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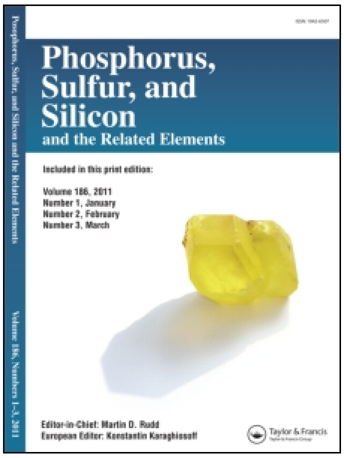

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Escapade into Metal Alkoxide Chemistry: Control of Aggregation Via Oxo and Hydroxide Ligands

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The high coordination numbers required by large elements (Ln, Ba...) favor the formation of closo oxo aggregates by desolvation of $M(OR)_n(ROH)_x$ solvates and subsequent non-hydrolytic condensation. Pentanuclear M_5O cores display a remarkable stability for large elements and can associate along an edge or an apex. Heteronuclear arrays are thus accessible from these aggregates by Lewis acid-base reactions or, for a better control of stoichiometry between the metals, by reactivity of the coordinated alcohol of a solvate. Functionalisation by polymerisable O-donors such as allylacetatoacetate (HAAA) provides species which can be converted into organic-inorganic arrays by copolymerisation reactions.

Keywords: metal alkoxides; clusters; polymerisable ligands; sol-gel; organic-inorganic

1. INTRODUCTION

Metal alkoxides are used as synthetic platforms for catalysis, organic synthesis and in material science as soluble and volatile precursors of metal oxides in chemical routes to advanced materials.[1] The structural characterization in the solid state of this class of compounds has only blossomed recently. This has led to reformulation of many homoleptic, *a priori* simple compounds- especially those based on large elements, to a better understanding in the "aging" processes and to insights in their transformation into more extended arrays.

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Homoleptic metal alkoxides are well known for their oligomerisation. The trend is however the formation of closo aggregates rather than rings and the decanuclear Y methoxyethoxide $Y_{10}(\eta^1\text{-}OR)_{10}(\mu,\eta^2\text{-}OR)_{20}$ ($R = C_2H_4OMe$) remains, after a decade, the largest $M(OR)_n$ oligomer.[2] The formation of closo aggregates is promoted by the μ,η^3- coordination mode of the OR ligand as well as by the facile formation of oxo ligands. Reactivity of these aggregates allows further tailoring -incorporation of another metal, of a functionality - and thus to meet material science needs. These aspects will be illustrated with representative examples mostly on lanthanides all based on high yield transformations.

2. DESOLVATING AND LINKING: FORMATION OF CLOSO HOMOMETALLIC AGGREGATES

Most metal alkoxides are prepared with excess of alcohol giving solvates. Although coordination of the alcohol molecules is assisted by intramolecular hydrogen bonding, these ligands are often labile, their loss during isolation can lead to a simple increase of oligomerization but also to drastic structural changes in the case of large elements. The first and most salient example was provided by the reformulation of yttrium isopropoxide as a pentanuclear oxoisopropoxide $Y_5O(OPr^i)_{13}$ **1**. Desolvation proceeds stepwise with successive isolation (and structural characterization) of the non-oxo $[Nd_4(\mu_3\text{-}OR)_2(\mu\text{-}OR)_4(OR)_6(ROH)_4]$ solvate, the oxoalkoxide solvate $[Nd_5(\mu_5\text{-}O)(OR)_{13}(ROH)_2$ [assembly between $Nd_4O(OR)_{10}$ and $Nd(OR)_3(ROH)_2]$ and the final $Ln_5(\mu_5\text{-}O)(\mu_3\text{-}OR)_4(\mu\text{-}OR)_4(OR)_5$ unit ($R = Pr^i$. A common feature of all species is the hexacoordination of the metal.[2]

This Ln_5 unit, a quite regular square pyramid with an encapsulated oxo ligand, (fig 1) is actually a basic framework for isopropoxides of heavy metals (M = Ln(III); Sc, In [3]). The oxo ligand is more versatile in terms of stereochemistry than a classical alkoxide ligand and can assemble up to six metals. The M_5 framework has also been observed for barium and recently for strontium [4]. Functional alkoxide ligands such as $OCH(CF_3)_2$ [5] or $OCHMeCH_2NMe_2$ [6] in association with the oxo ligand allow barium to reach high coordination numbers and solubility .

Thermal condensation of $La_3(O^tBu)_9(^tBuOH)_2$ affords the same framework and the first example for t-butoxides [7]. The formation of a

Zr nitridoimido cluster $Zr_5(\mu_5\text{-}N)(\mu_3\text{-}NH)_4(\mu\text{-}NH_2)_4(OCtBu_3)_5$ furthermore illustrates the special stability of this pentanuclear framework with a variety of ligands [8].

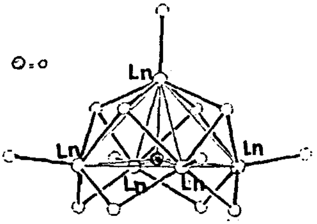


FIGURE 1: Molecular structure of $Ln_5O(OPr^i)_{13}$ (solid state and solution)

Solvates of tetravalent metal isopropoxides are more stable than those based on trivalent metals as illustrated by the isolation of $M_2(\mu\text{-}OR)_2(OR)_6(ROH)_2$ (M = Zr, Hf, Ce, Sn) [9]. However transformation of the cerium derivative **2** occurs already by heating the solid at 70°C for 15 mn giving $[Ce_4(\mu\text{-}O)(\mu_3\text{-}OR)_2(\mu\text{-}OR)_4(OR)_8]$ ($R = {}^iPr$) by assembly of two desolvated and thus unsaturated dimeric units along faces [10]. This process (eq. 1) generates a tetrahedron with a central oxo ligand and allows two of the Ce atoms to increase their coordination numbers from six to seven.

$$2Ce_2(OR)_8(ROH)_2 \rightarrow Ce_4(\mu\text{-}O)(\mu_3\text{-}OR)_2(\mu\text{-}OR)_4(OR)_8 + 4\ ROH + 2\ R_2O \qquad \text{(eq 1)}$$

The oxo ligand, difficult to detect since silent to usual spectroscopies such as ^1H or ^{13}C NMR, can originate by accidental hydrolysis, oxidation by dioxygen or ligand desoxygenation reactions. The preceeding example with elimination of dialkylether and alcohol supports desoxygenation, and thus non-hydrolytic condensation pathways.

3. TOWARD HETEROMETALLIC AGGREGATES

The formation of heterometallic species which can act as "single-source" precursors to multimetallic oxides is generally achieved by Lewis acide base reactions between alkoxides or other sources of oxides (carboxylates, β-diketonates) [11]. The stereolability of the M_5O_{14} core allows such reactions to proceed even at room temperature. X-Ray studies have proven that the pentanuclear core is retained in $YPr_4O(OR)_{13}$ and $TiSm_4O(OR)_{14}$ but the frameworks are different due to the versatility of the μ_5-oxo ligand, tetragonal pyramidal in the former, trigonal bipyramidal in the latter. The Ti-Sm species can be seen as a complex between the butterfly $Sm_4O(OR)_{10}$ moiety and $Ti(OR)_4$, the donor site being the oxo ligand. Similar species were obtained with $Ti(OR)_3Cl$ or $Zr_2(OR)_8(ROH)_2$. These species allow homogeneous incorporation of lanthanides into high indexes oxide matrices such as TiO_2 or ZrO_2 but, with the exception of the dimeric Ln-Zr aggregate, do not account for extension of the arrays. The structural complexity of the Ln_5 "monomer" can make characterization of the mixed-metal species tedious in the absence of single-crystals. The reaction between **1** and barium isopropoxide (reactants used for high Tc superconductors) provides an example. EXAFS studies associated with analytical and NMR (^{89}Y NMR: 217 and 214 ppm, 1:4) data account for retention of the Y_5 core. EXAFS data [Y(K) and $Ba(L_{III})$ edges] indicate that both metals are 6-coordinate in an Y-Ba array (Y....Ba distance of ~ 4.30 Å) (fig 2) in which square pyramids are connected by edges [12]. This array might originate from the assembly of the Y_5 core with two $Ba_3(OR)_6$ moieties. A fragment of such an array was actually observed by X-Ray for $Ba_2Sr_6O_2(OPh)_{14}(HMPA)_6$[13]

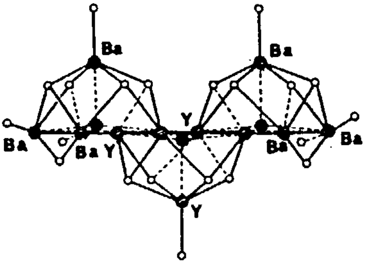


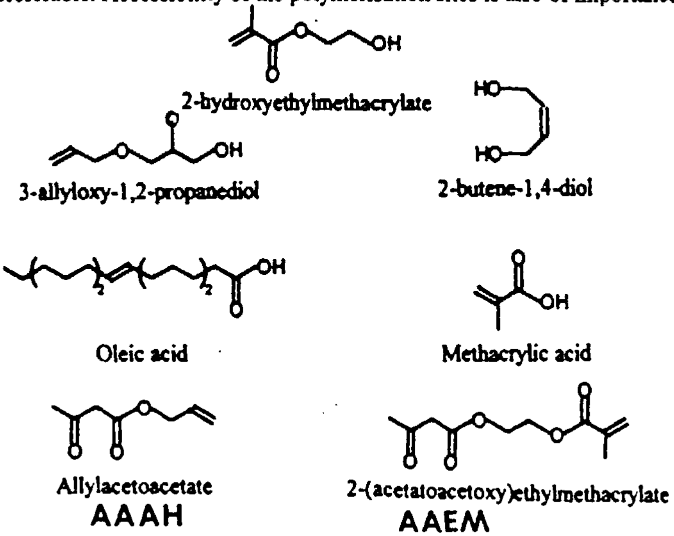
FIGURE 2 Structure of $Y_5Ba_6(\mu_5\text{-}O(\mu_3\text{-}OR)_{12}(\mu\text{-}OR)_2(OR)_7$ R= Pr^i

Lack -for some systems- of formation of heterometallic species by simple mixing as well as lack of control over the stoichiometry between the metals are the main drawbacks of the material science approach [11]. The connectivity between the metals can be forced by using the reactivity of a coördinated ligand and a reactive species of the other metal. Coordinated alcohol is the ligand of choice in terms of availability of reagents and by-product formation, allowing to proceed in situ. Thus whereas no Ba-Ce species could be formed by mixing **2** and barium isopropoxide, a species of the expected stoichiometry $[BaCe_2(OR)_{10}]_2$ was isolated with barium chips (eq 2). Its structure, based on 6-coordinate metals corresponds to the assembly of two triangular units deriving from the "trapping" of a barium atom by the two ROH ligands of **2**, whose acidity is enhanced by coordination [14]. Further tailoring of the properties (stability toward segregation for instance) of the heterometallic array can be achieved with polyols whose coordination modes- bridging-chelating- reinforces the assembly. Topological control can even be achieved if a constrained polyol such as triethanolamine is selected [2].

$$2\ Ce_2(OR)_8(ROH)_2 + 2Ba \rightarrow [BaCe_2(\mu_3\text{-}OR)_2(\mu OR)_3(OR)_5]_2(\mu\text{-}OR)_2 + 4\ ROH \qquad (eq\ 2)$$

4. ALKOXIDES WITH POLYMERISABLE LIGANDS: TOWARD ORGANIC-INORGANIC MATERIALS

Extended inorganic arrays derived from alkoxides result from formation of M-O-M bonds via hydrolytic or non-hydrolytic routes. Homo- or copolymerisation reactions involving an unsaturated ligand Z are required for extended organic arrays and access to hybrid materials [1b,c]. If covalent association between the networks is a goal, the M-Z linkage should resist to processing conditions and be stable thermodynamically and kinetically. This is achieved via Si-C bonds for silicon, but via oxygen for most other elements. Scheme 1 collects some common unsaturated ligands. Chelating or bridging-chelating ligation is preferable. Accessibility of the polymerisation sites is also of importance.



2-hydroxyethylmethacrylate

3-allyloxy-1,2-propanediol

2-butene-1,4-diol

Oleic acid

Methacrylic acid

Allylacetoacetate
AAAH

2-(acetatoacetoxy)ethylmethacrylate
AAEM

Scheme 1: Some unsaturated O-donor ligands

. β-diketones and related ligands are more prone to act as terminal-chelating ligands than as bridging ones and have thus been used as polymerisation lockers in sol-gel science [1a-c]. The reaction between $Y[N(SiMe_3)_2]_3$ (or **1**) and allylacetatoacetate (HAAA) (stoichiometry 1/3 and 1/13 respectively) afforded $Y_4(OH)_2(AAA)_{10}$, **(3)** whose structure (NMR evidence) is related to that of $M_4(\mu\text{-}OH)_2(acac)_{10}$ (M = Y or Nd) in which the 8-coordinated metals are in a plane.[2] **3** results probably from partial hydrolysis of $Y(AAA)_3$ giving $Y_2(OH)(AAA)_5$ which dimerises via hydroxo and AAA ligands. A cheaper route (used for bulky β-diketones) applied to $Y(NO_3)_3{,}6H_2O$, HAAA and NaOH in ethanol afforded $[Y_9(\mu_4\text{-}O)_2(\mu_3\text{-}OH)_8(\mu,n^2\text{-}AAA)_8(n^2\text{-}AAA)_8]^-$ (fig 3) [15]. This anion can be seen formally either as the assembly of two $Y_4(OH)_4(AAA)_8$ units resulting from hydrolysis of **3** (with loss of two bridging AAA ligands) connected by a YO_2^- anion or as two square pyramids connected by an apex. This molecular oxohydroxo cluster is related to $[Er_6(\mu_6\text{-}O)(\mu_3\text{-}OH)_8(H_2O)_{24}]^{8+}$ obtained by hydrolysis of $Er(NO_3)_3$ in basic aqueous media in the absence of additional ligands.[16] The AAA ligands skirting the basal plane of the square pyramid (as do the OR ligands in **1**) prevent aggregation to an octahedron.

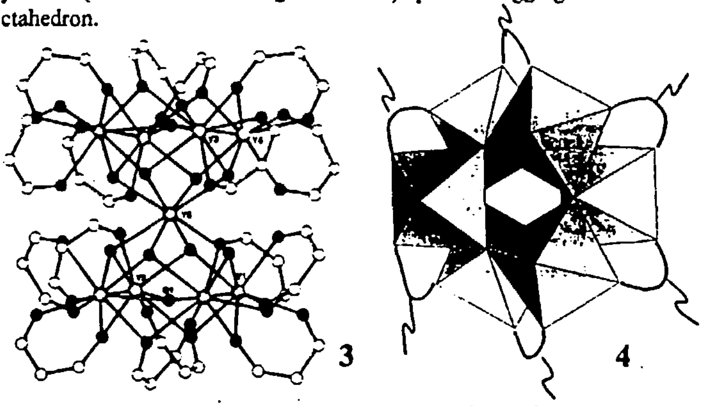


FIGURE 3: Oxo aggregates with polymerisable functionalities, $[Y_9(\mu_4\text{-}O)_2(\mu_3\text{-}OH)_8(\mu,n^2\text{-}AAA)_8(n^2\text{-}AAA)_8]^-$ (3) and $Ti_6(\mu_3\text{-}O)_3(\mu\text{-}O_2CR')_6(OR)_6$ (4)

Carboxylic acids are an alternative for introduction of polymerisable sites in a metal coordination sphere. The reaction between oleic acid and $Ti(OPr^i)_4$ (1:1 stoichiometry, azeotropic distillation) leads to an oil, $[Ti(OPr^i)_3(O_2CR')]$. The oleate ligand is also "masked " in surfactants such as monooleate sorbitan (Span 80) used for elaboration of microcellular materials [17]. $[TiO(OR)(R'CO_2)]_m$ [R' = $O_2C(CH_2)_7CH{=}CH(CH_2)_7Me$] (4) is obtained at room temperature by reacting $Ti(OPr^i)_4$ with Span 80 in hexane [18]. Preliminary results indicate that 4 is isostructural with $Ti_6O_6(OR)_6(R'CO_2)_6$ (R' = 2-phenoxybenzoate or acetate) (fig 3) [19]. The assembly of two staggered triangular units built by sharing vertices of octahedra and connected by carboxylates, minimizes steric repulsion for the aliphatic chains and provides a surrounding of three oxo ligands (at the shared edges) for Ti.

3 and 4 can be considered as oxides wrapped with polymerizable ligands. FT-IR data show that the unsaturated functionality ($\nu C{=}C$ at 1735 cm^{-1} for instance for 4) does not interact with the metal and should be available for further reactivity. Differential hydrolysis with respect to the OR ligand is observed in all cases [20]. ^1H NMR monitoring of Ti and Y derivatives allowed to establish a ranking in the hydrolytic susceptibility of the M-Z linkage namely AAEMA ~ AAA <acac << butenediolate (acac = acetylacetonate). The β-ketoesterate ligands as represented by 2-(methacryloyloxy)ethylacetatoacetate (AAEMA) and AAA- are actually quite labile. [18]

Homopolymerisation has been conducted in the presence of a radical initiator. As expected, the highest conversions were observed for the compounds whose unsaturated functionalities are the most accessible.[18] Copolymerisation with monomers such as styrene and divinylbenzene in the presence of Span 80 as surfactant for stabilisation of inverted emulsions was also investigated. The highest incorporation of metal oxide (with respect to added precursor) was observed for 4 which presents an unsaturated functionality similar to that of the surfactant; but also a high oxo surrounding which might increase the stability of the metallic species in processing conditions.

5. CONCLUSION

Large oxophilic metals have a trend to form soluble polynuclear oxo (or hydroxo) aggregates wrapped in an organic surrounding which can bear pendant functionalities. The extent of structural studies in alkoxide chemistry gives raise to the emergence of a library of building blocks and allows, to some extent, to predict their connectivity and resulting homo or heteronuclear frameworks. Among those elementary bricks, pentanuclear aggregates with an encapsulated electron rich atom display a remarkable stability. Beside stabilisation of closo aggregates, the oxo (or hydroxo) ligands allow to decrease the reactivity toward hydrolysis in accordance to material processing needs.

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