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Some aspects of homo and heterometallic alkoxides based on functional alcohols

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Abstract

Functional alkoxides find applications in chemistry as catalysts or for organic synthesis as well as in material science. They can provide stabilization toward hydrolysis, reduce oligomerization and, thus, give access to volatility, act as assembling ligands for the building up of mixed-metal species and to some extent control their stoichiometry. These aspects will be

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illustrated on non-silicon systems with alkoxide ligands bearing pendant ether, hydroxyl or amino functionalities, or unsaturated sites for organic cross-linking reactions. Fluoroalkoxides act often as functional groups via secondary M· · ·F bonds to electrophilic metals such as barium and will, thus, also be considered. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Alkoxides; Aminoalkoxides; Diolates; Mixed-metal alkoxides; MOCVD; Organic synthesis; Sol-gel; Unsaturated alkoxides

Abbreviations

acac	acetylacetonat
thd	2,2,6,6-tetramethylheptane-3,5-dionato
hfacac	1,1,1,5,5,5-hexafluoroacetylacetonato
TMEDA	tetramethylethylenediamine
OR_N	2-dimethylaminopropoxide
OR'_N	1,3-bis(dimethylamino)-2-propoxide

1. Introduction

Metal alkoxides based on functional alcohols are of interest to chemists and material scientists. The π-donor ability of the alkoxide ligand leads to stabilization of metals in high oxidation states [1,2]. Functional alkoxides cover a large variety of derivatives depending on the donor site namely oxygen, sulfur, nitrogen, phosphorus or unsaturation and a large body of literature is devoted to them. Such ligands offer the advantage of being relatively easily tailored with appendage, "spacer" and additional donor sites, the latter affording the possibility of forming complexes stabilized by intramolecular coordination [3,4]. Their flexibility might allow fine tuning of the reactivity of the metal centre for catalytic applications or to meet the requirements as precursors to advanced oxide materials via chemical routes. These involve solution routes such as sol-gel processing requiring solubility and appropriate rheology especially for coatings, and vapor-phase decomposition procedures, namely conventional and aerosol-assisted (AA) CVD [5,6]. The availability of intramolecular coordination sites allows the reduction of the nuclearity and, thus, provides the volatility needed for conventional metal organic vapor-phase deposition (MOCVD). The formation of mixed-metal species with a well-defined, fixed stoichiometry is another aspect of the possibilities opened up by the use of alkoxide ligands having pendant Lewis base centers.

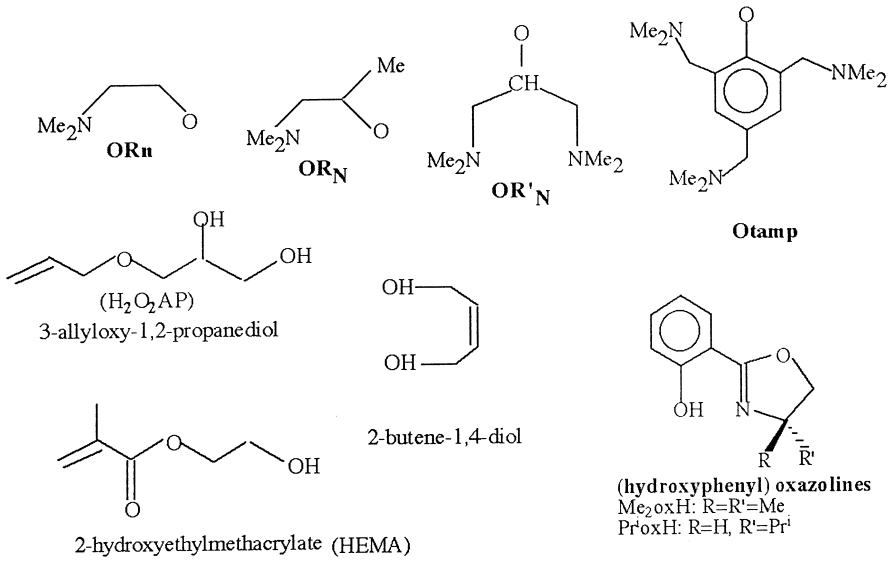
Functional alkoxides can be used as versatile ligands, especially if the spacer is flexible, for the building up of novel architectures and/or for more practical purposes. The latter are better stability toward ambient atmosphere and, thus, easier handling for industrial applications of either metal alkoxides or organometallics, especially those based on group 13 metals, stabilization of the catalytic species in enantiospecific and stereospecific synthesis, rheology or appropriate volatility during processing for

the obtaining of films by sol-gel techniques or conventional CVD, specific sites of reactivity for instance for access to organic–inorganic materials or control of stoichiometry. Qualitative data based on the comparison of temperatures of sublimation and molecular weight (MW) data indicate that the design of the ligand by increasing the number of donor sites appears a better strategy than achieving a mononuclear character by selecting bulky ligands at the price of a large number of carbon atoms [7,8].

We wish to illustrate some of these aspects focused on research in our group for sake of brevity. Examples will, thus, deal with non-silicon systems, namely metals in high oxidation states and involved in the formulation of high-tech materials, having functional alkoxide ligands with hard donor centers such as pendant O- or N-donor sites and/or unsaturated for organic cross-linking reactions. Fluorinated alkoxides do not display an obvious donor site, however they behave often as functional ligands via the formation of short, secondary M· · ·F bonds with elements such as alkaline earth metals or lanthanides, thus modifying strongly physical properties and reactivity of the metallic derivatives. Scheme 1 shows some representative examples of the various functional alkoxide ligands that we have used.

1.1. What are the properties required for practical applications?

Basic requirements for compounds destined to applications in material science or catalysis are purity, high yield synthetic routes, easy handling, facile storage and non-toxicity. In terms of transformation into materials, high ceramic yields and controlled conversion are desired. Suitable physical properties are solubility for sol-



Scheme 1. Some functional alkoxide ligands.

gel applications or "wet MOCVD", volatility and thus liquids or solids with low melting points for conventional MOCVD. Control of the hydrolysis rates, access to a suitable rheology (stable sols, homogeneous gels, viscosity etc.) especially for coatings and, for the materials required in their crystalline form, low temperatures of crystallization are additional requirements for applications. Special chemical functionalities such as donor–acceptor or polymerizable sites may be necessary for properties such as non-linear optics (NLO), microcellular materials or photopatterning. Multicomponent oxides such as electro-optical ceramics can be obtained either by using mixtures of precursors or by using "single source" precursors. The formulation of these MM′ species should then match the stoichiometry required by the formulation of the final material [9–11].

2. Homometallic derivatives

Homometallic alkoxides supported by functional alkoxide ligands have been mainly reported as a result of substitution reactions, starting from halides, usual and commercial alkoxides (ethoxides, isopropoxides) and C–C coupling reactions mediated by metal derivatives in low oxidation states. For the alcohol interchange reactions, the choice of the new alkoxide ligand is generally determined by the fact that the pK_a of the free modifying alcohol must be lower than that of the free alcohol corresponding to the initial alkoxide ligand [11]. Alcohol interchange reactions which generally require heating for classical alcohols if complete substitution is desired, occur quite easily at room temperature with most functional alcohols.

2.1. Alkoxyalkoxides

The electronegative alkoxide groups make the metal atoms highly prone to nucleophilic attack. Metal alkoxides $M(OR)_n$ are largely more hydrolysable than their silicon counterparts [5]. This is due to the more electrophilic character of the metal as well as a larger and more stereolabile coordination sphere. Several strategies have been developed in order to slow down hydrolysis rates. The focus on alkoxyalkoxide derivatives has largely resulted from the use of alkoxyalcohols in sol-gel processing in order to control hydrolysis rates and/or to provide appropriate rheology for coatings. Synthesis and X-ray characterization of a number of 2-methoxyethoxides—the parent alcohol being the most favored choice in sol-gel routes—have shown the trend of the OC_2H_4OMe group to act as a bridging–chelating ligand and, thus, to favor high nuclearity. The cyclic decamer $[Y(\mu,\eta^2\text{-}OC_2H_4OMe)_2(\mu,\eta^1\text{-}OC_2H_4OMe)]_{10}$ (**1**), obtained in high yield, either by alcohol exchange from the oxoisopropoxide $Y_5O(OPr^i)_{13}$ or by direct reaction between yttrium turnings and the alkoxyalcohol remains the homoleptic metal alkoxide having the largest nuclearity reported to date [12]. ^{89}Y NMR and molecular weight data account for retention of its high nuclearity in solution [13]. Besides its interest in material science, this compound presents a very high reactivity as compared with other classical initiators for ring-opening

polymerization reaction of lactones [14]. Giant aggregates such as $[M_9(\mu_3,\eta^2\text{-OR})_6(\mu_3,\eta^1\text{-OR})_2(\mu,\eta^2\text{-OR})_6(\mu,\eta^1\text{-OR})_2(OR)_2(OHR)_2]$ (M = Ca [15], Cd [16]), oxo clusters such as $[Gd_6(\mu_4\text{-O})(\mu_3,\eta^2\text{-OR})_4(\mu,\eta^2\text{-OR})_6(\mu,\eta1\text{-OR})_2(OR)_4]$ [17] (**2**) (Fig. 1), $[Lu_4(\mu_4\text{-O})(\mu_3\text{-OH})(\mu_3,\eta^2\text{-OR})_3(\mu,\eta^2\text{-OR})_3(\mu,\eta^1\text{-OR})(\eta1\text{-OR})_4]$ [18] or $[Ba_6(\mu_6\text{-O})(\mu_3,\eta2\text{-OR})_8(\eta^2\text{-OR})_2(OHR)_4]$ [19] (**3**) ($R = C_2H_4OMe$) are other examples of large oligomers, but which remain soluble. One can notice the preponderance of bridging μ_n,η^2- or μ_n,η^1- ($n = 2, 3$) ligation modes over the simple chelating one η^2. These ligation modes favor the stabilization of closo aggregates. For instance, the Gd_6 species can be considered as resulting from two $Gd_3(OR)_9$ units—trinuclear units are basic building blocks in lanthanide alkoxide chemistry—assembled orthogonally via a μ_4-oxo ligand. Additional connections are provided by four μ,η^2 methoxyethoxides leading to metals with high coordination numbers, namely seven and eight. The assembling character of the 2-methoxyethoxide ligand can also lead to the formation of infinite polymers as observed for $[Bi_2(\mu,\eta^1\text{-}OC_2H_4OMe)_4(\eta^1\text{-}OC_2H_4OMe)_2]_\infty$ or $[M(OC_2H_4OMe)_2]_\infty$ [M = Cu(II) [20], Pb(II) [21]] in the solid state. The Bi–O(Me) distances are quite long (2.90–3.10 Å) by comparison with those for the alkoxides (2.071(6)–2.573(6) Å), but shorter than the sum of the van der Waals radii (3.47 Å) [22]. The ether moieties are directed toward the open sites of the tetragonal pyramidal surrounding of the metal and offer secondary bonds. The overall structure can be considered as resulting from the self-assembly of $Bi(OR)_3$ units which proceeds with the stereochemically active lone pairs in *trans* positions leading, thus, to a zig-zag chain arrangement

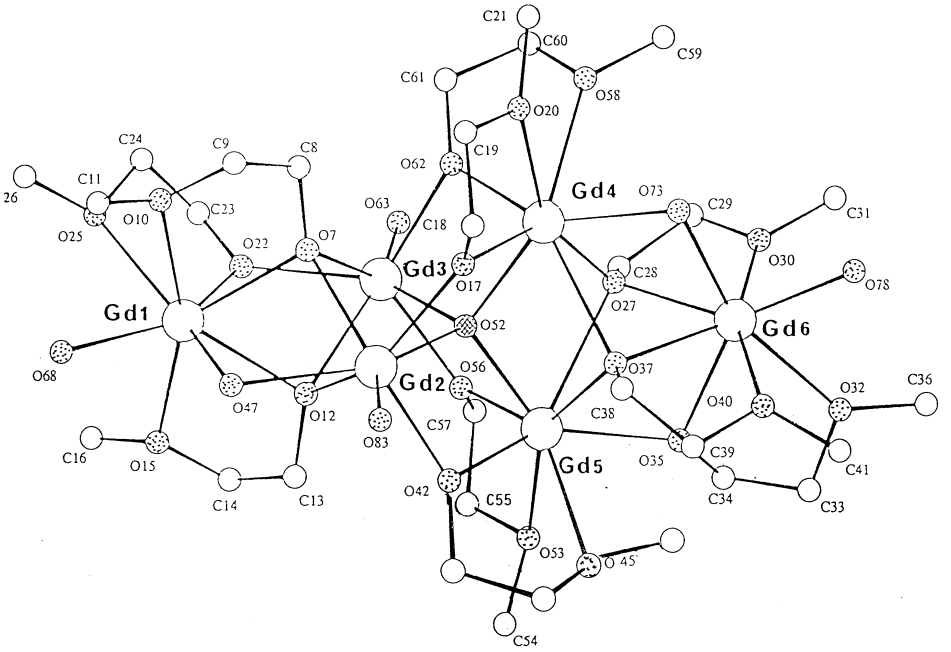


Fig. 1. Molecular structure of $Gd_6(\mu_4\text{-O})(\mu_3,\eta^2\text{-OR})_4(\mu,\eta^2\text{-OR})_6(\mu,\eta^1\text{-OR})_2(OR)_4$ ($R = C_2H_4OMe$).

(Fig. 2). The ether functionality is not involved in coordination for the lead species and polymerization is achieved via authentic μ,η^1-bridges [21]. The bismuth derivative breaks down into the basic dimeric units in solution, and is thus highly soluble even in pentane. A different situation is encountered for the copper and lead derivatives which remain polymeric and insoluble even in polar media.

The X-ray data that we have obtained on a variety of compounds show that the bond lengths usually vary according to $M–OR(t) < M–\mu–OR < M–\mu_3–OR < M–\mu OR'$, the metal–ether coordination bond being the longest. The high reactivity of 2-methoxyethanol and the variety of coordination modes established by X-ray and collected in Scheme 2 bring some insight into its behavior during sol-gel processing and its ability to promote the formation of gels. In general, about one-third of the ether functionalities remains dangling, probably for steric reasons. Another common feature is the increase of the metal coordination number, which in turn makes the metal less accessible to nucleophilic attack by water and the species more robust to hydrolysis. Yttrium is, for instance, six-coordinate in $Y_5(\mu_5\text{-}O)(OPr^i)_{13}$, but hepta-coordinated in $[Y(OC_2H_4OMe)_3]_{10}$. The chelating behavior remains restricted to a few examples, for instance the hexanuclear barium oxo species (**3**), the dioxo molybdenum derivative $MoO_2(\eta^2\text{-}OC_2H_4OMe)_2$ obtained by alcoholysis of $MoO(OEt)_4$ and subsequent elimination of diglyme over storage for 1–2 days [23] and $SeWCl_3(\eta^2\text{-}OC_2H_4OMe)$ resulting from the C–O cleavage of dimethoxyethane [24].

Although the 2-methoxyethoxide ligand is, in many cases, a means to achieve solubilization, more topological control might be necessary, for instance for copper(II). The tendency of the OC_2H_4OR' ligand to act as assembling moiety, can, to some extent, be controlled by steric hindrance at the Lewis base site and, thus, by the bulkiness of the R' group. Indeed, whereas the yttrium methoxyethoxide is a decamer, we have shown that the isopropoxyethoxide analog is only dimeric (L.G. Hubert-Pfalzgraf, unpublished results). Similarly, by contrast with the polymeric $[Cu(OC_2H_4OMe)_2]_\infty$ solubility in toluene was observed for $[Cu(OC_2H_4OBu^n)_2]_m$, but its nuclearity was not reported [25]. Reduction of the nuclearity can also be achieved by increasing the number of potential O-donor sites and, thus, of ether functionalities. Solubility was obtained for $[Cu(OC_2H_4OC_2H_4OMe)_2]_m$ assumed to be a pentanuclear species on the basis of molecular weight data [26]. Monomeric liquid barium species $Ba[O(OC_2H_4O)_nMe]_2$ ($n=2$, 3) have been reported [27], but they were non-volatile, as are most barium alkoxides.

Conventional MOCVD requires quite good volatility and stability for a constant mass transport. The poor tendency of the OC_2H_4OMe group to act as a η^2-chelating ligand makes it inappropriate for that purpose. Introduction of bulky substituents such as Bu^t in the $C\alpha$ position, thus increasing the cone angle, can, as well as increasing the number of donor sites, force chelation. Most efforts in tailor-made alcohols are due so far to the group of Herrmann [28,29]. A number of volatile alkoxides of divalent metals such as late transition metals (Fe, Co, Ni) and alkaline earth metals including barium was developed along this strategy using $OHCBu^t(CH_2OR)_2$ ($R=Et$, Pr^i) as trifunctional alcohols. The solvent-free alkaline earth metal alkoxides are dimeric in the solid state as well as in the gas phase, and

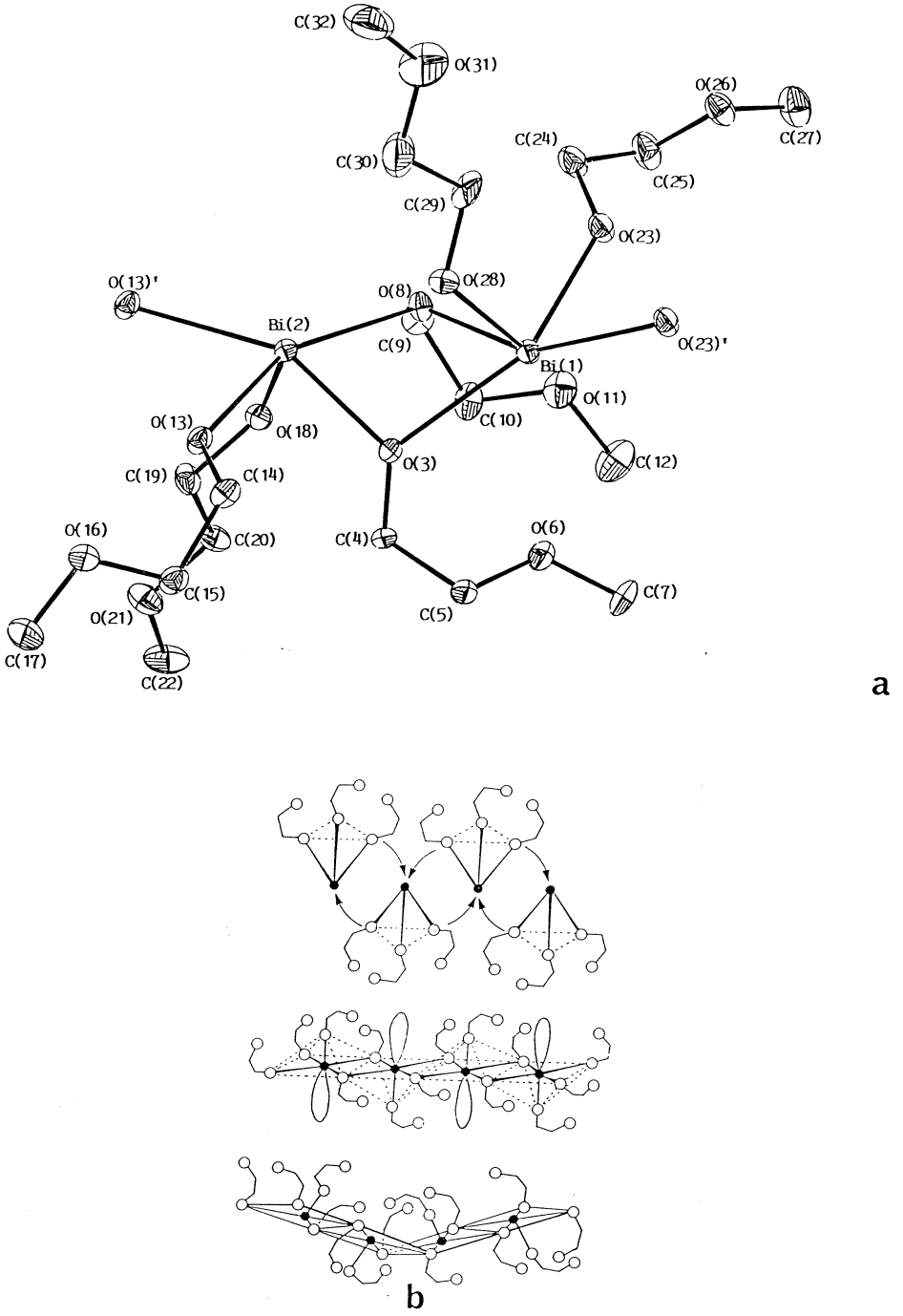
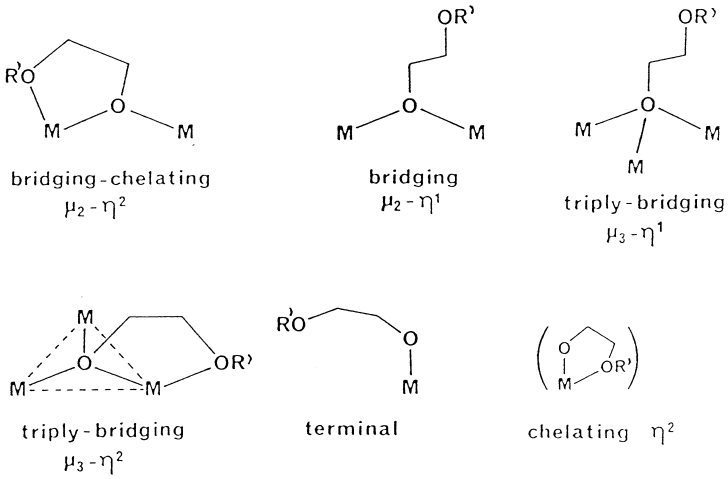


Fig. 2. (a) View of the asymmetric unit of $[Bi_2(\mu,\eta^1\text{-}OC_2H_4OMe)_4(\eta^1\text{-}OC_2H_4OMe)_2]_\infty$; (b) scheme of the assembly of the $Bi(OR)_3$ moieties into chains.



Scheme 2. Coordination modes of 2-methoxyethanol.

display well-defined sublimation temperatures (185 °C/7.5.10^{-3} Torr for R′=Pr^{i}). However, the moisture sensitivity of these precursors, all solids, might be a hurdle for applications.

2.2. Aminoalkoxides

Aminoalcohols represent another class of alcohols used to a large extent in sol-gel processing. Mono and diethanolamines, especially, were found to give access to media remaining homogeneous even for large hydrolysis ratios h ($h=[H_2O]/[M(OR)_n]$), up to 10, for instance for the $M(OR)_4$-deaH_2-H_2O-^{i}PrOH solutions (M=Ti, Zr) [30]. Various ethanolamines have also been used as sol stabilizers [31,32] and/or as a means to improve the microstructure of coatings [33].

Primary and secondary aminoalkoxides of type $OHCHRCH_2NMe_2$ have proven more efficient than 2-methoxyethoxide for breaking down aggregation and, thus, providing volatility. Praseodymium derivatives offer a contrasting example between 2-methoxyethoxide and aminoalkoxide derivatives [34]. Polynuclear oxo aggregates based on $Pr_4O_2(OC_2H_4OMe)_8$ units, as we established for $[Pr_8(\mu_4\text{-}O)_4(\mu_3,\eta^2\text{-}OR)_4(\mu,\eta^2\text{-}OR)_8(\mu,\eta^1\text{-}OR)_2(OR)_2(OPMe_3)_2]$, are formed with 2-methoxyethoxide (R=C_2H_4OMe), whereas the aminoalkoxide $[Pr(OC_2H_4NMe_2)_3]_3$ is stabilized as a trimer. The difference is also nicely illustrated with the copper(II) alkoxides: $Cu(OCHRCH_2NMe_2)_2$ (R=H, Me) are both monomeric and volatile, a feature in sharp contrast with the oligomeric or even polymeric alkoxyalkoxides. The same observation is valid for the Zn derivatives [35]. The volatility of the copper(II) aminoalkoxides was utilized to obtain metallic copper by pyrolysis at 300 °C under nitrogen at ambient pressure [36].

2.3. Mixed-ligand functional alkoxides: toward further tuning?

Alkoxyalcohols, alkoxyphenols and aminoalcohols have been used for intramolecular stabilization of organoaluminium and organogallium with the aim to obtain novel organometallic compounds for industrial uses [37,38]. Most reported mixed-ligand alkoxides derive, however, from the modification of metal alkoxides. Indeed, the essential feature of metal alkoxides is the lability of the M–OR bond [1,6]. This property is generally retained for functional alkoxides and modifications can occur easily. Aluminium [39,40] or lanthanide [41] functional alkoxides have for instance been used as initiators for ring-opening polymerization of lactides and lactones. Coordination of the metal center by the acyle oxygens of the polymer repeating units has been suggested for the intermediates.

Heteroleptic species are accessible in a controlled way for tailoring of properties. β-diketonatomethoxyethoxides, for instance, were synthesized as part of efforts to improve properties of precursors for MOCVD applications. Since β-diketonates act essentially as chelating ligands, we explored the partial substitution of alkoxide ligands by them as a means to reduce oligomerization and thus to increase volatility. $[Y_3(OC_2H_4OMe)_5(acac)_4]$ [42] and $[Cu(\beta\text{-dik})(OC_2H_4OMe)]_4$ [β-dik = acac [43] or hfacac [44–46]] are representative examples of the volatile compounds obtained. The same approach was less successful for barium. Barium alkoxides, including derivatives supported by fluorinated or functional primary alkoxides are generally either non volatile, or volatile in conditions too drastic for CVD applications, since they correspond to oligomers. Barium β-diketonatoalkoxides remain of high nuclearity, usually four or five, even for functional alkoxide ligands. The pentanuclear cluster $[Ba_5(\mu_5\text{-}OH)(\mu,\eta^2\text{-thd})_4(\eta^2\text{-thd})(\mu_3,\eta^2\text{-}OCHMeCH_2NMe_2)_4]$ whose structure is related to that of $Y_5O(OPr^i)_{13}$ illustrates that trend [47]. Polynuclear aggregates were also obtained for non-oxo species such as $[H_2Ba_4(thd)_6(\mu_3,\eta^2\text{-}OC_2H_4OPr^i)_4]$[2][48], and $[Ca_4(thd)_6(\mu_3,\eta^2\text{-}OC_2H_4NMe_2)_4]$ [49]. Finally, if such compounds can display properties pertinent for sol-gel applications, the combination of bifunctional alkoxide and β-diketonate ligands has generally not achieved better volatibility and/or stability of barium derivatives. TGA data show that the alkoxide ligand is generally more thermally labile than the β-diketonate.

The trifunctional alcohol, 1,3-bis-(dimethylamino)-2-propanol $OHCH(CH_2NMe)_2$ (R'_NOH) has been used as a cross-linking and complexing reagent in solutions routes to high T_c superconductors [50]. This approach has generated a variety of homo or heteroleptic alkoxides based on Cu(II), Sr, Bi and trivalent lanthanides (Y, La, Pr, Nd), the ancillary ligands being fluorinated acetate or hexafluoracetylacetone [51]. We envisioned that the flexibility of this potential tridentate should allow encapsulation of barium and provide volatility. However, the corresponding barium aminoalkoxide was insoluble. Its modification by tetramethylheptanedione afforded a solvate $[Ba(OR'_N)(thd)(R'_NOH)]$ [7,8]. This monomeric compound displays interesting properties, namely a low melting point and high volatility, since it distils at 130 °C/10^{-3} mm Hg. The volatility probably finds origin in its relatively low molecu-

[2] H_2 stands for hydroxyl hydrogens, but which could not be located.

lar weight, but like other volatile barium alkoxides, the moisture sensitivity is a hurdle for MOCVD applications. The related yttrium β-diketonatoaminoalkoxide $[Y(\mu,\eta^2\text{-}OR'_N)(\eta^2\text{-}thd)_2]_2$ was obtained from ligand exchange between the preceeding Ba species and $Y(thd)_3$. The molecular structure shows that the alkoxide ligands are bridging as expected, but only one amino donor site tethers the metal which is seven-coordinated [7,8].

2.4. Functional aryloxides: effect of bulkiness, rigidity and donor sites

Aryloxides with bulky substituents in positions 2 and 6 have been largely used in order to enforce a mononuclear character for species based on large metals [52]. In some cases, additional linkages to metal(s) were provided via C–H activation reactions [53] and/or π-bonding of pendant phenyl groups as for 2,6-diphenylphenoxide [54]. A very unusual coordination behavior of a phenoxide ligand acting as a 10-electron donor toward five ruthenium atoms has been reported [55]. However, functional aryloxides are essentially phenoxides with potentially intramolecularly coordinating ortho-substituents [3]. They combine steric shielding, are less flexible than aliphatic functional alkoxides and provide electron donation. 2,6-(dimethylaminomethyl)methyl-4-phenoxide and 2,4,6-tris(dimethylaminomethyl)phenoxide (O-tamp) are the most accessible and, thus, used ligands.

The O-tamp ligand has been reported as a bridging, tridentate ligand in

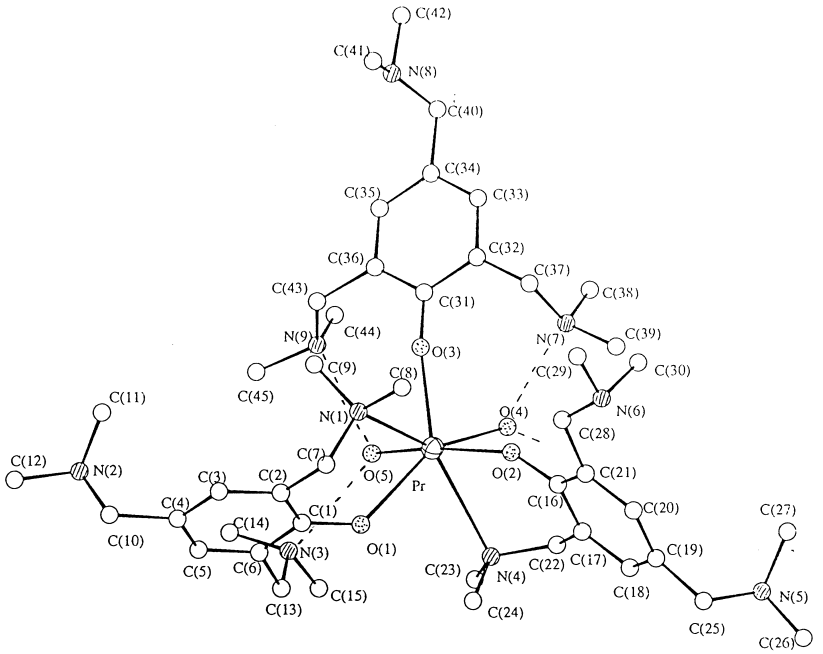


Fig. 3. Molecular structure of $Pr(O\text{-}tamp)_3(H_2O)_2$, dotted lines indicate H-bonding.

$Ba_4(\mu_4\text{-}O)(O\text{-}tamp)_6$ achieving, thus, seven-coordination for barium [56]. By using this potential tetradentate, we were able to stabilize praseodymium(III) as a mononuclear adduct $Pr[OC_6H_2(CH_2NMe)_3\text{-}2,4,6]_3(H_2O)_2$ (**4**) [57]. Its molecular structure (Fig. 3) shows two types of ligation modes for the O-tamp ligand, one monodentate and two bidentate, one ortho-dimethylaminomethyl group being linked to the metal. This ensures heptacoordination (five O-donors, two N-donors) for praseodymium which has a distorted pentagonal bipyramidal surrounding. The striking feature is the presence of two water molecules as ligands. Those are involved in intra as well as intermolecular hydrogen bonding with the nitrogen sites. Water (probably due to the hygroscopic phenol) appears actually as a better ligand than THF which was used as the reaction medium. These results indicate that aryloxides with potential donor sites are, like fluoroalkoxides, able to form stable complexes with water and are, thus, less hydrolyzable than classical alkoxides. One can notice that although the O-tamp ligand can limit the molecular complexity, this is achieved at the price of the large number of atoms, thus increasing the molecular weight of the resulting complex [7,8]. The hygroscopic character of the phenol might also favor hydrogen bonding, another unfavorable feature for the volatility.

Phenols incorporating the oxazoline skeleton, namely 2-(2-hydroxyphenyl)-2-oxazolines can be prepared easily as achiral and homochiral ligands via the tuning of the substituents (Scheme 1). Such bidentate ligands appeared, thus, attractive to us for access to molecules which could be handled on the open bench, inert to ligand exchange reactions and whose physical properties could met the requirements for conventional and/or aerosol-assisted CVD [7,8]. Such compounds could also have a potential for asymmetric synthesis and since the ligands are related to naturally occuring moieties, biomedical applications can be expected for some metals [58]. Volatile Ce(IV) and Cu(II) derivatives have been obtained. $Ce(Me_2ox)_4$ and $Ce(Pr^iHox)_4$, for instance, were formed by alcohol exchange reactions applied to $Ce_2(OPr^i)_8(Pr^iOH)_2$. Volatility and stability properties toward ambient atmosphere are in the favor of the isopropoxide substituted oxazoline derivative (sublimation 180 °C versus 200 °C under 3.10^{-4} Torr) [7,8].

2.5. Fluorinated alkoxides: a way to acceed to volatile species?

Fluorinated ligands are known to improve volatility and this has been largely applied with fluorinated β-diketonates [6–8]. Fluorinated secondary and ternary groups such as hexafluoroisopropoxide $OCH(CF_3)_2$ (HFIP) or per-t-fluorobutoxide $C(CF_3)_3$ (PFTP) are the most familar examples of alkoxides. Such metallic compounds were recently developed and/or reinvestigated for yttrium and lanthanides (La, Pr, Eu) [5,59] barium, zirconium and sodium [60]. A common feature is the high Lewis acidity which results in the retention of solvents, even non polar ones such as benzene, reactants and/or side products such as ammonia or water in the metal coordination sphere. The yttrium and trivalent lanthanide derivatives are monomeric or dimeric and volatile. However, we could not achieve notable volatility for barium. The usual high nuclearity of barium alkoxides was retained as illustrated by the pentanuclear core of $[Ba_5(\mu_5\text{-}OH)(HFIP)_9(THF)_4(H_2O)]$ [61]. Secondary barium–fluorine interactions [2.99(2)–3.31(2) Å] ensure high coordination numbers

from nine to 11 for the barium centers. Pure BaF_2 was obtained by thermal decomposition of the aggregate.

2.6. Derivatives of polyols

2.6.1. Diolates

A number of derivatives obtained by alcohol exchange reactions between $M(OR)_n$ (M = Al, Ti, Nb, Ta, Ln, etc.) and various α,β-diols (propane-1,2 or 1,3-diols, butane-2,3-diol, etc.) have been reported [1,62–65]. Most of those compounds have remained poorly characterized; monomeric and/or dimeric structures were assumed on the basis of molecular weight data. The consideration of diols as alternatives to the toxic 2-methoxyethanol in sol-gel processing [66–69], the possibility to acceed easily (about 1 h reaction time) to soluble oxide precursors, namely anions, by reacting oxides such as SiO_2 [70], GeO_2 [71], TiO_2 [72], Al_2O_3 [73] and diols in basic media (alkali metal hydroxides) under azeotropic distillation conditions, has led to a renewed interest in the recent years.

Surprisingly, ethyleneglycolate derivatives were obtained by C–O bond cleavage reactions of 2-hydroxyethylmethacrylate induced by oxophilic metal centers (Eq. (1)). These reactions, which occur in mild conditions—room temperature over a few hours—lead to the formation of heteroleptic ethyleneglycolate derivatives. For instance, the pentanuclear species $Ti_5(OC_2H_4O)_5(OPr^i)_{10}$ (**5**) was obtained by reacting $Ti(OPr^i)_4$ and $OHC_2H_4OC(O)CMe=CH_2$ (HEMA) in 1:1 stoichiometry [74]. This soluble cluster displays several unprecedented structural features, namely five-, six- and seven-coordinate Ti centers as well as four types of ligation modes of the ethyleneglycolate ligands [Fig. 4(a)]. These correspond to μ,η^2- chelating doubly-bridging, two types of triply-bridging μ_3,η^2- and a μ_4,η^2- fly-over manner, respectively. These C–O bond cleavage reactions mediated by electrophilic metal centers are favored by coordinative unsaturation and proceed more easily for the monomeric $Ti(OPr^i)_4$ species than the $[Ti(OEt)_4]_3$ trimer. A centrosymmetric tetranuclear niobium ethyleneglycolate $Nb_4(\mu,\eta^2\text{-}OC_2H_4O)_4(\mu\text{-}OC_2H_4O)_4(OPr^i)_{10}$ (**6**) was obtained in similar conditions by reacting niobium isopropoxide and HEMA. The diolate ligands arrange themself around six- and seven-coordinated metals with the central heptacoordinated metals displaying a distorted bipyramidal pentagonal surrounding [Fig. 4(b)] [75,76].

$$M(OPr^i)_n + OHC_2H_4OC(O)CMe=CH_2 \begin{cases} \xrightarrow{M=Ti} 1/5Ti_5(OC_2H_4O)_5(OPr^i)_{10} + \ldots \\ \xrightarrow{M=Nb} 1/4Nb_4(OC_2H_4O)_5(OPr^i)_{10} + \ldots \end{cases} \quad (1)$$

More simple ligation modes have been observed for the $[Ti(\eta^2-OC_2H_4O)]_3^{2-}$ anion, derived from titanium dioxide and ethyleneglycol in the presence of sodium hydroxide [72]. This anion was also found (as hydrogen-bonded pairs to nine-coordinate $[Ba(HOC_2H_4OH)_4(H_2O)]^{2+}$ cations) in a compound formulated as

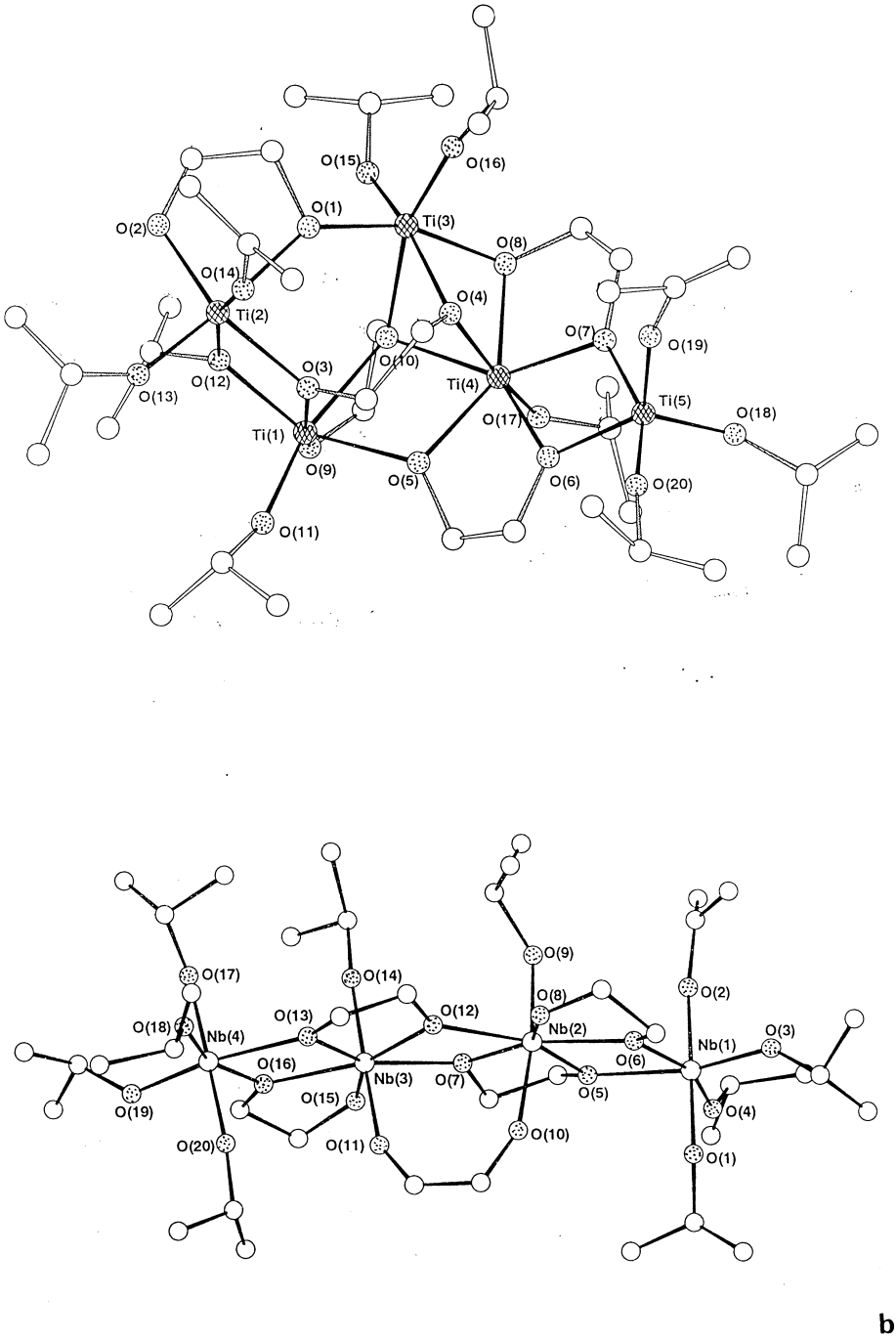


Fig. 4. (a)Molecular structure of $Ti_5(OPr^i)_9(\mu\text{-}OPr^i)(\mu,\eta^2\text{-}OC_2H_4O)(\mu_3,\eta^2\text{-}OC_2H_4O)_3(\mu_4,\eta^2\text{-}OC_2H_4O)$; (b) Ball-and-stick drawing of the molecular structure of $Nb_4(\mu,\eta^2\text{-}OC_2H_4O)_4(\mu\text{-}OC_2H_4O)(OPr^i)_{10}$.

$BaTi(C_2H_4O_2)_2,4C_2H_6O_2,H_2O$ which was isolated in high yield from reaction of ethyleneglycol with BaO (or Ba metal) and TiO_2 (or titanium isopropoxide) [77].

The pinacolate ligand is another common diolate. Its usual coordination mode has been reported as a η^2-chelating behavior [78]. A less common behavior is illustrated by the $[(\eta^5\text{-Cp})TiCl(pin)]_2$ dimer presenting a 10-membered ring. It results from the heating of $[(\eta^5\text{-Cp})TiCl(\eta^2\text{-}O_2C_2Me_4)]$, assumed to be a monomer on the basis of cryoscopic measurements [79,80]. The rearrangement of the kinetic product into the thermodynamic dimeric one was attributed to repulsions between the cyclopentadienyl ring and the methyl substituents. These observations suggest the possibility of tailoring ligation modes either by ancillary ligands or by substituents.

We isolated soluble, polynuclear niobium oxopinacolate derivatives by reactions between niobium alkoxides and pinacol ($pinH_2$). $[Nb_3(\mu\text{-}O)_2(\mu,\eta^2\text{-pin})_2(\mu\text{-pin})_4H]$ (**7**) and $[Nb_4(\mu\text{-}O)_2(\mu_3\text{-}O)_2(\mu,\eta^2\text{-pin})_2(OPr^i)_8]$ (**8**) were obtained from ethoxide and isopropoxide in 1:4 and 1:2 stoichiometry respectively and structurally characterized (Fig. 5) [75,76]. The trinuclear species is based on a bent, open shell polyhedron, [angle Nb(2)–Nb(1)–Nb(2′) = 102.13(2)°], build up around six-coordinated metals. Those are assembled by bridging pinacolate and oxo ligands. The electroneutrality of the compound requires an hydroxyl functionality. The short contact of 2.48 Å

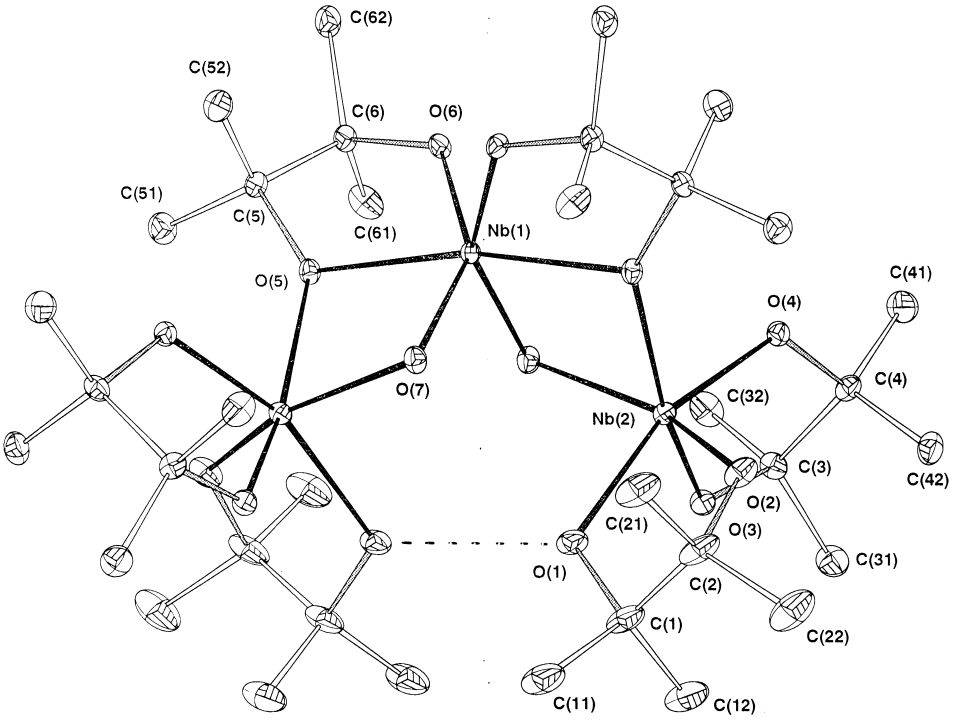
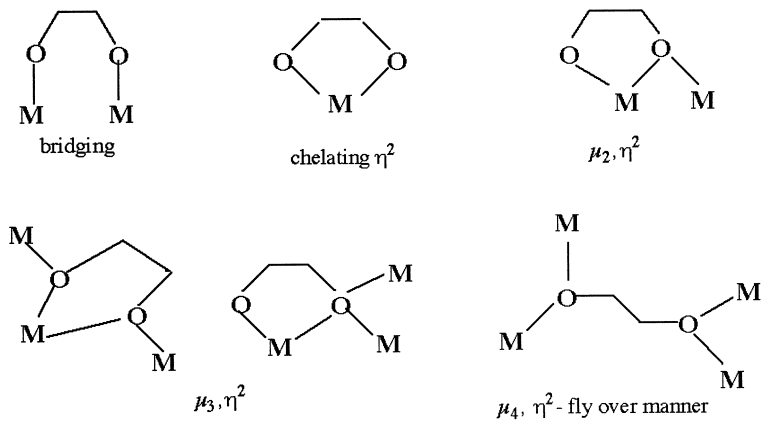


Fig. 5. ORTEP drawing of $Nb_3(\mu\text{-}O)_2(\mu\text{-pin})_4(\mu,\eta^2\text{-pin})_2H$. The dotted line indicates H-bonding. Selected distances: Nb· · ·Nb = 3.202(4) Å; Nb–O = 1.907(2)–2.128(2) Å.

between O(1) and O′(1) provides a clue and is in favor of the presence of an hydrogen atom. The tetranuclear pinacolate species is based on a quite regular rhombus. As observed for the trinuclear cluster, all metals are six-coordinated, but their stereochemisty is severely distorted, especially for the metals linked to the chelating ligand [<O–Nb(2)–O = 71.5(2)–162.6(3)°]. The bond lengths vary according to Nb–OPr^i < Nbμ–O < Nbμ$_3$–O ≈ Nb–O(pin). The structure can formally be considered as resulting from the assembly of two dimeric $Nb_2(\mu\text{–pin})(\mu\text{–OR})(OR)_7$ units with elimination of dialkylether. An insoluble derivative was obtained if the same reaction was carried out in 1:4 stoichiometry showing the influence of the OR group. The bite angles of the pinacolate ligands have values around 74° and are comparable with those of ethyleneglycolate. All these novel species **5**, **6**, **7**, **8**, are more resistant to hydrolysis than the parent homoleptic alkoxides and are converted into gels by hydrolysis-polycondensation, while the latter give precipitates as a result of uncontrolled hydrolysis. Our results on the pinacolate and ethyleneglycolate derivatives show that these simple ligands can give rise to a rich coordination chemistry, especially if the metal is able to adopt a variety of coordination numbers and that the molecular structures are more complex than anticipated. The variety of coordination modes of flexible diolate ligands is expressed in Scheme 3.

The use of transition metal alkoxides for enantioselective and stereospecific catalysis or synthesis also requires stabilization of the metallic species. Bidentate diolates derived from dialkyl tartrate [81,82], 2,2′-methylene-bis(6-tbutyl-4-methylphenol) [83–85] ($mbmpH_2$) or from the 1,1-binaphtol ligand R_2BINOL (R = H, Me, etc.) have been the most commonly used, especially for titanium [86,87] and for rare earth metals [88]. A large number of heteroleptic titanium diolates have been prepared using standard routes applied to $TiCl_4$ or Ti(OPr^i)$_4$, respectively [86,87]. Whereas most compounds are monomeric, a trinuclear species, namely $Ti_3(\mu,\eta^2\text{-}R_2BINO)_2(\eta^2\text{-}R_2BINO)(\mu\text{-}OPr^i)_2(OPr^i)_4$ (R = ^{t}BuMe$_2$Si) has been reported. One can notice that it displays a solid-state structure quite different from



Scheme 3. Coordination modes of diolates, especially ethyleneglycolates.

that of **7**. The bulkiness of the diolate ligands imposes their distribution over all metals and some isopropoxides behave as assembling ligands, although diolate ligands are usually more assembling than common OR groups, as seen previously with ethyleneglycolates and pinacolates.

2.6.2. Derivatives of triols

The ability of triethanolamine $N(C_2H_4OH)_3$ ($teaH_3$) to stabilize transition metal alkoxides such as those of titanium toward hydrolysis has been recognized for some time. The extensive possibilities of hydrogen bonding (intra and intermolecular via the non-deprotonated hydroxyls) favor the formation of gels, but they are defavorable to a facile elimination of the organic residues if crystalline materials are required. That ligand is, thus, often less favorable for access to high-tech materials than diethanolamine, although the precursor solutions are more easy to handle and display a larger range of stability toward precipitation. $TeaH_3$ acts always as a tetradentate ligand, but the extent of its deprotonation is function of the metal oxidation's state. A soluble eight-coordinate barium triethanolamine derivative $Ba(teaH_2)_2$ was obtained by us by alcohol interchange reactions applied to the insoluble barium methoxide [89]. Despite encapsulation of the metal leading to a mononuclear complex, volatility was low as a result of intermolecular hydrogen bonding of the residual hydroxyl groups with the solvent of crystallization, ethanol. Triethanolamine was also able to achieve solubilization of late transition metal alkoxides such as copper(II) [90]. However, the lower coordination number required by this metal imposes a different coordination mode of the functional alkoxide. The compound that we isolated was actually a tetranuclear solvate $[Cu(\mu\text{-}teaH_2)]_4$,3$teaH_3$ (Fig. 6). Tetranuclear Cu(II) derivatives display generally a cubane type framework. The constrained triethanolamine ligand, due to the pyramidal nitrogen atom, favors an eight-membered Cu_4O_4 ring where the copper atoms have a distorted square pyramidal surrounding. A comparable coordination behavior, but involving complete deprotonation of the triol, was observed for $[(tea)Al_2Me_3]_2$ [91] or $[Ti(tea)(\mu\text{-}OPr^i)]_2$ [92–96]. Beside tuning of the rheology of a system via H-bonding, non deprotonated hydroxyl sites can also be used for anchoring of another metal (see Section 3.3).

1,1,1-tris(hydroxymethyl)propane and 1,1,1-tris (hydroxymethyl)ethane $RC(CH_2OH)_3$ [R = Et (THMPH3), Me ($THMEH_3$)] are the other triols which have received the most attention so far for limiting hydrolytic susceptibility. In contrast with triethanolamine, their reactions with titanium and zirconium isopropoxides in 1:1 stoichiometry afforded insoluble compounds [97,98]. Soluble, crystalline materials were obtained when the stoichiometry triol/$M(OR)_4$ was optimized to 1:2. Tetranuclear aggregates $(THME)_2M_4(OPr^i)_{10}$ and $(THMP)_2M_4(OPr^i)_{10}$ (M = Ti, Zr) based on a typical fused M_3O_{12} arrangement were characterized, the greater flexibility of these triol type ligands—with respect to $teaH_3$—allows them to span four metals via two μ_3- and one μ_2- bonds. The films of lead zirconate titanate (PZT) prepared by using these novel molecules displayed less shrinkage, macroscopic cracking and porosity as compared with the films obtained from non-modified Ti

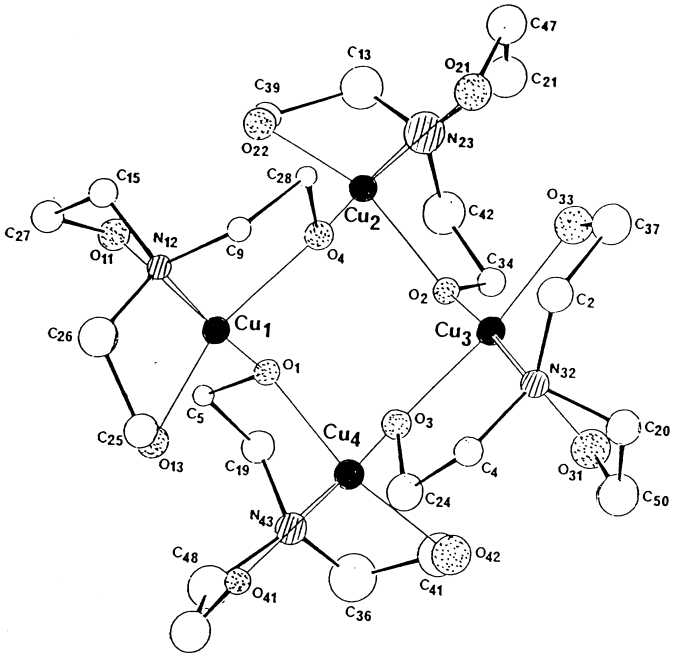


Fig. 6. Ball-and-stick drawing of the tetranuclear core of $[Cu(\mu\text{-}teaH_2)]_4,3teaH_3$ [Cu–O = 1.85(3)–2.47(4)] [Cu(4)–O(41)], Cu–N = 1.89(6)–2.09(6) Å.

or Zr isopropoxides. However, their non-uniformity calls for further optimization of the precursors.

2.7. *Unsaturated alkoxides: a potential for organic cross-linking reactants*

There have been very few reports of alkoxides derived from unsaturated alcohols. Such alkoxides $M(OR)_n$ have been for many years restricted to main group elements such as boron, aluminium ($R = CH_2CH{=}CHMe$, $CMeCH{=}CH_2$ or $CH_2CMeC{=}CH_2$), germanium ($R = CH_2CH{=}CHMe$ or $CH_2CMeC{=}CH_2$) and silicon [62–65,99]. Characterization was based on IR and ^1H NMR mainly. Unsaturated transition metal alkoxides were mostly limited to enolates although a vinoxytitanium species $[Ti(OPr^i)_2(OCH{=}CH_2)_2]$ and $[Ti(OCH_2CH{=}CH_2)_4]_2$ were reported from the reaction of $Ti(OPr^i)_4$ and acetaldehyde [100] or 2-propen-1-ol [101], respectively. Enolates have been extensively used in metal-mediated organic synthesis [102]. Their formation has been reported to occur by a variety of synthetic routes such as deshydrogenation of alkoxides [35], sometimes subsequent to THF ring-opening reactions [103], acyl rearrangements [104], insertion of carbonyl derivatives such as ketones into metal–carbon bonds [105,106], or ketenes into metal alkoxide ones [107]. The recent interest in hybrid (organic–inorganic) materials has boosted the search for derivatives bearing unsaturated ligands which can contribute

to the formation of the organic network [108–110]. A number of silicon alkoxides were shown to be valuable candidates for the formation of non-shrinkable composites [111,112].

We have obtained a trinuclear oxo species $Ti_3(\mu_3\text{-}O)_2(OPr^i)_5(OCMe{=}CH_2)_3(Pr^iOH)$ (**9**) by a non-hydrolytic condensation process, namely the reaction between $Ti(OPr^i)_4$ and acetone [113]. Such condensations are based on the formation of an enolate intermediate which is expected to undergo C–C coupling reactions forming an unstable adolate which eliminates mesityle oxide leading to the M–OH linkage for growth of the metal oxide network [114]. The formation of the aldolate was reported as the rate determining step for the formation of zinc oxide. We observed no evolution into gels and/or oxide precipitation for the titanium species in the reaction medium with large excess of acetone over several months. These condensations reactions rely on the basicity of the metal alkoxide; no enolate intermediate could be isolated in similar conditions for lanthanide derivatives since extensive M–O–M condensations occur.

Access to alkoxides with unsaturated functionalities—which are a means to obtain class II hybrid materials [108–110]—might require a more careful selection of the reactants for oxophilic metals than for elements such as silicon. For instance, whereas 2-hydroxyethylmethacrylate derivatives were easily obtained for silicon, reactions between HEMA and various metal alkoxides $M(OPr^i)_n$ (M = Al, Ti, Nb) are characterized, as exposed previously, by C–O bond cleavage reactions of the acyle group, thus leading to the loss of the polymerizable sites [74]. Allyloxy-1,2-propanediol (APO_2H_2) and 1,4-butene-*cis*-diol are better choices for selective alcohol exchange reactions. Compounds of formula $Ti(APO_2)_2$ and $Ti(OPr^i)_2(APO_2)_2$ were obtained by reacting the diol and titanium isopropoxide in 1:2 and 1:1 stoichiometry respectively. A similar reaction between $Ti(OPr^i)_4$ and the butenediol in 1:1 stoichiometry afforded a tetranuclear species. Its molecular structure corresponds to $[Ti_4(OPr^i)_8(\mu_3,\eta^2\text{-}OCH_2CH{=}CHCH_2O)_2(\mu,\eta^2\text{-}OCH_2CH{=}CHCH_2O)_2]$ with Ti···Ti distances of 3.274(5) Å av. The central titanium atoms which bear diolate ligands and one terminal isopropoxide are six-coordinate, whereas the other titanium atoms are only five-coordinate. The framework is, thus, related to that of the niobium ethyleneglycolate **6** [Fig. 4(b)] showing that the higher rigidity of the unsaturated diolate does not affect the assembly [115]. The novel unsatured titanium alkoxides have been used for the obtaining of doped microcellular organic materials via copolymerization reactions in biphasic media [116].

3. Mixed-metal derivatives

3.1. General features

Single-source precursors in which different metals M and M′ are associated within a same molecule are accessible by a variety of strategies. They can be obtained either by Lewis acid–base reactions or by a more rational way based on the reactivity of a functional group. They can be exploited for the increase of solubility, of the

stability toward moisture and/or dioxygen, and, if the right set of ligands has been selected, of the volatility [7–10]. A more homogeneous microstructure and a lower temperature of crystallization of the materials issued from their transformation can be expected. The heterometallic concept has also shown its potential in asymmetric catalysis with group 13 metals or lanthanides associated to alkali metals [117,118]. Such complexes can function both as a Broenstedt base and as a Lewis acid; in fact, like an enzyme. The different metals play different roles to enhance the reactivity of both partners leading to a multifunctional catalyst.

The simplest approach to mixed-metal species is based on the mixing of precursors of different metals, namely metal alkoxides or metal alkoxides associated to other oxide precursors such as carboxylates, β-diketonates, nitrates for material science purposes or to halides or alkyl derivatives for systems destined to catalytic applications. A general feature is that the stoichiometry of the mixed-metal species, if stable and isolable is determined a posteriori. A number of mixed-metal alkoxides based mostly on the isopropoxide ligand has been developed by the group of Mehrotra [62–65,119]. The breakthrough for functional alcohols was the isolation of $[Ba_2Cu_2(OR)_4(acac)_4(ROH)_2]$ ($R = C_2H_4OMe$) from reaction between $[Cu(acac)(OR)]_2$ and barium 2-methoxyethoxide (2:1.5 stoichiometry) in the parent alcohol [120]. A terheterometallic species, $Cu_3Ba_2YO_3(OC_2H_4OMe)_7$, was claimed to be formed by simple mixing in solutions used for processing of high T_c superconductors [121], but such a formulation is highly speculative in view of the difficulties to associate three different metals [122].

Most structurally characterized heterometallic functional alkoxides remain based on alkali metals [23,28,29]. $[Ni(\eta^2\text{-}OCHMeCH_2NMe_2)_2ClLi(Pr^iOH)]_2$ offers an example of an heterometallic species involving alkali metals (Fig. 7). We obtained it by alcoholysis of "$[Ni(OPr^i)_2]$" prepared by anodic dissolution using lithium chloride as electrolyte [123]. This unanticipated observation indicates how easy it can be to incorporate small ligands such as Li^+—giving "ate" compounds into metallic cores. It can be described formally as a $[Ni(OR)_2Cl]^-$ fragment with pentacoordinated nickel atoms in a distorted tetragonal pyramidal surrounding, assembled by $[Li(Pr^iOH)]^+$ illustrating, thus, a cooperative anion–cation binding, but the species is molecular and soluble in organic media.

2-methoxyethanol has so far been the solvent of choice for access to multicomponent oxides such as high T_c superconductors, dielectrics or ferroelectrics, namely lead, barium or bismuth titanates. However, by contrast with the homometallic systems, structural data on mixed-metal species based on the unique OC_2H_4OMe ligand remain scarce and restricted to $[Ba_4Ti_{13}(\mu_3\text{-}O)_{12}(\mu_5\text{-}O)_6(\mu_1,\eta^1\text{-}OR)_{12}(\mu_1,\mu_3,\eta^2\text{-}OR)_{12}]$. This species, isolated in 30% yield (based on Ti) after 2 months from the hydrolysis of barium and titanium methoxyethoxides dissolved in the parent alcohol [124], shows that important modifications can occur on the way to the material especially over long periods of time.

Mixed-metal functional alkoxides have also been prepared by alcohol exchange reactions applied to MM′ species supported by usual OR ligands. Retention of the stoichiometry has generally been assumed although evidence for this is mostly missing in the absence of isolation and unequivocal characterization. As observed

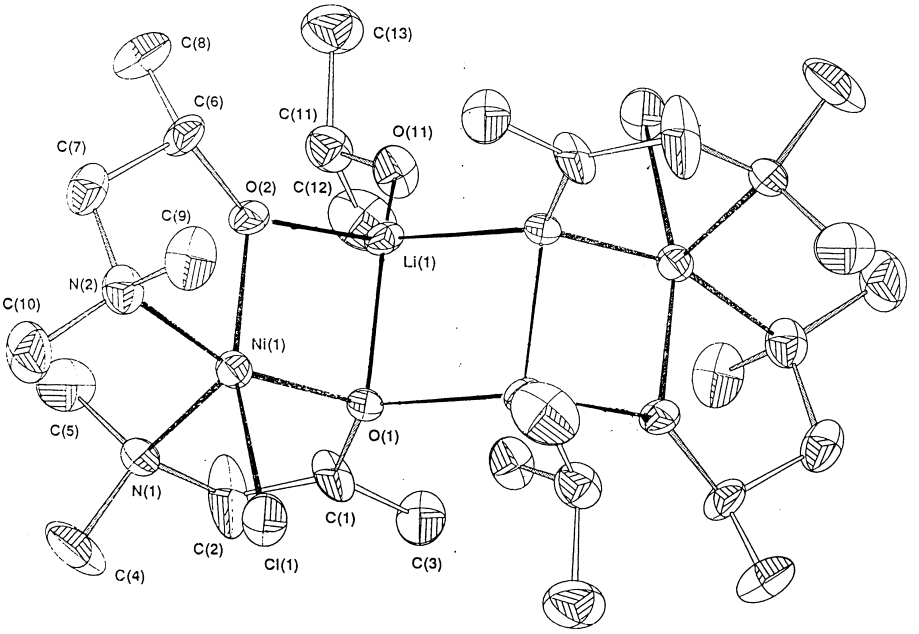


Fig. 7. ORTEP drawing of $[Ni(\eta^2\text{-}OCHMeCH_2NMe)_2ClLi(Pr^iOH)]_2$.

for mixed-metal species based on usual OR groups, change of the M:M′ stoichiometry is favored by extrusion of insoluble species. Thus, while 2-methoxyethanol is generally a good choice as solvent for sol-gel processing, its addition to $Pb_6Nb_4(\mu_4\text{-}O)(OEt)_{24}$, a precursor for the PNM $[Pb(Nb_{1/3}Mg_{2/3})O_3]$ ceramic, leads to alteration of the Pb:Nb stoichiometry as a result of the precipitation of $[Pb(OC_2H_4OMe)_2]_\infty$ [125].

The reactions between metal alkoxides and other oxide precursors represent another aspect of the Lewis acid–base approach to mixed-metal species. The presence of ancillary ligands different from OR makes the issue of the reaction dependent on the experimental conditions as noticed previously with usual alkoxides. The nature of the solvent can be crucial. The addition of isopropanol to a medium that we assumed to contain a BaCu species of 1:1 stoichiometry $[BaCu(OR_N)_2(thd)_2]_m$ afforded a crystalline material of formula $[Ba_2Cu(\mu_3,\eta^2\text{-}OR_N)_2(\mu,\eta^2\text{-}thd)_2(\eta^2\text{-}thd)(Pr^iOH)_2]$ (**10**) together with the homoleptic copper(II) aminoalkoxide [126]. Copper is five-coordinate, whereas the barium centers display coordination numbers of seven and eight [Fig. 8(a)].

As seen previously, sterically encumbered aryloxide ligands can reduce the hydrolytic susceptibility. This feature is of value for AACVD applications [7,8]. An aryloxide with potentially chelating aminomethyl arms such as the 2,4,6-tris(dimethylaminomethyl)phenoxide could also act as an efficient bridging "pincer" ligand. The reaction between $Cu(O\text{-}tamp)_2$ and $Ba_4(thd)_8$. (1:1 Ba:Cu stoichiomety) in hexane afforded $[BaCu(thd)_2(O\text{-}tamp)_2(H_2O)]$ (**11**) [Fig. 8(b)]

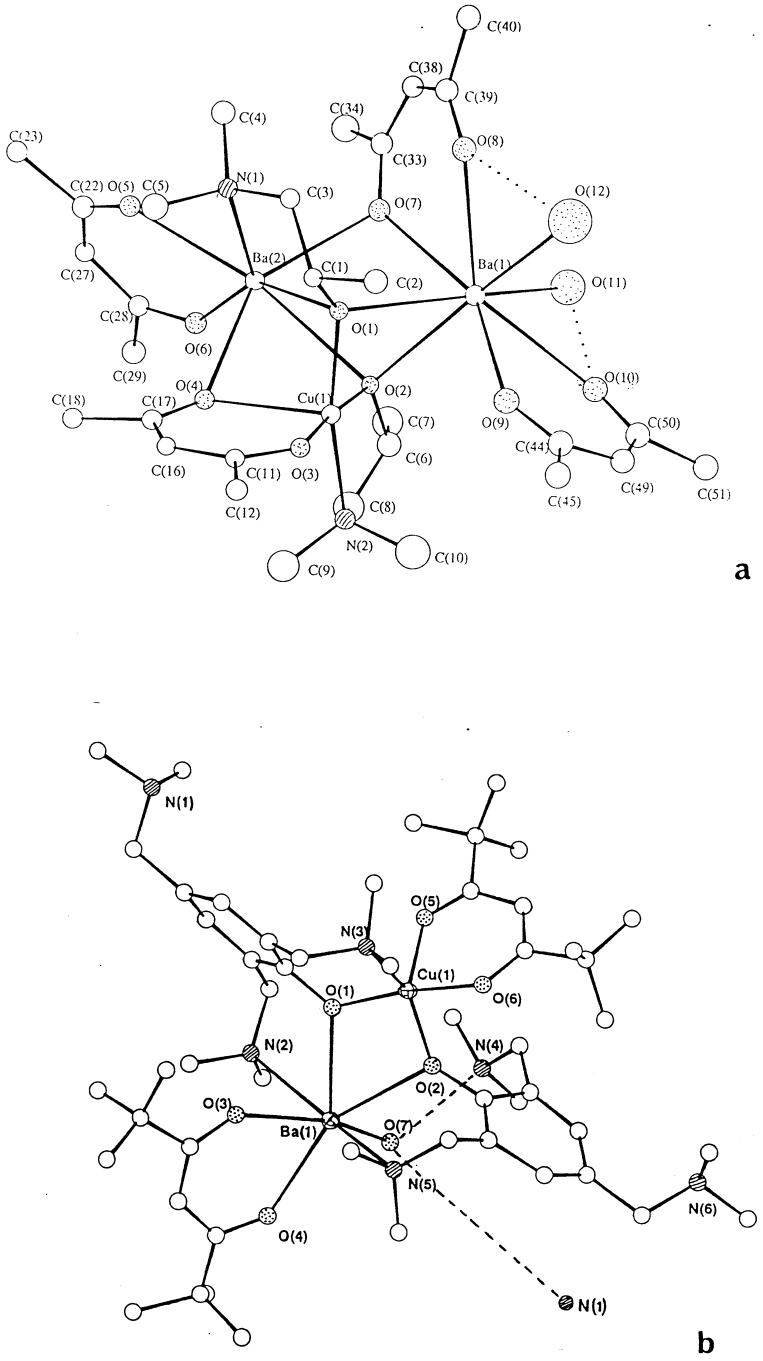
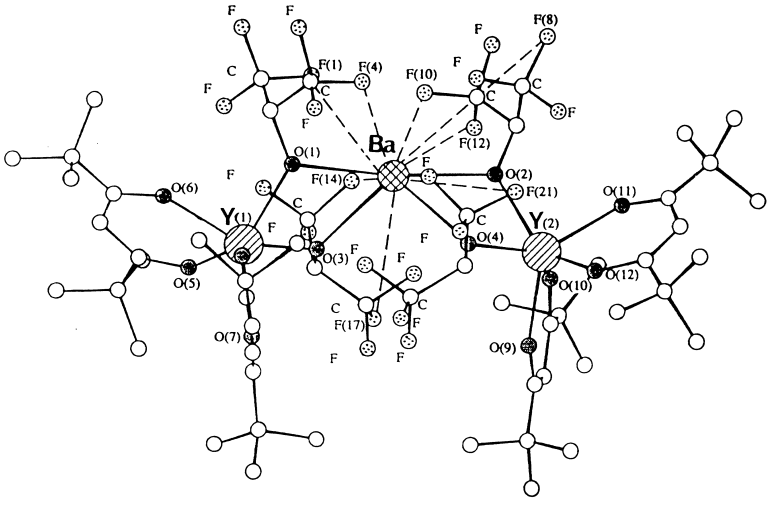


Fig. 8. (a) Molecular structures of Ba–Cu heteroleptic species: (a) $[Ba_2Cu(\mu_3,\eta^2\text{-}OR_N)_2(\mu,\eta^2\text{-thd})_2(\eta^2\text{-thd})(Pr^iOH)_2]$; (b) $[BaCu(thd)_2(O\text{-tamp})_2(H_2O)]$ Ba · · · Cu = 3.680(3); Ba–O = 2.57(2), 2.67(1), 2.11(2); Cu–N = 2.14(2).

[7,8]. The presence of water favors crystallization in high yield (90%), but is not necessary for the formation of a Ba–Cu derivative. Each metal bears a chelating tetramethylheptanedionate ligand, the aryloxide ligands act as assembling moieties via the oxygen atom, but the metals are also clamped together by the nitrogen donor functionalities. The Ba–N(2) and Cu–N(3) coordination bonds lead to a tridentate aryloxide. The other aryloxide is of μ,η^2- type and only one nitrogen center acts as an effective Lewis base. As observed for (**10**), the additional neutral ligand is linked to barium. The barium atom is seven-coordinate and the copper center five-coordinate with a tetragonal pyramidal surrounding. The steric crowding around barium makes the compound air stable but the presence of intermolecular hydrogen-bonding with the adjacent nitrogen sites of the aryloxide is prejudiciable to its volatility. The difference in the stoichiometry and, thus, in the structure of the Ba–Cu β-diketonatoalkoxide species (**10**) and (**11**) is probably related to the higher nuclearity of the initial mixed-metal species [before the addition of isopropanol for (**10**)] and, thus, on the number of donor sites and/or bulk of the alkoxide type ligand.

3.2. Access to volatile mixed-metal species?

Requirements for classical MOCVD imply the use of assembling ligands forming strong bridges between the metals. The tendency of fluorinated alkoxide ligands to form secondary M···F interactions for oxophilic metals can be exploited for an increase of the stability. Indeed, such ligands have been able to retain the association between different metals in the vapor phase and to stabilize volatile species [9,10]. This is best illustrated with systems related to high T_c superconductors. Volatility and stability can be tuned by modification of the coordination sphere by chelating ligands such as β-diketonate ones for instance as illustrated with Y–Ba fluoroisopropoxide species. $[Ba_2Y(HFIP)_7(THF)_3]$ is volatile (200 °C/10^{-3} Torr, decomposition ≈ 200 °C), whereas $[Y_2Ba(thd)_4(\mu\text{-}HFIP)_4]$ (**12**) sublimes at 150 °C/10^{-3} Torr, but decomposes at only 170 °C. Other volatile heterometallic species, namely $[BaCu_2(thd)_2(HFIP)_4]$ (**13**) and $[YCu(thd)_3(HFIP)_2]$ (**14**) have been obtained in high yield [127]. Their vapor pressures are higher than those observed for homometallic tetramethylheptanedionates (Fig. 9a) and the association between the metals is retained in the vapor, as shown by mass spectrometry. Secondary Ba···F bonds complement the barium coordination sphere, allowing the metal to reach a coordination number of 12. The Ba^{2+} center is actually encapsulated between two $Y(HFIP)_2(thd)_2$- units (Fig. 9b). The coordination sphere of the central barium atom can be modified by various Lewis bases, decreasing the number of Ba···F interactions due to the fluoroisopropoxide groups which, in fact, act as hemi-labile ligands. Complexes such as $[Y_2Ba(thd)_4(HFIP)_4L_2]$ (L = TMEDA or Me_2CO) have been isolated [127]. The stability and volatility of the Y_2Ba species can, thus, be tuned and the temperature window for effective use increased. One can also notice that Ba···F interactions in the solid state and/or in the vapor phase do not always imply fluoride residues in the final material. However, large differences in the stability are observed for the two mixed-metal precursors, (**13**) and (**14**), required for the $YBa_2Cu_3O_{7-x}$ composition and the



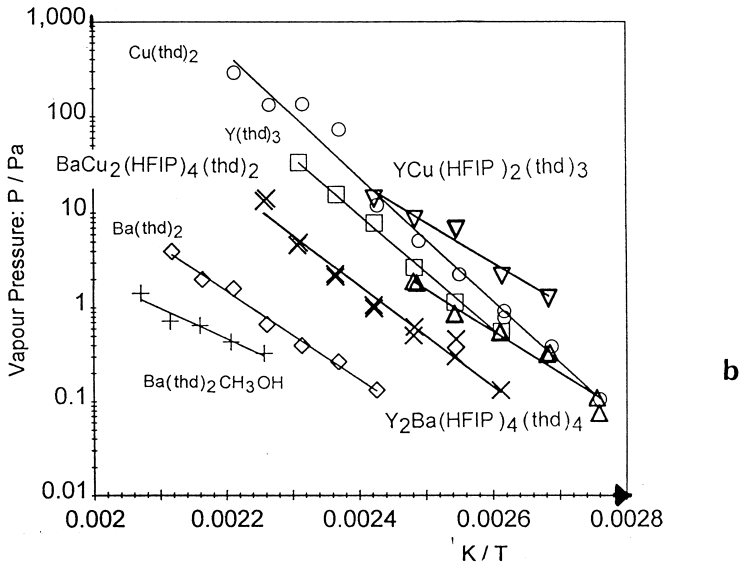


Fig. 9. (a) Molecular structure of $Y_2Ba(thd)_4(HFIP)_4$; (b) comparison of the vapor pressure data with these of the homoleptic tetramethylheptanedionates.

parameters for the obtaining of films are, thus, difficult to adjust. Most of the YBa species are hygroscopic; $[Y_2Ba(thd)_4(HFIP)_4(THF)_2(H_2O)]$ has for instance been obtained, and this affects the long-term stability and the reproducibility of the thermal behavior. Another feature is that superconducting properties of the layers

derived from fluorinated precursors are generally poor, even in the absence of fluoride contamination. The concept of the use of fluorinated ligands for improving volatility has, thus, strong limitations for oxide materials. Fluorinated precursors can, however, find applications for fluoride glasses or photonic materials [128,129].

If β-diketonate ligands are a means to increase volatility, they can also favor segregation between the metals in solution. The use of THF acting as a Lewis base can be sufficient for dissociation into homometallic species in the case of simple OR groups such as tertiobutoxide [126], especially if copper is one of the metals. Mixed-metal β-diketonatoalkoxides based on functional alkoxides are more stable toward dissociation. Reactions between β-diketonates and copper aminoalkoxides were, thus, investigated. Subtle differences in the alkoxide group can, however, affect the course of the reaction as illustrated by the Y–Cu and Pr–Cu systems [7,8]. The mixing of $Y(thd)_3$ and $Cu(OCHMeCH_2NMe_2)_2$ provides a single species, $YCu(thd)_3(OR_N)_2$, by self-assembly. The use of $Cu(OC_2H_4NMe_2)_2$ leads to the formation of a mixed-metal species, but also of yttrium and copper β-diketonatoalkoxides resulting from redistribution reactions. Two mixed-metal species of different stoichiometry (1:1 and 1:2) have been isolated for the Pr–Cu system. The copper-rich derivatives, $PrCu_2(thd)_3(ORn)_4$ sublimes (140 °C/10^{-4} Torr) with elimination of copper alkoxide giving the more stable $PrCu(thd)_3(ORn)_2$ species. Its structure (Fig. 10) shows that the aminoalcohol acts as an assembling μ,η^2-ligand. The nitrogen donor sites interact with the lanthanide, allowing the metal to be eight-coordinate. The diketonate ligands are terminal and chelating. A benefit of these heterometallic species is their stability toward moisture

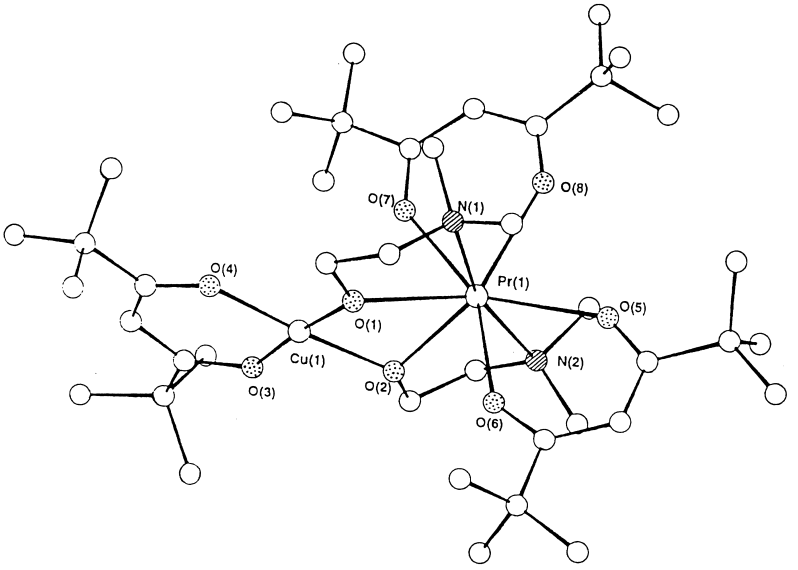


Fig. 10. Molecular structure of $PrCu(\mu,\eta^2\text{-}OCHMeCH_2NMe)_2(\eta^2\text{-}thd)_3$. Selected distances (Å): Pr· · ·Cu = 3.345(1); Pr–N = 2.695(9) av.; Pr–O = 2.368(7)–2.460(7); Cu–O = 1.896(7)–1.910(7).

by comparison to the hygroscopic nature of $Y(thd)_3$ or $[Pr_2(thd)_6]$ and the hydrolysable character of copper alkoxides. The mixing of an appropriate set of precursors can, thus, be a means to enhance the stability of the metallic species, for instance, for AACVD applications. The volatility of the $MCu(thd)_3(OR_N)_2$ (M = Pr, Y) species (sublimation 130 °C/10^{-4} Torr and 150 °C/10^{-4} Torr, respectively) is also compatible with their use for conventional CVD. These compounds represent, to the best of our knowledge, the first examples of volatile and structurally characterized mixed-metal β-diketonatoalkoxides supported by non-fluorinated ligands.

3.3. Toward control of the stoichiometry?

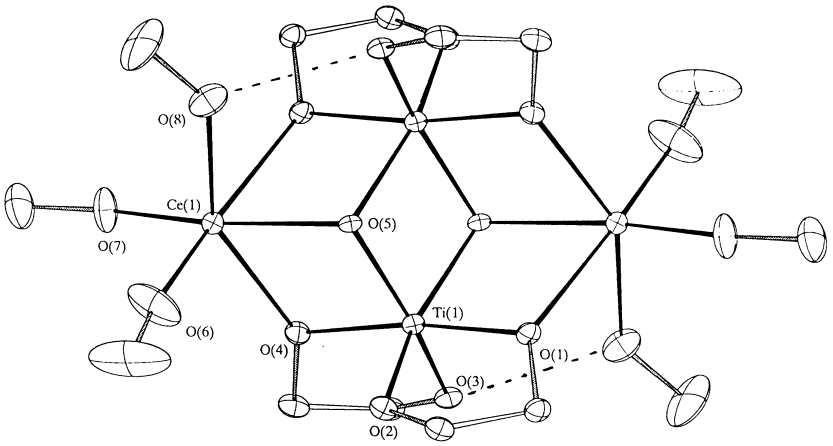
The target of the synthesis of "single-source" precursors is a species in which the metals display the stoichiometry required by the formulation of a specific material. Control of the stoichiometry for the association of two different metals supposes using the reactivity of a functional group. Metathesis reactions imply metal halides and an heterometallic alkoxide usually based on an alkali metal. Such synthons remain limited for functional alcohols. A more versatile approach is to take advantage of the reactivity of coordinated ligands and, thus, to use metalloligands. A number of metal alkoxides are isolated as solvates. Typical examples are isopropoxides such as for instance $M_2(OPr^i)_8(Pr^iOH)_2$ (M = Zr, Hf, Ce, Sn) or butoxides such as $Ln_3(O^tBu)_9(^tBuOH)_2$ (Ln = Y, La, etc.). The acidity of the hydroxyls is enhanced by coordination. This enables their reactivity with species having labile ligands such as silylamides, alkyl derivatives or even electropositive metals such as barium [130–132]. The synthetic utility of such solvates has been reported.

What about the availability of solvates based on functional alcohols? The addition of diols or polyols in appropriate stoichiometry to metal alkoxides might afford species whose IR spectra show the presence of absorption bands attributed to residual hydroxyl functionalities. These are often broad, suggesting hydrogen bonding which is also responsible of the frequent insolubility observed for such species. Are these hydroxyl functionalities latent sites of reactivity? Is the control of the stoichiometry effective? These are some of the questions which have to be addressed.

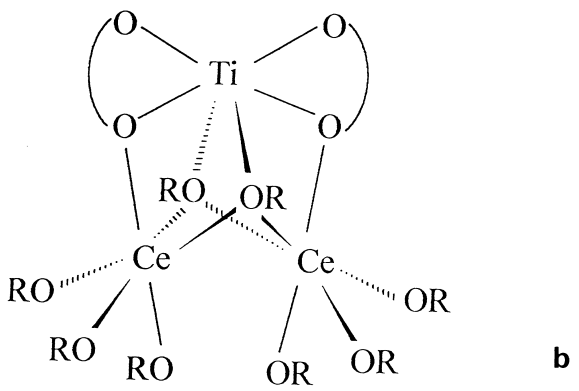
The reaction between the insoluble lanthanum atrane $[La(tea)_2H_3]_m$ and niobium isopropoxide illustrates the potential of this approach [133]. The reaction proceeds smoothly at room temperature in a non polar solvent such as toluene giving $La(tea)_2Nb_3(OPr^i)_{12}$ (Eq. (2)). The constrained triethanolamine directs the topology of the complex, the central atrane acting as a template for the assembly. The complex is also volatile. However, if triethanolamine is valuable for stabilization toward moisture, the relatively high temperatures required for elimination of this tetradentate ligand are less attractive. The well-known $LaLi_3(BINO)_3$ catalyst which displays a similar stoichiometry was prepared in one step from lanthanum isopropoxide by exposure to three equivalents of BINO and addition of three equivalents of butyllithium [128,129]. It can be considered as resulting from the elimination of butane between $La(BINO)_3H_3$ and the lithium alkyl.

$$La(tea)_2H_3 + 3Nb(OPr^i)_5 \rightarrow LaNb_3(tea)_2(OPr^i)_{12} + 3Pr^iOH \quad (2)$$

Alternatives using more thermally labile polyols were also investigated [75,76]. The reaction between a cerium pinacolate of empirical formula $[Ce_2O(pin)_4H_2]_m$ and titanium isopropoxide is another example of the strategy (Eq. (3)). $Ce_2Ti_2O_2(pin)_4(OPr^i)_4(Pr^iOH)_2$ (**15**) was obtained and structurally characterized [Fig. 11(a)]. The overall Ce_2Ti_2 framework corresponds to the usual rhombus observed for derivatives of 1:1 stoichiometry, with pinacolate and trigonal oxo moieties as assembling ligands. By contrast with the LaNb system, the reaction



a



b

Fig. 11. (a) Molecular structure of $Ce_2Ti_2O_2(\mu,\eta^2\text{-pin})_4(OPr^i)_4(Pr^iOH)_2$, dotted lines indicate H-bonding [O(8)···O(3′)=2.73 Å]. Other distances (Å): Ti···Ti=3.050(3); Ce···Ti=3.40(2); Ce–O= 2.051(7)–2.431(7); Ti–O=1.856(6)–2.026(6); (b) structure of $Ce_2Ti(pin)_2(OPr^i)_8$.

proceeds with notable modification, namely redistribution of the pinacolate and isopropoxide ligands between the two different metals and generation of another oxo ligand. The electroneutrality of (**15**) implies the presence of two remaining hydroxyls. The Ce–O bond lengths and small Ce–O–C angles are in the favor of two isopropoxide being actually isopropanol molecules. The hydrogens interact also with the adjacent oxygens of the pinacolate ligands. Despite all these modifications, the stoichiometry is dictated by complete deprotonation of the pinacolate ligand. The dissolution of titanium pinacolate $[Ti(pinH)(pin)(OPr^i)]_m$ in the presence of cerium isopropoxide $Ce_2(OPr^i)_8(Pr^iOH)_2$ proceeded in a 1:1 stoichiometry affording $Ce_2Ti(pin)_2(OPr^i)_8$ (Eq. (4)). Unfortunately, no suitable crystals could be grown so far for X-ray studies. Variable temperature ^1H NMR data are consistent with a $Ce_2Ti(\mu,\eta^2\text{-pin})_2(\mu_3\text{-}OPr^i)_2(OPr^i)_6$ structure [Fig. 11(b)] in which all metals are six-coordinate, as observed for the Ce_2Ti_2 species. The assembly between these two homometallic fragments requires less structural modifications than for the previous example. An analogous synthetic route was used for a Ce_2Nb_2 species which was prepared by reacting $Nb_2O(pin)_4H_2(OPr^i)_2$ and $Ce_2(OPr^i)_8(Pr^iOH)_2$. The pinacolate ligands remain on the niobium centers. The interesting feature of all those reactions is that, whereas no reactions were observed between $Ce_2(OPr^i)_8(Pr^iOH)_2$ with either $Ti(OPr^i)_4$ or $Nb(OPr^i)_5$ at room temperature, the presence of pinacolate ligands in the metal coordination sphere of any of the metals allows the building up of mixed-metal species in mild conditions. The reactions proceed in higher yields if no ligand exchange reaction is necessary in the process.

$$1/m[Ce_2O(pin)_4H_2]_m + 2Ti(OPr^i)_4 \rightarrow Ce_2Ti_2O_2(pin)_4(OPr^i)_4(Pr^iOH)_2 + \ldots \quad (3)$$

$$1/m[Ti(pinH)(pin)(OPr^i)]_m + Ce_2(OPr^i)_8(Pr^iOH)_2 \rightarrow Ce_2Ti(pin)_2(OPr^i)_8 + 3Pr^iOH \quad (4)$$

Dangling donor functionalities can a priori also be exploited as reactive sites for the anchoring of another metal. The preceeding examples with amino donor sites show, however, that the control of the stoichiometry is quite limited. Better control of the stoichiometry is achieved when the dangling donor sites have characteristics inappropriate for coordination to the initial metal (i.e. hard metal and soft donor).

4. Conclusions and outlook

Functional alkoxide ligands are easily accessible and can serve several purposes such as achieve solubility and stabilize the metallic species toward oxidation, handling and/or undesired precipitation during the polycondensation process. O,N chelation and, thus, aminoalkoxides are usually more effective than alkoxyalkoxides in decreasing hydrolysis rates, breaking aggregation and, thus, for inducing volatility. Higher coordination numbers are generally achieved by using functional ligands. 2-methoxyethoxide ligands and diolates such as pinacolate or ethyleneglycolate can

display a large number of coordination modes and, thus, give rise to aggregates of various frameworks and nuclearity.

Mixed-metal species show frameworks similar to those observed with usual alkoxide ligands, since the geometry is essentially governed by the stoichiometry between the metals. The reactivity of coordinated ligands namely alcohols has proven an useful way to control the geometry between metals for usual OR groups provide the solvate is stable in solution. The same strategy is less operative for functional alcohols, since solvates are often heteroleptic species and ligands redistribution reactions might modify the issue of the reaction. Selectivity is recovered for less labile systems such as these based on the constrained triethanolamine. Glyoximes are other ligands which can serve the same purpose. The versatility of coordination modes of functional alkoxides with dangling donor sites, the excess of coordinative ability can actually be a hurdle for control of the MM′ stoichiometry. Classical routes based on metathetical reactions appear, thus, preferable if a specific stoichiometry is needed. The development of metal alkoxides with unsaturated groups is still in its infancy, but growing interest is expected in view of the numerous applications which can be envisioned. Pyrolysis of precursors based on functional alkoxides has a potential for access to non-oxide ceramics [6,134] and should be further exploited.

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