, chelating; μ_2, η^2; μ_3, η^2; μ_4, μ_2-fly-over types. In the absence of X-ray crystallographic data, it would therefore be difficult to predict in some cases precisely the connectivity at least of simple (unsubstituted) glycolate ligands. Interestingly, even with ethyleneglycolate selectivity in its η^2-coordination mode could be achieved if the number of diolate groups attached to the metal are sufficient to satisfy the maximum coordination number of the metal via η^2, chelation (cf. Fig. 14). In complexes derived from 2-methyl-2,4-pentanediol (hexyleneglycol), and 2,5-dimethyl-2,5-hexanediol, the limited possibilities of their coordination modes [13,17,23] makes plausible predictions (on the basis of spectroscopic particularly the concerned metal NMR data) about their possible connectivities more convincing.

Structurally constrained polyols such as di- and tri-ethanolamines exhibit greater selectivity in their ligating behavior. For example, di- and tri-ethanolamines generally depict tri- and tetra-dentate ligating behavior. The metal derivative of such ligands, therefore, depict lower degree of association and hydrolyzability than their simple alkoxides.

Keeping the above facts in mind, plausible bonding modes of glycolate, di- and tri-ethanolaminate are depicted in Fig. 6.

An interesting observation [7] was made in mid-1970s that although alkaline earth metals dissolve very slowly in alcohols probably due to the low solubility of their simple binary alkoxides, their dissolution is highly facilitated by the presence of alkoxides of other metals, like Al, Zr,



(a) [87]

(R = Me, Bu^t, Ph, *c*-hexyl, H)

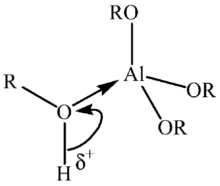
(b) [88]

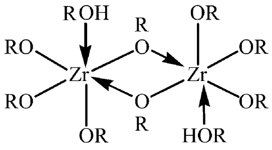
(c) [87]

(d) [101]

Fig. 5. X-ray crystallographically determined structures of a few selected homometallic triethanolaminate derivatives.

Nb, and Ta yielding soluble heterobimetallic alkoxides of the types: $[\mathrm{M}\{\mathrm{Al}(\mathrm{O}\text{-}i\text{-}\mathrm{Pr}_4\}]$, $[\mathrm{M}\{\mathrm{Zr}_2(\mathrm{O}\text{-}i\text{-}\mathrm{Pr}_9\}_2]$, and $[\mathrm{M}\{\mathrm{Nb}(\mathrm{O}\text{-}i\text{-}\mathrm{Pr})_6\}_2]$. In order to explain such behavior, it was suggested by Caulton and Hubert-Pfalzgraf [11] that the coordination of ROH through its oxygen atom enhances the acidity and reactivity of the alcohol molecule coordinated to the metal in alkoxide systems as depicted below:





Taking a clue from the above, the possibility has been explored for the formation of an entirely novel type of heterometallic alkoxide complex (see Tables 1–3) by utilizing the higher reactivity of the coordinated (OH) group(s) in homometallic complexes of the types (Fig. 6A–I) (where M is a di-, tri-, tetra-, or penta-valent metal).

Systematic efforts have been made in our laboratories for anchoring another metal via reactions with alkoxides of other metals such as aluminum, titanium, zirconium, niobium, or tantalum. These have led to the formation of many new and novel heterometallic complexes, such as those represented by structures (**J**)–(**M**) as well as (**N**), and (**Q**).

These results are summarized in the following sub-sections. Our efforts in these directions were further encouraged by the reported synthesis (Eqs. (18) and (19), and X-ray structure (Fig. 7) of an interesting La–Nb product $[\mathrm{La}\{\mathrm{OCH}_2\mathrm{CH}_2)_3\mathrm{N}\}_2\ \{\mathrm{Nb}(\mathrm{O}\text{-}i\text{-}\mathrm{Pr})_4\}_3]$ [22]:

$$\mathrm{La(O\text{-}}i\mathrm{\text{-}Pr)_3 + 2\text{-}teaH_3 \rightarrow La(teaH)(teaH_2) + 3Pr\text{-}}i\mathrm{\text{-}OH} \tag{18}$$

$$\mathrm{La(teaH)(teaH_2) + 3Nb(O\text{-}}i\mathrm{\text{-}Pr)_5 \rightarrow [La\{tea\}_2\{Nb(O\text{-}}i\mathrm{\text{-}Pr)_4\}_3] + 3Pr\text{-}}i\mathrm{\text{-}OH} \tag{19}$$

The molecular structure of $[\mathrm{La}\{\mathrm{tea}\}_2\{\mathrm{Nb}(\mathrm{O}\text{-}i\text{-}\mathrm{Pr})_4\}_3]$ (Fig. 7) is based on a central ‘diatrane’ core with eight-coordinate lanthanum while all niobium atoms are six-coordinate.

3.2. Heterometallic glycolate-alkoxide derivatives

Glycols are highly reactive towards metal alkoxides (cf. Section 2.1) to form homo- and hetero-leptic homometallic complexes.

The former type of derivative has attracted considerable interest in recent years due to their ability (a) to function as templates for the synthesis of heterometallic coordination systems, (b) to chelate and bridge different metal atoms, and (c) to depict lower steric demand in comparison to two alkoxo groups.

Another interesting feature of the homometal glycolates is the variety of their structural types [13,17,23] which is generally influenced by (a) the nature of the metal and its valency state, (b) the type of glycolate moiety, and (c) the stoichiometric ratios of reactants.

Table 1
Heterobimetallic glycolate complexes

Compound	Colour and state	Available characterization data	Reference
$BaCu(OG^1O)_3-(HOG^1OH)_3$	Deep blue crystals	Anal, X-ray	[108]
$BaCu(OG^1O)_2-(HOGOH)_6$ G^1: CH_2CH_2	Deep blue crystals	Anal, X-ray	[108]
$MAl_2(OG^2O)_2-(O-i-Pr)_4$ M: Mg, Ca, Sr, Ba G^2: CMe_2CMe_2	White solid	Anal, MW, IR, NMR (^1H,^{13}C,^{27}Al)	[27]
$MAl_2(OG^3O)_2(O-i-Pr)_4$ M: Mg, Ca, Sr G^3: $CHMeCH_2CMe_2$	Colourless solid	Anal, MW, IR, NMR (^1H, ^{13}C,^{27}Al)	[26]
M: Ba	Yellow solid	Anal, MN, IR, NM (^1H, ^{13}C, ^{27}Al)	[26]
M: Sn(II)	Colourless solid	Anal, MW, IR, NMR (^1H,^{13}C,^{27}Al,^{119}Sn)	
$Ce_2Ti(OG^2O)_2-(O-i-Pr)_8$	Yellow crystals	Anal IR, NMR (^1H,^{13}C)	[37]
$Ce_2Ti_2O_2(OG^2O)-(O-i-Pr)_4(HO-i-Pr)_2$	Yellow crystals	Anal, IR, NMR, X-ray	[37]
$Ce_2Nb_2O(OG^2O)_6-(OG^2OH)_2(O-i-Pr)_6$	Yellow crystals	Anal IR, NMR (^1H,^{13}C)	[37]
$Ce_2Ti_2O_2(OG^2O)_4-(O-i-Pr)_6$	Yellow crystals	Anal, IR, NMR, X-ray	[37]
$TiTa_2(OG^4O)_3-(O-i-Pr)_8$ G^4: $CMe_2CH_2CH_2CMe_2$	White solid	Anal, MW,IR, NMR (^1H, ^{13}C)	[39]
$TiTa_2(OG^2O)_3-(O-i-Pr)_8$	White solid	Anal, MW, IR, NMR (^1H,^{13}C)	[39]
$TiAl_2(OG^3O)_3-(O-i-Pr)_4$	White solid	Anal, MW, IR, NMR (^1H,^{13}C,^{27}Al)	[33]
$TiAl_2(OG^2O)_3-(O-i-Pr)_4$	White solid	Anal, MW, IR, NMR (^1H,^{13}C,^{27}Al)	[39]
$TiAl_2(OG^4O)_4-(O-i-Pr)_4$	White solid	Anal, MW, IR, NMR (^1H,^{13}C,^{27}Al)	[39]
$TiAl_2(OG^3O)_5$	White solid	Anal, MW, IR, NMR (^1H,^{13}C,^{27}Al)	[33]
$Na_2Ti(OG^1O)_3-(HOG^1OH)_4$	Colourless crystals	IR, NMR (^1H, ^{13}C), X-ray	[109]
$K_2Ti(OG^1O)_3-(HOG^1OH)_{2.5}$	Colourless crystals	IR, NMR (^1H, ^{13}C), X-ray	[109]
$ZrTi_2(OG^4O)_3-(O-i-Pr)_6$	White solid	Anal, MW, IR, NMR (^1H,^{13}C)	[39]
$Zr_2Ti(OG^2O)_4-(OG^2O_4)_2(O-i-Pr)_2$	White solid	Anal, ^1H NMR, X-ray	[36]
$Zr_2Ti_2(OG^2O)_6-(O-i-Pr)_4$	White powder	Anal, ^1H NMR, X-ray	[36]
$ZrNb_2(OG^4O)_3-(O-i-Pr)_8$	White solid	Anal, MW, IR, NMR (^1H,^{13}C)	[39]
$ZrTa_2(OG^4O)_3-(O-i-Pr)_8$	White solid	Anal, MW, IR, NMR (^1H,^{13}C)	[39]
$ZrAl_2(OG^4O)_3-(O-i-Pr)_4$	White solid	Anal, MW, IR, NMR (^1H,^{13}C,^{27}Al)	[39]
$ZrAl_2(OG^3O)_3-(O-i-Pr)_4$	White solid	Anal, MW, IR, NMR (^1H,^{13}C,^{27}Al)	[33]
$ZrAl_2(OG^3O)_3-$	White crystalline solid	Anal, MW, IR, NMR (^1H,^{13}C,^{27}Al)	[33]
$NbAl(OG^3O)_3-(O-i-Pr)_2$	White solid	Anal, MW, IR, NMR (^1H,^{13}C,^{27}Al)	[33]
$NbAl(OG^3O)_4$	White solid	Anal, MW, IR, NMR (^1H,^{13}C,^{27}Al)	[33]
$SnAl_2(OG^3O)_3-(O-i-Pr)_4$	White crystalline solid	Anal, MW, IR, NMR (^1H,^{13}C,^{27}Al,^{119}Sn)	[33]
$SnAl_2(OG^3O)_5$	White solid	Anal, MW, IR, NMR (^1H,^{13}C,^{27}Al,^{119}Sn)	[33]
$AlNb(OG^3O)_2-(O-i-Pr)_4$	Colourless viscous	Anal, MW, IR, NMR (^1H,^{13}C,^{27}Al)	[33]
$Na_2Al(OG^1O)_2-(OG^1OH)(HOG^1OH)_4$	White crystalline needles	^{27}Al NMR, X-ray	[110]
$Na_2Al(OG^1O)_2-(OG^1O)(HOG^1OH)_5$	White hexagonal plates	TGA, ^{27}Al NMR, X-ray	[110]
$Na_3Al_3(OG^1O)_5-(OG^1OH)_2(HOG^1OH)_6$	White crystalline solid	^{27}Al NMR, X-ray	[110]
$LiSi(OG^1O)_2-(OG^1OH)$	Colourless microcrystalline solid	TGA, ^{29}Si NMR, X-ray	[114]
$Na_2Si_2(OG^1O)_5$	White solid	TGA, ^{29}Si NMR	[114]
$SbAl(OG^3O)_2-(O-i-Pr)_2$	White solid	Anal, MW, IR, NMR (^1H,^{13}C,^{27}Al)	[33]
$SbAl(OG^3O)_3$	White solid	Anal, MW, IR, NMR (^1H,^{13}C,^{27}Al)	[33]
$SbNb(OG^3O)_2$ $-(O-i-Pr)_4$	White solid	Anal, MW, IR, NMR (^1H,^{13}C)	[33]

Anal: elemental analytical data, MW: molecular weight data, IR: infrared spectral data, NMR: nuclear magnetic resonance data (^1H: proton NMR data, ^{13}C: carbon-13 NMR data, ^{27}Al: aluminium-27 NMR data, ^{29}Si: silicon-29 NMR data, ^{119}Sn: tin-119 NMR data), X-ray: single crystal X-ray crystallographic studies, TGA: thermogravimetric analysis.

Table 2
Heterobimetallic diethanolaminate complexes

Compound	Colour and state	Available characterization data	Reference
$MAl_2(dea)_2(O-i-Pr)_4$ M: Mg, Ca, Sr, Ba	Colourless solid	Anal, MW, IR, NMR (^1H, ^{13}C, ^{27}Al)	[66]
$MTi_2(dea)_2(O-i-Pr)_6$ M: Mg, Ca, Sr, Ba	Colourless solid	Anal, MW, IR, NMR (^1H, ^{13}C)	[107b]
$MZr_2(dea)_2(O-i-Pr)_6$ M: Mg, Ca, Sr, Ba	Colourless solid	Anal, MW, IR, NMR (^1H, ^{13}C)	[107b]
$TiAl_2(dea)_3(O-i-Pr)_4$	Light yellow crystalline solid	Anal, MW, IR, NMR (^1H, ^{13}C)	[33]
$ZrAl_2(dea)_3(O-i-Pr)_4$	White crystalline solid	Anal, MW, IR, NMR (^1H, ^{13}C)	[33]
$NbAl(dea)_2(O-i-Pr)_4$	Light yellow crystalline solid	Anal, MW, IR, NMR (^1H, ^{13}C, ^{27}Al)	[33]
$SnAl_2(dea)_3(O-i-Pr)_4$	White crystalline solid	Anal, MW, IR, NMR (^1H, ^{13}C, ^{27}Al, ^{119}Sn)	[33]
$SnAl(dea)_2(O-i-Pr)_2$	White solid	Anal, MW, IR, NMR (^1H, ^{13}C, ^{27}Al)	[33]

dea: diethanolaminate (2-).

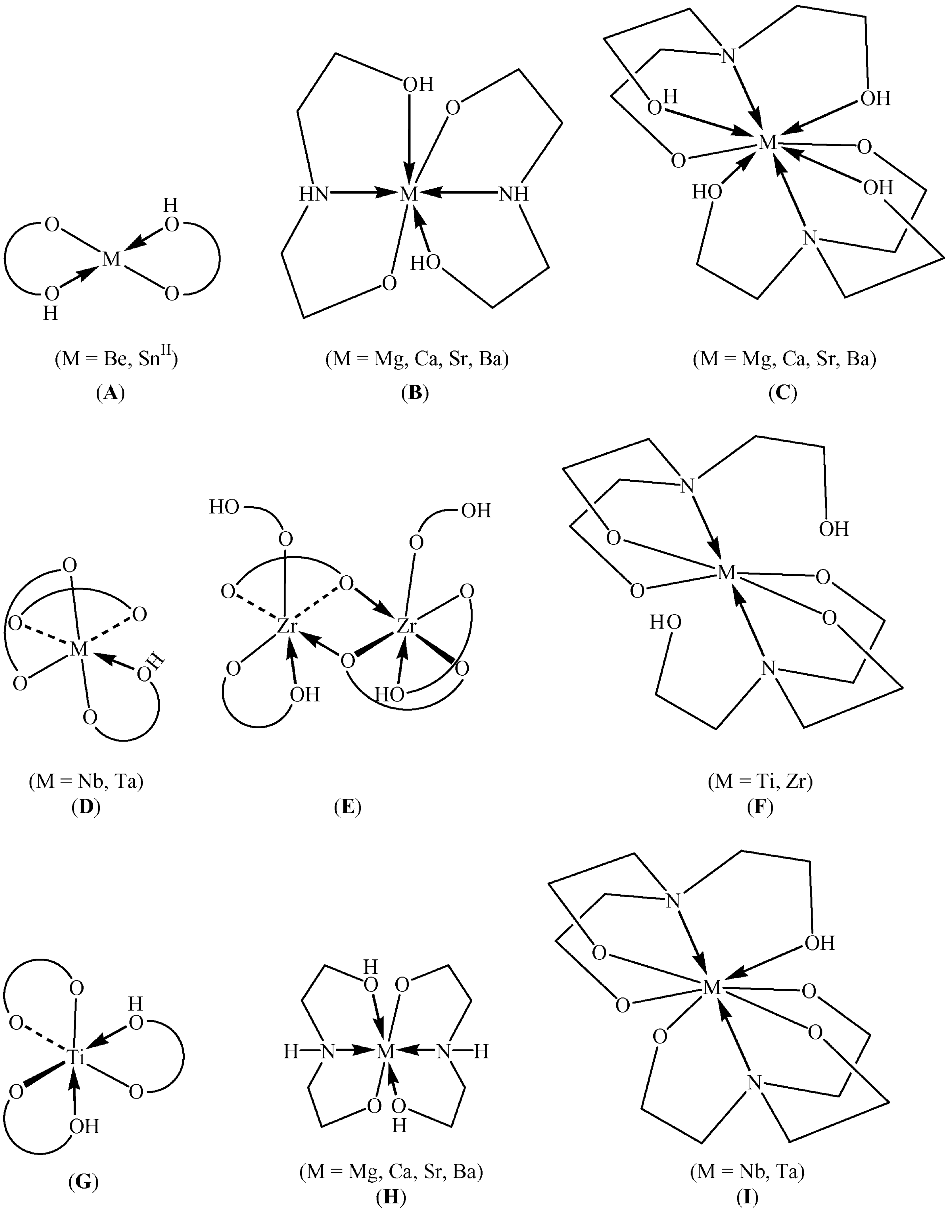
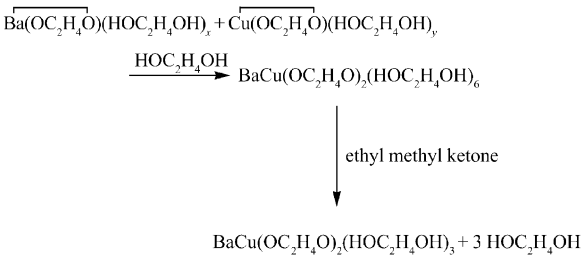


Fig. 6. Simplified, ball-and-stick drawings of some homoleptic derivatives of glycols, di- and tri-ethanolamines, which are used as starting materials for the synthesis of novel heterometallic coordination systems.

These interesting features have prompted us [25–27,33–35,38,39,106] and others [36,37,108] to investigate reactions of homometallic glycolate complexes containing coordinated hydroxy group(s) of dihydroxy alcohols with different metal alkoxides in order to obtain many novel and interesting heterometallic glycolate systems according to the reactions shown in Scheme 5, widening our search for single source precursors for the desired heterometal oxide ceramic materials [109].

In addition to products illustrated in Scheme 5 for the synthesis of heterobimetallic glycolate complexes, some interesting X-ray crystallographically characterized heterometal ethyleneglycolates of barium [108], titanium [110a], aluminum [110b], silicon [111–114], and antimony [107a], have also been prepared according to the reactions (Eqs. (20)–(26)) illustrated below:



$$\mathrm{Ba(\overline{OC_2H_4O})(HOC_2H_4OH)_x + Cu(\overline{OC_2H_4O})(HOC_2H_4OH)_y \xrightarrow{HOC_2H_4OH} BaCu(OC_2H_4O)_2(HOC_2H_4OH)_6 \Big\downarrow {\scriptstyle \text{ethyl methyl ketone}} \; BaCu(OC_2H_4O)_2(HOC_2H_4OH)_3 + 3\,HOC_2H_4OH} \quad (20)$$

Table 3
Heterobimetallic triethanolaminate complexes

Compound	Colour and state	Available characterization data	Reference
$Mal_4(tea)_2(O\text{-}i\text{-}Pr)_8$ M: Mg, Sr, Ba	Yellowish solid	Anal, MW, IR, NMR (^1H, ^{13}C, ^{27}Al)	[84]
$MTi_4(tea)_2(O\text{-}i\text{-}Pr)_{12}$ M: Mg, Ca, Sr, Ba	White solid	Anal, MW, IR, ^1H NMR	[38]
$MZr_4(tea)_2(O\text{-}i\text{-}Pr)_{12}$ M: Mg, Ca, Sr, Ba	White solid	Anal, MW, IR, ^1H NMR	[38]
$MNb_4(tea)_2(O\text{-}i\text{-}Pr)_{16}$ M: Mg, Ca, Sr, Ba	White solid	Anal, MW, IR, NMR (^1H, ^{13}C)	[38,131]
$MTa_4(tea)_2(O\text{-}i\text{-}Pr)_{16}$ M: Mg, Ca, Sr, Ba	White solid	Anal, MW, IR, NMR (^1H, ^{13}C)	[38,131]
$LaNb_3(tea)_2(O\text{-}i\text{-}Pr)_{12}$	Colourless rhombic crystals	Anal, ^1H NMR, X-ray	[22]
$TiAl_2(tea)_2(O\text{-}i\text{-}Pr)_4$	White solid	Anal, MW, IR, NMR (^1H, ^{27}Al)	[98]
$TiNb_2(tea)_2(O\text{-}i\text{-}Pr)_8$	White viscous liquid	Anal, MW, IR, ^1H NMR	[98]
$TiTa_2(tea)_2(O\text{-}i\text{-}Pr)_8$	White viscous liquid	Anal, MW, IR, ^1H NMR	[98]
$TiAl_2(tea)_2(OC_2H_4OMe)_2$	White solid	Anal, MW, IR, NMR (^1H, ^{27}Al)	[98]
$TiAl_2(tea)_2(OC_2H_4OEt)_4$	White solid	Anal, MW, IR, NMR (^1H, ^{27}Al)	[98]
$TiAl_2(tea)_2(OC_2H_4NH_2CH_2Ph)_4$	Light yellow viscous liquid	Anal, MW, IR, NMR (^1H, ^{27}Al)	[98]
$TiAl_2(tea)_2\text{-}(OC_2H_4NHMe)_4$	White solid	Anal, MW, IR, NMR (^1H, ^{27}Al)	[98]
$TiAl_2(tea)_2(acac)_4$	White solid	Anal, MW, IR, NMR (^1H, ^{27}Al)	[98]
$TiAl_2(tea)_2(OC_2H_4O)_4$	White solid	Anal, MW, IR, NMR (^1H, ^{27}Al)	[98]
$TiAl_2(tea)_2(O\text{-}t\text{-}Bu)_4$	White solid	Anal, MW, IR, NMR (^1H, ^{27}Al)	[98]
$TiTa_2(tea)_2(O\text{-}t\text{-}Bu)_8$	White viscous liquid	Anal, MW, IR, NMR (^1H)	[98]
$ZrAl_2(tea)_2(O\text{-}i\text{-}Pr)_4$	White solid	Anal, MW, IR, NMR (^1H, ^{27}Al)	[99]
$ZrAl_2(tea)_2(acac)_4$	White solid	Anal, MW, IR, NMR (^1H, ^{27}Al)	[99]
$ZrAl_2(tea)_2(OC_2H_4OMe)_4$	White solid	Anal, MW, IR, NMR (^1H, ^{27}Al)	[99]
$ZrAl_2(tea)_2(OC_2H_4OMe)_2\text{-}(O\text{-}i\text{-}Pr)_2$	White solid	Anal, MW, IR, NMR (^1H, ^{27}Al)	[99]
$NbAl(tea)_2\text{-}(OC_2H_4OMe)_2$	White solid	Anal, MW, IR, NMR (^1H, ^{27}Al)	[44]
$NbAl(tea)_2(OC_2H_4OEt)_2$	White solid	Anal, MW, IR, NMR (^1H, ^{27}Al)	[44]
$NbAl(tea)_2(O\text{-}i\text{-}Pr)_8$	White solid	Anal, MW, IR, NMR (^1H, ^{27}Al)	[44]
$NbAl(tea)_2(acac)_2$	White solid	Anal, MW, IR, NMR (^1H, ^{27}Al)	[44]

acac: acetylacetonate; tea: triethanolaminate (3-).

$$\begin{tikzcd}
Ti(O\text{-}i\text{-}Pr)_4 + 7\,HOC_2H_4OH + 2\,NaOH \arrow[r, "{-4\,HO\text{-}i\text{-}Pr,\ -2\,H_2O}"'] & Na_2Ti\overline{(OCH_2CH_2O)}_3.4HOC_2H_4OH \\
TiO_2 + 7\,HOC_2H_4OH + 2\,NaOH \arrow[r, "PhMe", "THF"'] & {} \arrow[u, "-4\,H_2O"']
\end{tikzcd} \qquad (21)$$

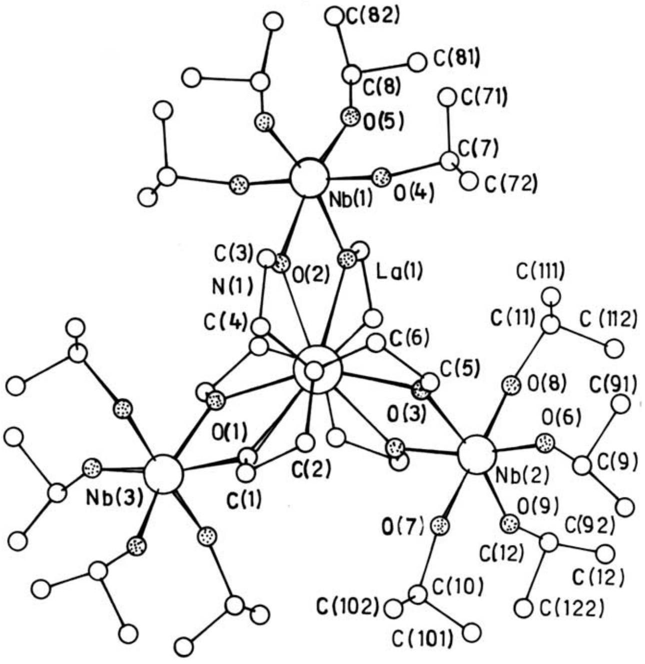


Fig. 7. Crystal structure of $[La\{tea\}_2\{Nb(O\text{-}i\text{-}Pr)_4\}_3]$ (from Ref. [22]).

$$Al(O\text{-}i\text{-}Pr)_3 + 7\,HOC_2H_4OH + 2\,NaOH \xrightarrow[-2\,H_2O]{-3\,HO\text{-}i\text{-}Pr,} Na_2Al\overline{(OCH_2CH_2O)}_2(OC_2H_4OH).4HOC_2H_4OH \qquad (22)$$

$$Al_2O_3 + 15\,HOC_2H_4OH + 4\,NaOH \longrightarrow Na_2Al\overline{(OCH_2CH_2O)}_2(OC_2H_4OH).4HOC_2H_4OH + Na_2Al(OCH_2CH_2O)_2(OC_2H_4OH).5HOC_2H_4OH + 7\,H_2O \qquad (23)$$

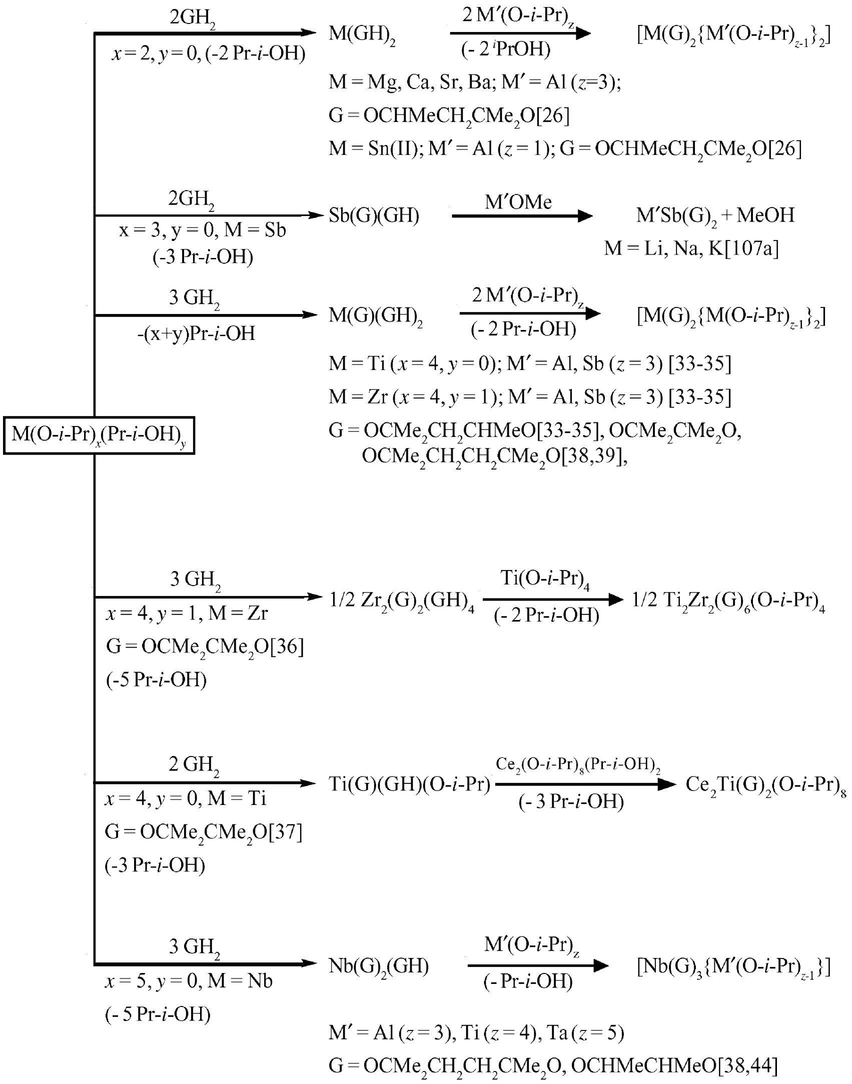
$$SiO_2 + 3\,HOC_2H_4OH + MOH \longrightarrow MSi\underline{(OCH_2CH_2O)}_2(OC_2H_4OH) + 3\,H_2O \qquad (24)$$

$$2SiO_2 + 5HOC_2H_4OH + 2MOH \rightarrow M_2Si_2(OCH_2CH_2O)_5 + 6H_2O \qquad (25)$$

M: Li, Na, K, or Cs.

$$Sb(OCMe_2CMe_2O)(OCMe_2CMe_2OH) + MOCH_3 \xrightarrow{MeOH} MSb\overline{(OCMe_2CMe_2O)}_3 + MeOH \qquad (26)$$

M: Li, Na, or K.



Scheme 5. Synthesis of heterobimetallic glycolate complexes.

The spectroscopic (IR, NMR) and colligative properties of heterometallic glycolate complexes listed in Table 1 have been studied during the last 2–3 years and plausible bonding modes for some of these (**J**)–(**M**) have also been suggested. From ^{27}Al NMR investigations on derivatives of the types (**J**), (**K**), and (**M**), which exhibit broad signals centered in the δ 60–66 ppm region [26,27,33,39,44], a tetra-coordinate aluminum center is indicated consistent with their structural formulations. The ^{119}Sn (δ −655) and ^{27}Al (δ 35) NMR signals [33] for $\overline{\mathrm{Sn\{OCHMeCH_2CMe_2O}}\mathrm{\}_3\{Al)(O\text{-}\mathit{i}\text{-}Pr)_2\}}$ indicate that tin(IV) and Al(III) centres are six- and four-coordinate, respectively, which is consistent with the proposed structure (**K**) when M: Sn.

The novelty of the structural features as shown in (**J**)–(**M**), have been confirmed by single crystal X-ray crystallography for the following complexes.

$BaCu(OC_2H_4O)_2(HOC_2H_4OH)_3$ (Fig. 8), $BaCu(OC_2H_4O)_2(HOC_2H_4OH)_6$ (Fig. 9), $TiZr_2(OCMe_2CMe_2O)_4(OC$-

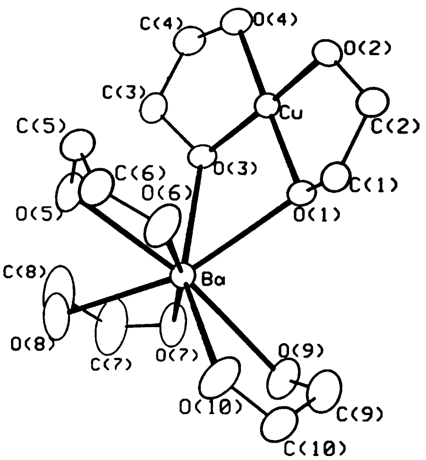
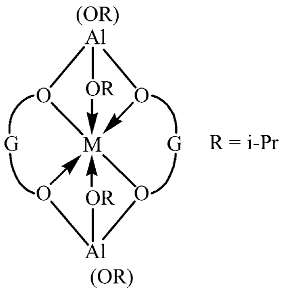
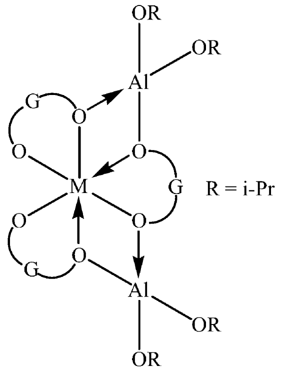


Fig. 8. ORTEP drawing of the $BaCu(OC_2H_4O)_2(HOC_2H_4OH)_3$ molecule (from Ref. [108]).



M = Mg, Ca, Sr, Ba
when G = $CHMeCH_2CMe_2$[26], CMe_2CMe_2[27]

(**J**)



M = Ti, Zr, Sn; G = $CHMeCH_2CMe_2$ [33]
$CMe_2CH_2CH_2CMe_2$ [39]
CMe_2CMe_2 [39]

(**K**)

$Me_2CMe_2CMe_2OH)_2(O\text{-}i\text{-}Pr)_2$ (Fig. 10), $Ti_2Zr_2(OCMe_2O)_6(O\text{-}i\text{-}Pr)_4{\cdot}2CHCl_3$ (Fig. 11), $Ce_2Ti_2(\mu_3\text{-}O)_2(\mu,\eta^2\text{-}OCMe_2CMe_2O)_4(O\text{-}i\text{-}Pr)_4(Pr\text{-}i\text{-}OH)_2$ (Fig. 12) and $Ce_2Nb_2(\mu_3\text{-}O)_2(\mu,\eta^2\text{-}OCMe_2CMe_2O)_4(O\text{-}i\text{-}Pr)_6$ (Fig. 13) as well as ionic complexes such as $K_2Ti(OCOC_2H_4O){\cdot}2.5HOC_2H_4OH$ (Fig. 14), $Na_2Al(OC_2H_4O)_2(OC_2H_4OH).(HOC_2H_4OH)_4$, $Na_2Al(OC_2H_4O)_2(OC_2H_4OH){\cdot}(HOC_2H_4OH)_5$, $Na_3Al_3(OC_2H_4O)_5(OC_2H_4OH)_2{\cdot}(HOC_2H_4OH)_6$, $M[Si(Si(OC_2H_4O)_2(OC_2H_4OH)]$ and $M_2[Si_2(OC_2H_4O)_5$ (M: Li, Na, K or Cs).

Out of these, the structures of only seven complexes are illustrated for brevity in the Figs. 8–14.

The molecule $BaCu(OC_2H_4O)_2(C_2H_4OH)_3$ (Fig. 8) consists of a $Cu(OC_2H_4O)_2{}^{2-}$ unit by the sharing of two oxygen atoms, O(1) and O(3), as shown in Fig. 8. All ethyleneglycol or glycolate ligands bind the copper or barium in a bidentate fashion. Copper and barium atoms are in nearly square planar and distorted cubic environment, respectively.

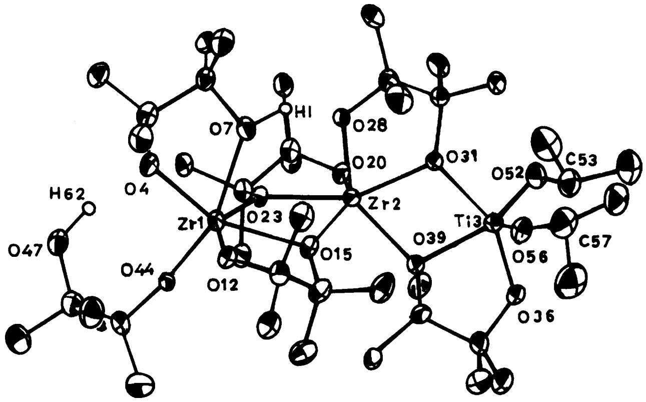


Fig. 10. ORTEP representation of $TiZr_2(OCMe_2CMe_2O)_4(OCMe_2CMe_2OH)_2(O\text{-}i\text{-}Pr)_2$ (from Ref. [36]).

In contrast to $BaCu(OC_2H_4O)_2(HOC_2H_4OH)_3$, the structure of $BaCu(HOC_2H_4OH)_6(OC_2H_4O)_2$ (Fig. 9), contains discrete $Cu(OC_2H_4O)_2{}^{2-}$ and $Ba(HOC_2H_4OH)_6{}^{2+}$ units: barium is coordinated by nine oxygen atoms of the six ethyleneglycol molecules, three of which are bonded in bidentate fashion whereas the remaining three are bonded in a monodentate manner. The bonding environment around barium and copper may be described as a trigonal prism

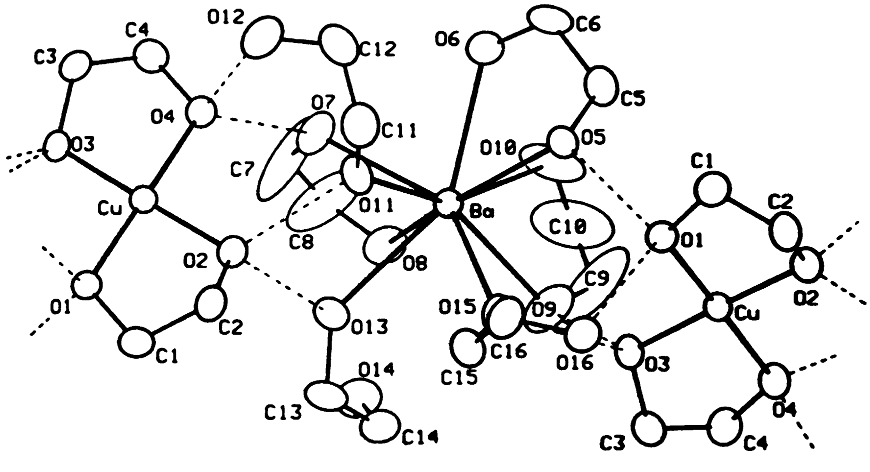


Fig. 9. ORTEP drawing showing a hydrogen-bonded chain of $Cu(OC_2H_4O)_2{}^{2-}$ and $Ba(HOC_2H_4OH)_6{}^{2+}$ units in $BaCu(OC_2H_4O)_2(HOC_2H_4OH)_6$ (from Ref. [108]).

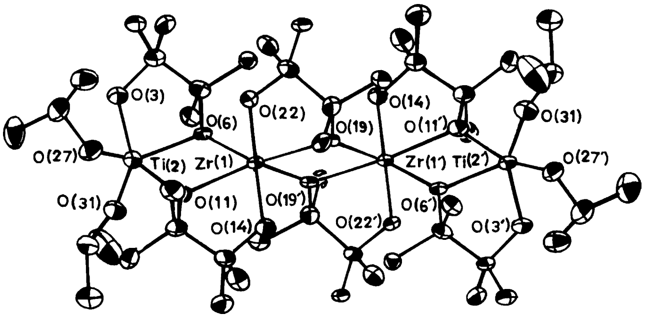


Fig. 11. ORTEP representation of $Ti_2Zr_2(OCMe_2CMe_2O)_6(O\text{-}i\text{-}Pr)_4$ (from Ref. [36]).

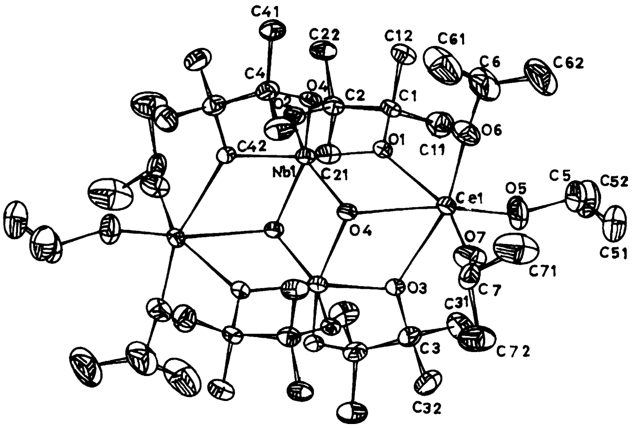


Fig. 13. Crystal structure of $Ce_2Nb_2O_2(OCMe_2CMe_2O)_4(O\text{-}i\text{-}Pr)_6$ (from Ref. [37]).

of oxygen atoms with the remaining oxygen atoms capping the rectangular faces and square planar arrangement, respectively.

The solid state structure of $TiZr_2(OCMe_2CMe_2O)_4(OCMe_2CMe_2OH)_2(O\text{-}i\text{-}Pr)_2$ (Fig. 10) which crystallizes out of THF in the space group $P2_1/c$ shows that each zirconium is six-coordinate, while the titanium has coordination number five. The six pinacolate moieties are present in five types of bonding environment: one $OCMe_2CMe_2OH$ group is bonded to zirconium by a single oxygen (η^1) while its pendant hydroxyl group is involved in hydrogen bonding. The second $OCMe_2CMe_2OH$ group chelates (η^2) zirconium. The four dianionic pinacolate groups are chelating one metal and bridging to a second metal (η^2-μ_2). Out of these four pinacolate ligands, two are chelating bridging zirconium, one is chelating zirconium while bridging to titanium and the last is chelating titanium and bridging to zirconium.

The X-ray crystallographically determined structure of $TiZr_2(OCMe_2CMe_2O)_6(O\text{-}i\text{-}Pr)_4$ (Fig. 11) which crystallizes in the centrosymmetric space group $P\bar{1}$, shows that each of the pinacolate ligands is chelating a single metal and bridged by a single oxygen to a second metal (η^2-μ_2). Out of six pinacolate ligands, two are chelating to zirconium and bridging to a second zirconium atom while two more are chelating zirconium but bridging to titanium centres. The remaining two pinacolates are chelating titanium and bridging zirconium. The isopropoxide groups are terminally bonded only to titanium (two to each). The coordination environments around zirconium and titanium are 6 and 5, respectively.

The molecular structure of $[Ce_2Ti_2(\mu_3\text{-}O)_2(\mu,\eta^2\text{-}OCMe_2CMe_2O)_4(O\text{-}i\text{-}Pr)_4(Pr\text{-}i\text{-}OH)_2]$ (Fig. 12) is based on a centrosymmetrical rhombus compressed along the Ti··· Ti axis. The cerium and titanium metals are all six-coordinated and are connected by bridging-chelating pinacolate and trigonal oxo-ligands. The electroneutrality of the complex is consistent with the presence of two isopropyl alcohol molecules.

The complex $Ce_2Nb_2(\mu_3\text{-}O)_2(\mu,\eta^2\text{-}OCMe_2CMe_2O)_4(O\text{-}i\text{-}Pr)_6$ (Fig. 13) displays a framework similar to that of cerium–titanium complex (Fig. 12), the niobium centers bearing the pinacolate ligands (Fig. 13) and all (Ce, Nb) metals are six-coordinate with distorted stereochemistry.

The structure of anionic titanium tris(ethyleneglycolate) complex (Fig. 14) shows considerable distortion from octahedral coordination about the titanium, consistent with the narrow bite angle of the glycolate ligand. The structure

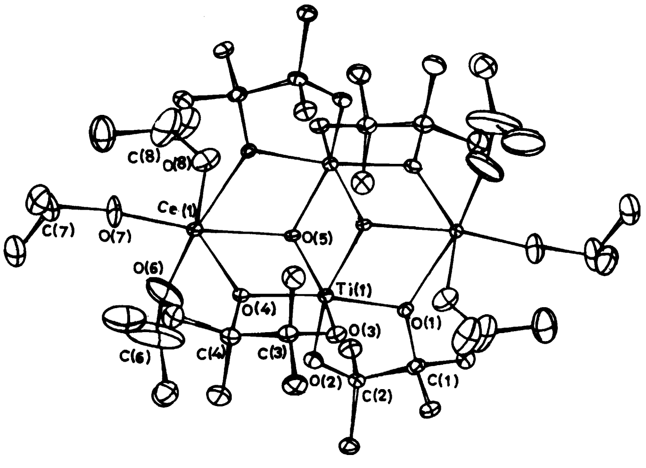


Fig. 12. Crystal structure of $[Ce_2Ti_2(\mu_3\text{-}O)_2(\mu,\eta^2\text{-}OCMe_2CMe_2O)_4(O\text{-}i\text{-}Pr)_4(Pr\text{-}i\text{-}OH)_2]$ (from Ref. [37]]).

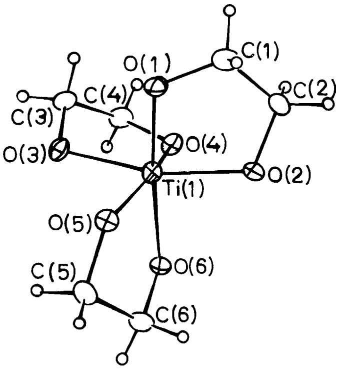


Fig. 14. Crystal structure of the anionic part of $K_2Ti(OC_2H_4O)_3{\cdot}2.5HOC_2H_4OH$ (from Ref. [110a]).

shown in Fig. 14 contains a single enantiomer of Δ chirality.

In conclusion, a series of synthetic and spectroscopic studies as well as single-crystal X-ray crystallographic investigations on heterometallic glycolate complexes have revealed the emergence of a number of fascinating and intricate heterometallic coordination systems. It is still an active field in which novel and exciting developments may be expected.

3.3. Heterobimetallic diethanolaminate–alkoxides

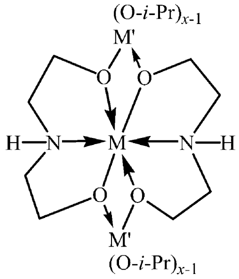
The complexing ability of diethanolamine, $HN(CH_2CH_2OH)_2$ has been much investigated for the preparation of homometallic complexes [17,24,115,116], an account of which has already been presented in Section 2.2. However, their heterometallic analogues have become accessible only during the last 5–6 years [33–35,66].

The reactions of diethanolamine with metal alkoxides in the desired molar ratios in benzene, followed by treatment of the resulting insoluble homometallic complexes with different metal alkoxides, yield hydrocarbon-soluble heterobimetallic diethanolaminate–alkoxide complexes (see Scheme 6).

An alternative route for the synthesis of heterobimetallic diethanolaminates of alkaline earth metals has been the interaction $M\{Al(O\text{-}i\text{-}Pr)_4\}_2$ (M: Mg, Ca, Sr, Ba) with diethanolamine in 1:2 molar ratio in benzene [66].

$$M\{Al(O\text{-}i\text{-}Pr)_4\}_2 + \text{dea}\,H_2 \xrightarrow{\text{Benzene}} M\{Al(O\text{-}i\text{-}Pr)_2(\text{dea})\}_2 + 4HO\text{-}i\text{-}Pr \qquad (27)$$

The molecular formulae of these (see Table 2) novel complexes, which are soluble in common organic solvents (e.g., benzene, toluene, carbon tetrachloride, dichloromethane, or hexane) have been elucidated [66,107] by elemental analyses and spectroscopic data as well as ebullioscopic determination of the molecular weights. Although structural data even on homometal diethanolamine complexes are rare [13,17], the complexes of the types $[M(\text{dea})_2\{Al(O\text{-}i\text{-}Pr)_2\}_2]$ and $[M(\text{dea})_2\{M'(O\text{-}i\text{-}Pr)_{x-1}\}_2]$ (where M: Mg, Ca, Sr, Ba and M′: Al ($x = 3$) [66], Ti($x - 4$) [107a], Zr($x = 4$) [107b], Nb($x = 5$) [107c], or Ta ($x = 5$) [107c] all show similar IR and NMR spectra [65,107b,107c] indicating close similarity in their structural (**N**) features. For example, complexes of the type $[M(\text{dea})_2\{Al(O\text{-}i\text{-}Pr)_2\}_2]$ show (i) infrared absorptions characteristic of both the isopropoxy groups (1175–1140, 1130–1096 cm^{-1} νOPr-*i*, 1080–1032 cm^{-1} νC–O) and the diethanolaminate groups (3190–3160 cm^{-1} νN–H; 2940–2905 cm^{-1} *n*C–H) as well as νM–O and νAl–O in the 580–436 and 675–610 cm^{-1} regions, respectively, involving a lowering of 85–115 cm^{-1} in the νN–H compared with the parent ligand (νN–H, 3275 cm^{-1}), which supports the involvement of nitrogen in intramolecular coordination, (ii) ^1H NMR signals at δ 2.42–2.64 (br; NCH_2), 2.86–3.00 (br, OCH_3), 3.60–3.85 (br, NH), 1.20–1.26 (d, $CH\mathbf{Me}_2$), and 4.10–4.36 (sept, $C\mathbf{H}Me_2$), and (iii) ^{27}Al NMR chemical shifts in the δ 58–66 ppm region, characteristic of four-coordinate aluminium compounds (cf. structure (**N**)).

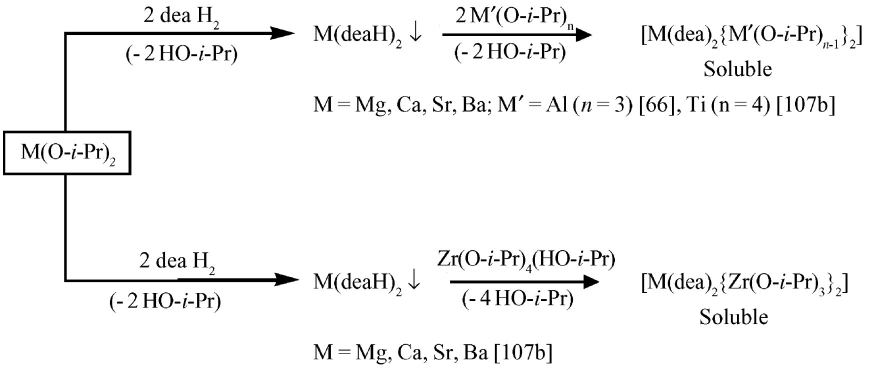


M = Mg, Ca, Sr, Ba
M' = Al (x = 3) [66]; Ti, Zr (x = 4) [107b];
Nb, Ta (x = 5) [107c]

(**N**)

3.4. Heterobimetallic triethanolaminate alkoxides

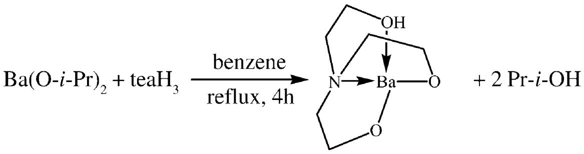
Tri-ethanolamine as a tetradenate ligand has attracted growing attention [104] in metal coordination chemistry. Homometal tri-ethanolamine complexes are known for most of the elements of the periodic table including main group elements [81–83,100–102,117,118], transition metals [87,88,92,119–128], and lanthanides [22,129]. These complexes have shown considerable potential for a variety



Scheme 6. Synthesis of heterobimetallic diethanolaminate complexes.

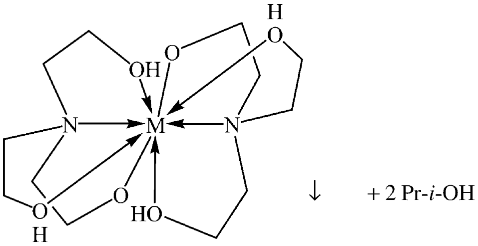
of purposes, such as biological activities of enzymes [92], low temperature metal organic chemical vapor deposition (MOCVD) techniques [130] and supramolecular chemistry [124], etc. Surprisingly, in spite of considerable preliminary investigations on such derivatives in the authors' laboratories, the ability of such homometal complexes containing one or more free/coordinated hydroxy group(s) of the triethanolaminate moiety to synthesize heterometallic coordination complexes does not appear to have been reported prior to the synthesis and X-ray crystallographic characterization [22] of $[La\{tea\}_2\{Nb(O\text{-}i\text{-}Pr)_4\}_3]$ by Hubert-Pfalzgraf and coworkers in 1994. However, the same has encouraged a flurry of activities (particularly in the chemical laboratories of the University of Rajasthan, Jaipur) [13,17] in this area during the past decade, which has led to the synthesis and characterization (mainly by elemental analyses, molecular weight measurements and spectroscopic studies) of many novel types of heterometallic alkoxide–triethanolaminate coordination systems, an account of which is summarized in the following pages.

Equimolar reaction of $Ba(O\text{-}i\text{-}Pr)_2$ with $teaH_3$ in refluxing benzene affords an insoluble homometallic derivative (Eq. (28)):



(**O**) (28)

The reactions of $M(O\text{-}i\text{-}Pr)_2$ (M: Ca, Sr, Ba, Sn(II)) even with two equivalents of tri-ethanolamine in benzene yield colorless insoluble, and non-volatile solids of composition $M\{teaH_2\}_2$ (Eq. (29)):

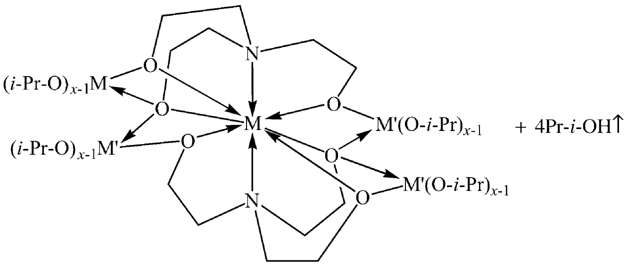


Insoluble

(**P**) (29)

The reactions in 1:1 molar ratio of (**O**) (Eq. (30)) and 1:4 molar ratio of (**P**) (Eq. (31)) with a metal isopropoxide in reluxing benzene afford respectively insoluble and soluble compounds.

$$(O) + Al(O\text{-}i\text{-}Pr)_3 \xrightarrow[\text{reflux},7\,\text{h}]{\text{benzene}} \frac{1}{x}[\{Al(O\text{-}i\text{-}Pr)_2\} \times \{Ba[(OC_2H_4)_3N]\}_{x\,\text{insoluble}} \downarrow + \text{Pr-}i\text{-OH} \uparrow \qquad (30)$$



Soluble, monomeric, volatile solids (31)

where, M: Ca, Sr, Ba, Sn(II); M′: Al [84], Ti [98], Zr [99], Nb [44], Ta [44] (**Q**).

Despite the insolubility in organic solvents (e.g., benzene, toluene, *n*-hexane, carbon tetrachloride, dichloromethane, etc.) of the homometallic triethanolaminate starting materials (**P**) due to intermolecular hydrogen bonding, the heterometallic complexes formed by interactions with different metal alkoxides are soluble in the above-mentioned organic solvents. In fact, the dissolution of insoluble starting materials on reaction with a different metal alkoxide provides confirmatory evidence for the formation of heterometallic species.

All of these novel heterometal coordination compounds of the type (**Q**) (Table 3) have been characterized by elemental analyses, molecular weight measurements, and spectroscopic [IR and NMR (^{1}H, ^{13}C, ^{27}Al)] studies.

4. Conclusion and future outlook

A perusal of the brief account of novel types of heterometallic alkoxides, which can be obtained by the reactions of coordinated hydroxy groups in the chelate derivatives of a number of metals, shows that it has been so far limited to only three types of polyols, i.e., glycols, di- and triethanolamines.

Heterometallic complexes of these polyols are comparatively less hydrolyzable than their parent homometal alkoxides. Although in a number of instances the ligand connectivity and arrangement of different metal atoms in heteronuclear molecular species can be envisaged from the structural features of the precursor homometal complexes of the polyols, yet examples are also known wherein the arrangement of ligands follows a different course of bonding modes [23,56,57]. However, in all of these heterometallic coordination systems, ligands arrange themselves around the metal centres in such a manner as to provide coordinative saturation to all the metals present in the molecular species. An other noteworthy feature is that homometal alkoxides are generally polynuclear species due to intermolecular association involving alkoxide bridges, whereas similar complexes of di- and tri-ols generally tend to be mono- or di-nuclear and only in a few cases examples of tri- or poly-nuclear species are known. Furthermore, it has already been demonstrated in earlier sections that metal complexes of glycols as well as di- and tri-ethanolamines provide stabilization toward hydrolysis, lower the oligomerization tendency, act as assembling ligands for building up novel heterometallic alkoxide coordination systems and to some extent control their stoichiometry.

It may be expected that information collated and collected in this review article would encourage investigation of more metals are other similar chelating ligands with more than three hydroxy groups. The authors are aware of investigations initiated in two different laboratories employing carbohydrates [132] and a novel ligand tris(2-hydroxy-3,5-dimethylbenzyl)amine [106,133].

This brief review is centered mainly around the synthetic and structural features of the derivatives of new polyol ligands. However, in view of the extra-ordinary suitability of metal alkoxides in general as precursors for oxide-ceramic materials by the sol–gel [134] as well as MOCVD [10] processes, a brief mention is being made in these directions also. Heterometal alkoxide systems in general have been shown to be better precursors than mixtures of their component homometal species [12,135].

Among the homo- and hetero-metallic glycolate derivatives [57,136], pinacolates [137] could be expected to be better precursors for oxide ceramic materials due to their simpler structures arising from steric factors, which should tend to make them more soluble in organic solvents and might even lead to volatility in exceptional cases. Within the di- and tri-ethanolaminates, the elimination of the latter (under processing conditions) from their derivatives might be comparatively less facile due to the tetradentate ligating mode. However, these derivatives could be utilized for mesopore formation and for obtaining special porous materials [138].

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