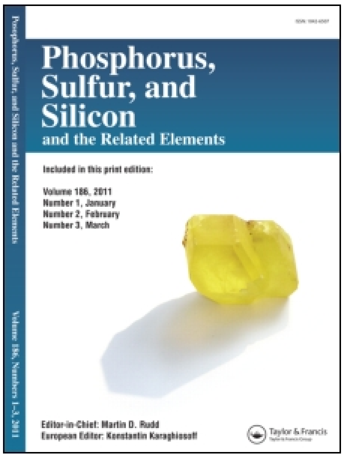

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Monoorganotin Oxo-Clusters : Versatile Nanobuilding Blocks for Hybrid Organic-Inorganic Materials

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The combination at the nanosize level of inorganic and organic components in a single material makes accessible an immense new area of materials science. Among other soft chemistry processes, sol-gel chemistry offers a versatile access to chemically designed new hybrid organic-inorganic materials. Yet, it might be inappropriate to prepare "model" hybrid materials, in which the structure of the organic and inorganic domains, together with those of their interface, are perfectly defined. Such systems, required to understand, optimize, and control the structure-properties relationship, can be alternatively prepared by assembling well-defined preformed inorganic nanobuilding blocks.

The molecular structures and syntheses of two types of organotin oxo-clusters, $\{(RSn)_{12}O_{14}(OH)_6\}^{2+}(X^-)_2$ ("Tin-12") and $\{RSnO(O_2CR')\}_6$ ("Tin-6") are presented. Various strategies to assemble them are discussed to illustrate the versatility of such nanobuilding blocks in the synthesis of hybrid systems with iono-covalent or ionic organic/inorganic interfaces.

Keywords: monoorganotin oxo-clusters; hybrid organic-inorganic materials; ^{119}Sn NMR; $\{(RSn)_{12}O_{14}(OH)_6\}^{2+}$; $\{RSnO(O_2CR')\}_6$

INTRODUCTION

Combining organic and inorganic components, over a length scale ranging from a few Angstroms to a few tens of nanometers, the so-called hybrid organic-inorganic materials have shown great potentialities in many domains such as optics, protective coatings, microionics, membranes, catalysis.[1] Very diverse systems can be considered as hybrid materials :

organic molecules (e.g. dyes) embedded in inorganic glassy matrices, siloxanes, interpenetrating organic and metal oxo-polymers, *in situ* generated nanometric inorganic fillers in organic polymers, just to mention few of them ; and therefore scientists of different communities are involved in such a topic.

The interest for these materials lies in their dual nature which has already offered improved or new properties.[1] Indeed, one can expect for such materials properties which depend not only on their dual chemical nature, but also on synergetic effects related to the very large and complex organic/inorganic interface developed in these nanocomposites. The nature of the interactions taking place at this interface has actually been used to group in two main classes the very broad spectrum of hybrid materials.[1h] Class I corresponds to all the systems where there are no covalent or iono-covalent bonds between the organic and inorganic components. In such materials, the various components only exchange interactions such as van der Waals forces, hydrogen bonding or electrostatic attraction. On the contrary, in class II materials, at least part of the organic and inorganic components are linked through strong chemical bonds (covalent or iono-covalent).

Several hybrid materials, such as polysilsesquioxanes (T-resins)[2], have been known and used for a long time, yet a tremendous increase in the variety and complexity of the combinations between organic and inorganic components has appeared over the last decade.[1] The synthesis of most of these new systems has been made possible following "soft chemistry" approaches such as sol-gel process,[3] in which the inorganic polymerization, initiated by hydrolysis, of molecular precursors, such as metal alkoxides,[4] in organic solvents and at very moderate temperatures, allows the synthesis of metal oxo/hydroxo-polymers. Chemical parameters such as the hydrolysis ratio, the use of complexing ligands or catalysts (H^+, nucleophile) allow the control of the reactions involved in inorganic polymerization. The outcomes can be as different as metal oxo-clusters, colloidal solutions (sols) or gels.[3] In this later case, the three-dimensional extension of some of the metal oxo-polymers reaches a macroscopic size trapping the solvent and smaller inorganic polymers, what results in highly visco-elastic systems.[3,5] Originally this process was, and still is, used to prepare purely inorganic materials, such as glasses or multi-component ceramics, by firing dried sols or gels.[3,6] Yet, the fairly mild chemical and thermal conditions under which a mineral framework can be generated up to the sol or gel state make the all process compatible with most of the organic components, from small molecules to polymers.[1] Inorganic and organic polymerizations can even be performed at the same time, allowing, when both components exhibit a good affinity, interpenetration of both polymers at an almost molecular level.[1a,m] The rheology of sols or gels is also a definite advantage as it generally allows one to shape hybrid systems into fibers, films or monolithic pieces, what clearly gives a status of materials.[3a] In this solution process, the final drying, during which the solvent is removed, should also be paid much attention as chemical reactions are generally not fully completed at this stage[5a] and stresses induced by capillary pressure can result in the formation of cracks in the final materials.[7]

Despite the clear advantages of sol-gel process to design new hybrid materials, some drawbacks can be mentioned. These materials generally exhibit rather ill-defined nanostructures which likely arise from size polydispersity and composition fluctuations in the components. Moreover, the control of the interactions taking place at the organic/inorganic interface can be difficult to achieve, especially in class I materials. All this has of course not limited the preparation of many hybrid materials relevant to specific applications, yet, the understanding of the structure-properties relationship might have suffered from it. Model hybrid materials of fairly well-defined composition and nanostructure are therefore of academic importance.

One way to achieve some control over the growth and morphology of inorganic materials, obtained from molecular precursors, is the use of organic templates which self organize into complex structures.[8] An other possible approach can be found in a two steps process where perfectly well-defined inorganic or already hybrid entities, named building blocks, are first prepared and then assembled in a controlled way.[9] For this goal, metal oxo-clusters represent versatile building blocks in the nanometric size domain, as exemplified by the materials build from the $[RSiO_{1.5}]_8$ cubane type derivatives.[9] Two important points should be kept in mind in this approach : i) the existence on the building blocks of at least one function which will allow one to assemble, or even better self assemble, these discrete species into a material, ii) the structural stability of the building blocks all along the process. Actually, this strategy is somehow closely related to the approach classically used in polymer science : the synthesis of complex monomers, from basic chemicals, followed by a controlled polymerization step.

On an academic point of view, tin based compounds are interesting for hybrid organic-inorganic materials as tin gathers several chemical features. Tin and sp^3-carbon form fairly stable covalent bonds which allow an access to class II materials. Tin shares this feature with silicon which is the most studied element for hybrid materials. Moreover, tin shares also with many elements, whose oxides are of great industrial relevance (Ti, Zr, Al, etc.), some chemical behaviors such an easy expansion of its coordination number above its valence and a good affinity for many complexing ligands (carboxylate, ß-diketonates, etc.) which are commonly used to chemically link the organic and inorganic components in class II hybrid materials when the metal centers form too ionic bonds with carbon (e.g. transition metals).[10] Finally for characterization, tin derivatives can be efficiently probed by solution or solid state NMR (^{119}Sn or ^{117}Sn isotope),[11] what is of paramount importance to follow a process all the way from the precursors to the final materials.

With the concern of a nanobuilding blocks approach to hybrid organic-inorganic materials, many monoorganotin clusters of known molecular structure [12-18] could be used as long as they possess an assembling function. In this paper, examples based on two oxo-clusters, the "Tin-12" $\{(RSn)_{12}O_{14}(OH)_6\}^{2+}(X^-)_2$ and "Tin-6" $\{RSnO(O_2CR')\}_6$, will be discussed. First, their molecular structure and syntheses will be presented, then, various strategies to assemble them will be illustrated. It is interesting to note that the possible use of "Tin-6" clusters to prepare novel materials was already briefly mentioned 6 years ago by K.C. Kumara Swamy et al.[19]

STRUCTURE AND SYNTHESES OF THE NBB

The "Tin-12" Oxo-Hydroxo-Cluster

The first description of a "Tin-12" was made by H. Puff and H. Reuter when they published the structures of $\{(Pr^iSn)_{12}O_{14}(OH)_6\}Cl_2 \cdot L$ with $L = 3H_2O$, 2DMF and $4H_2O \cdot 4DMPU$.[14] Since, the structures of $\{(BuSn)_{12}O_{14}(OH)_6\}Cl_2 \cdot 2H_2O$,[16] $\{(BuSn)_{12}O_{14}(OH)_6\}(OH)_2 \cdot 4HOPr^i$[17] and $\{(BuSn)_{12}O_{14}(OH)_6\}(PTS)_2 \cdot Diox$[18] (PTS : $4\text{-}(CH_3)C_6H_4SO_3^-$) have been reported. All these compounds are based on the same "Tin-12" oxo-hydroxo-organotin core which is represented in Figure 1. The cluster core is almost spherical and contains twelve tin atoms linked by μ_3-O and μ_2-OH bridges. All the organic moieties bound to a tin point toward the outside of the Sn-O-Sn framework. Six tin atoms are five-coordinate (square pyramid) and the six others are six-coordinate (distorted octahedra). The μ_2-OH bridges are only bound to the latter. This cluster can be described by considering three subunits. The first one is a hexameric crown, "$[RSnO_2]_6$", which contains only five-coordinate tin atoms. The two others are trimers, "$[RSn(OH)]_3O$", based on six-coordinate tin atoms. The complete oxo-cluster framework is obtained by capping each side of the crown by a trimer. It is of importance to note that this cluster is a dication. The hydrogen bonds observed in the all structures, solved by single crystal X-ray diffraction, between the charge compensating anions and the bridging hydroxy groups, likely indicates that the 2+ charge is equally located at both cage poles, formed by the "$[RSn(OH)]_3O$" trimers. It is interesting to note that this molecular structure is also found for other metal oxo-clusters : $\{(Pr^iOTi)_{12}O_{16}(OPr^i)_4\}$ [20] and $\{(VO)_{12}O_{12}F_2(OH)_6\}^{6-}$.[21]

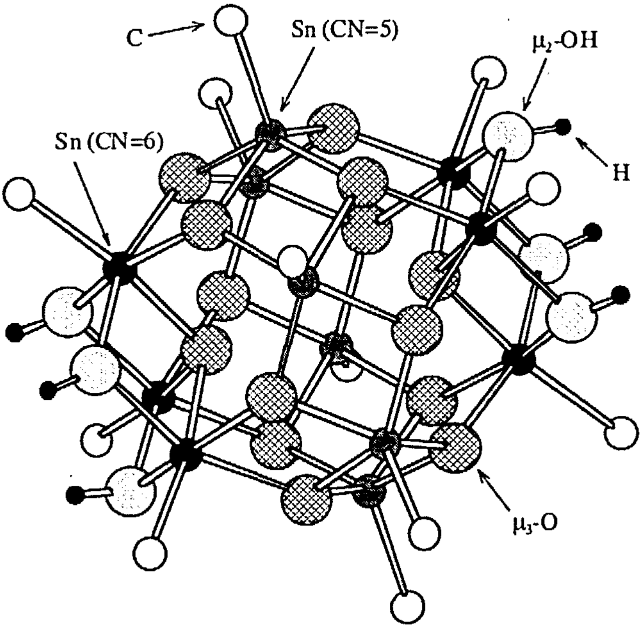

FIGURE 1 - Molecular structure of $\{(RSn)_{12}(\mu_3\text{-}O)_{14}(\mu_2\text{-}OH)_6\}^{2+}$ (only the carbon atoms directly bound to tin have been drawn).

Different crystalline compounds based on the "Tin-12" cluster have been studied by solid state ^{119}Sn NMR as they represent interesting references.[17,18,22] Figure 2 presents the ^{119}Sn MAS NMR spectra of $\{(BuSn)_{12}O_{14}(OH)_6\}(OH)_2 \cdot 4HOPr^i$ and $\{(BuSn)_{12}O_{14}(OH)_6\}(PTS)_2 \cdot Diox$. These spectra exhibit many resonances but most of them are spinning side bands, even at a rotation of 13 kHz on a 300 MHz spectrometer, and can be fully simulated by only considering chemical shift anisotropy (Fig. 2).[11c-e] Moreover, the simulation step allows the relative quantification of each site. Thus, ^{119}Sn MAS NMR on $\{(BuSn)_{12}O_{14}(OH)_6\}(OH)_2 \cdot 4HOPr^i$ shows only four unequivalent environments for tin: two at high frequency corresponding to five coordinate and two at low frequency to six-coordinate.[17] An equal amount of each coordination is observed as well as a 2:4 population ratio inside each coordination, in agreement with the inversion center and pseudo mirror plane which are present in the crystalline structure.[17] The difference in isotropic chemical shift is larger for the six-coordinate environments as they are more directly influenced by the localization of the charge compensating hydroxyl groups which are hydrogen bond to a unique μ_2-OH bridge at each pole.[17] For $\{(BuSn)_{12}O_{14}(OH)_6\}(PTS)_2 \cdot$Diox, ^{119}Sn MAS NMR shows an equal amount of five and six-fold coordination, but each split in three sites.[18] This result agrees again with the only centrosymmetric character of the structure. In this compound some of the five-coordinate tin atoms exhibit a donor-acceptor interaction with the oxygen atoms of the 1,4-dioxane molecules, what makes them more shielded.[18] Here, on the contrary to $\{(BuSn)_{12}O_{14}(OH)_6\}(OH)_2 \cdot 4HOPr^i$, each μ_2-OH bridge at the cage poles is hydrogen bonded to an oxygen atom of the sulfonate anions, making therefore the environments of the six-coordinate tin atoms very similar and, thus, the differences of their isotropic chemical shifts are quite small.[18] These two examples show that ^{119}Sn MAS NMR can not only evidence the presence of "Tin-12" clusters, but also clarify the interactions that these dications exchange with their charge compensating anions or with other surrounding molecules.

The ^{119}Sn NMR is also very informative on the behavior of "Tin-12" based compounds in solution.[16-18,23-25] The ^{119}Sn NMR spectra of $\{(RSn)_{12}O_{14}(OH)_6\}X_2$ present only two narrow resonances: one for five coordinate tin atoms at high frequency and one for six-coordinate at low frequency. Each resonance is flanked by satellites which arise from $^2J_{Sn\text{-}Sn}$ couplings correlated to the different connection paths existing between two adjacent tin atoms in the molecular structure of the "Tin-12" dications. Therefore, ^{119}Sn NMR indicates that the cluster framework is fully preserved in solution. Moreover, the presence of only two resonances indicates that structural constraints of the solid state have been released in solution, giving to the "Tin-12" clusters a D_{3d} symmetry.[16-18,23-25] Yet, the species characterized in solution, at least in solvents of low dielectric

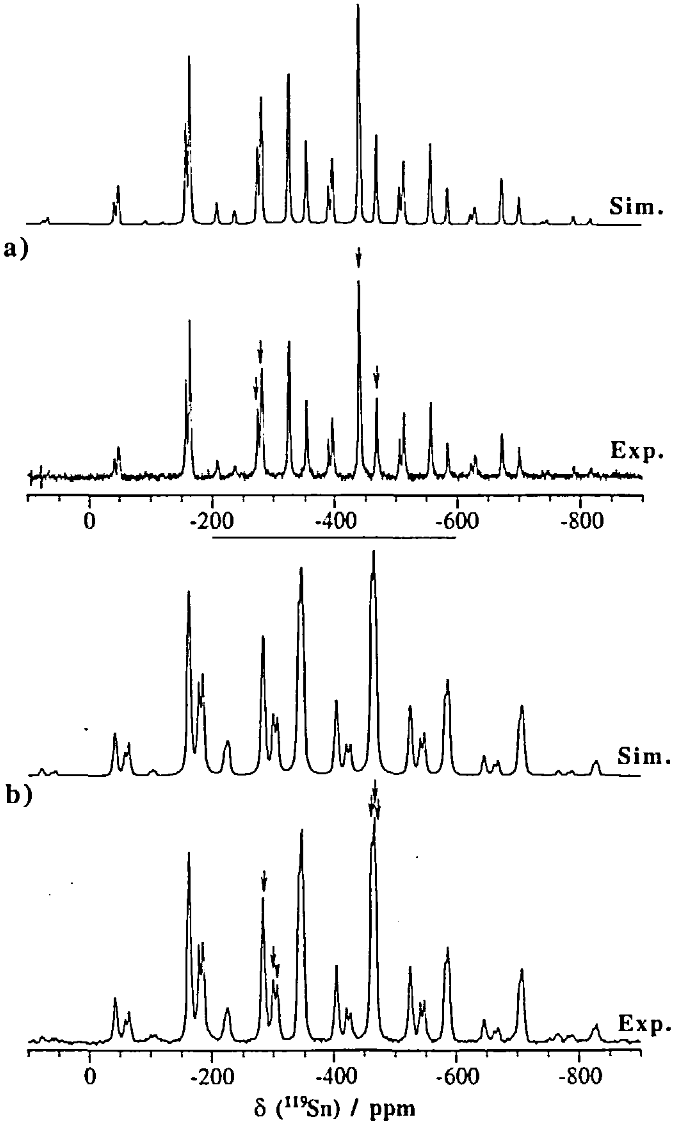

FIGURE 2 - Experimental and simulated ^{119}Sn MAS NMR spectra of (a) $\{(BuSn)_{12}O_{14}(OH)_6\}(OH)_2 \cdot 4HOPr^i$ and (b) $\{(BuSn)_{12}O_{14}(OH)_6\}(PTS)_2 \cdot$Diox, at 111.9 MHz with $\nu_{MAS} = 13$ kHz (isotropic resonances are pointed with arrows).

constant, are not free dications but ions triplets $\{(BuSn)_{12}O_{14}(OH)_6\}X_2$. Indeed, different charge compensating anions can lead to different chemical shifts, especially for the six-coordinate tin atoms which are closer to the cage poles.[16-18,23-25] The ^{119}Sn chemical shifts in solution are also in very good agreement with the averages of the isotropic chemical shifts measured in the solid state, where the anions are known to be hydrogen bond to the cage poles.[17,18,23,25] Finally, a 2D ^{31}P-^{1}H HOESY NMR experiment performed on $\{(BuSn)_{12}O_{14}(OH)_6\}(O_2PPh)_2$ has shown that, in CD_2Cl_2, the diphenylphosphinates were almost as close as they could come to the cage poles.[23]

Several syntheses of the "Tin-12" cluster have been described. They are of two types: hydrolysis-condensation of organotin molecular precursors (eq. 1-2) [14,16,17,26] or condensation of oxo-hydroxo-organotin polymers in the presence of sulfonic acid (eq. 3).[18,24]

$$RSnCl_3 \xrightarrow{H_2O/KOH} \{(RSn)_{12}O_{14}(OH)_6\}Cl_2 \qquad (1)$$

$$RSnX_3 \xrightarrow{H_2O} \{(RSn)_{12}O_{14}(OH)_6\}(OH)_2 \qquad (2)$$

$$X = OR' \text{ or } C{\equiv}C\text{-}R'$$

$$RSnO(OH) \xrightarrow{HO_3SR'} \{(RSn)_{12}O_{14}(OH)_6\}(O_3SR')_2 \qquad (3)$$

The two first reactions are fast and take place at room temperature, while the third one has to be performed at the reflux of toluene for two days. These differences arise from the higher reactivity of soluble molecular precursors compared to almost insoluble polymer species. The yield and the charge compensating anions depend on the precursor and reaction involved. The simple characterization of the crude reaction products by solution ^{119}Sn NMR generally seems to indicate that the "Tin-12" cluster is always the only formed species. Yet, quantitative solution ^{119}Sn NMR, solid state ^{119}Sn MAS NMR, size exclusion chromatography and crystallization yields are all in agreement with the simultaneous formation of ill-defined soluble organotin oxo-polymers.[18,24,27] These latter species have not been yet clearly characterized but they seem mostly based on six-coordinate tin atoms. Therefore, the preparation of pure "Tin-12" based compounds by the reactions described above always required a crystallization step to eliminate these oxo-polymers.

Exchanging the charge compensating anions can also offer an access to other "Tin-12" compounds.[23-25,28] The various studies performed on butyltin derivatives show that hydroxyl are the more versatile starting anions (eq. 4).

$$\{(BuSn)_{12}O_{14}(OH)_6\}(OH)_2 + 2\,HY \xrightarrow{-2H_2O} \{(BuSn)_{12}O_{14}(OH)_6\}Y_2 \qquad (4)$$

$$\text{for } Y = RSO_3^-, Cl^-, RCO_2^-, R_2PO_2^-$$

This reaction is total, yet with the more complexing anions (RCO_2^-, $R_2PO_2^-$) the stoichiometry has to be carefully controlled as an excess of acid results in the formation of other clusters such as $[BuSnO(O_2CR)]_6$ or $\{[BuSnOH(O_2PR_2)]_3O\}(O_2PR_2)$.[12,23,25] On the contrary, when "Tin-12" compounds with anions related to strong acids are used as starting materials ($X = Cl^-$ or $R'SO_3^-$), two equivalents of a weaker acid do not allow exchange but already lead to the partial cleavage of the cluster by nucleophilic complexing ligands (eq. 5-5').[23,24]

$$\{(BuSn)_{12}O_{14}(OH)_6\}X_2 + 2\,HO_2CR \longrightarrow \tfrac{1}{3}\{BuSnO(O_2CR)\}_6 + \tfrac{5}{6}\{(BuSn)_{12}O_{14}(OH)_6\}X_2 + \tfrac{1}{3}HX \qquad (5)$$

$$\{(BuSn)_{12}O_{14}(OH)_6\}X_2 + 2\,HO_2PR_2 \longrightarrow \tfrac{3}{4}\{[BuSnOH(O_2PR_2)]_3O\}(O_2PR_2) + \tfrac{45}{48}\{(BuSn)_{12}O_{14}(OH)_6\}X_2 + \tfrac{1}{8}HX \qquad (5')$$

Interestingly, as $\{(BuSn)_{12}O_{14}(OH)_6\}(PTS)_2$ is easily prepared in large quantities,[18] exchanging the p-toluenesulfonates by hydroxyl anions is possible upon reaction with tetramethylammonium hydroxyde (eq. 6).[24]

$$\{(BuSn)_{12}O_{14}(OH)_6\}(PTS)_2 + 2\,(CH_3)_4NOH \xrightarrow{HOPr^i} \{(BuSn)_{12}O_{14}(OH)_6\}(OH)_2 \qquad (6)$$

Exchange reactions can also allow the association of "Tin-12" clusters with inorganic polyanions (e.g. vanadates). Insoluble amorphous solids were obtained by reacting, in a dichloromethane/water two phases system, $\{(BuSn)_{12}O_{14}(OH)_6\}Cl_2$ with MVO_3 (M : Na^+, K^+, NH_4^+). These solids in which the clusters framework is fully preserved correspond to the formula $\{(BuSn)_{12}O_{14}(OH)_6\}V_2O_6$.[27]

The "Tin-12" based compounds exhibit enough physical and chemical stability in many organic solvents to be considered as possible nanobuilding blocks. Their functionalization, needed for their assembling, will be discussed along with the assembling strategies (*vide infra*).

The "Tin-6" Oxo-Carboxylate-Cluster

The "Tin-6" compounds are among the many organotin oxo-clusters where complexing ligands are directly bound to tin.[12] The first description of this molecular structure was made on a phenyltin derivative, $\{PhSnO(O_2CC_6H_{11})\}_6$, obtained serendipitously.[29] Since, several other monoorganotin derivatives, mainly butyltin, have been proved to adopt the same oxo-carboxylato framework which is presented in Figure 3.[12,30] This molecular structure, where all tin atoms are six-coordinate (distorted octahedra), exhibits a hexagonal prismatic or "drum" arrangement made of two interconnected "$[Sn\text{-}O]_3$" rings in which all the oxygen atoms are triply bridging. The carboxylate groups are located on the six side square faces of the "drum", each bridging two tin atoms. This results in a fairly anisotropic overall shape as the six carbons atoms of the carboxylates are almost coplanar, while the organic moieties bound to tin point outside the top or bottom hexagonal faces of the "drum". More recently, this "drum" structure was reported for two oxo-carboxylato-alkoxides, one of tin and one of titanium : $\{(^tBuOSn)O(O_2CCH_3)\}_6$,[31] and $\{(Pr^iOTi)O(O_2CH)\}_6$.[32]

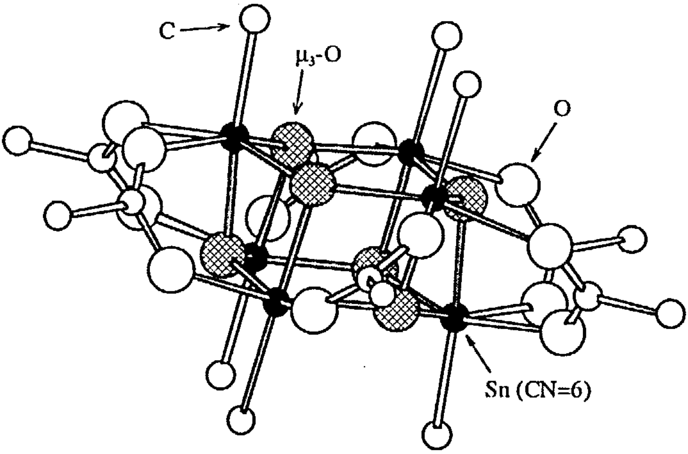

FIGURE 3 - Molecular structure of $\{RSn(\mu_3\text{-}O)(\mu_2\text{-}O_2CR')\}_6$ (only the carbon atoms bound to a tin or a carboxylate group have been drawn).

The molecular structure of $\{RSnO(O_2CR')\}_6$ is preserved in solution as easily evidenced by ^{119}Sn NMR experiments.[12,16,25] These clusters are characterized by a single chemical shift, around -485 ppm for butyltin derivatives, flanked by coupling satellites which mainly consist in two pairs. The two different $^2J_{Sn-Sn}$ couplings arise from two different connection paths in the cluster: inside a "$[Sn-O]_3$" hexagonal face and inside a "$[Sn-O]_2$" square face. As for the "Tin-12" clusters, the solution state releases, likely through the "breathing" of the Sn-O-Sn framework, the structural constraints of the solid state and gives to the "Tin-6" clusters a D_{3d} symmetry.

Two main syntheses of "Tin-6" clusters have been reported: the condensation of oxo-hydroxo-organotin polymers (organostannonic acids) with carboxylic acids (eq. 7) [12] and the condensation of "Tin-12" clusters also with carboxylic acids (eq. 8).[16,25]

$$6\,RSnO(OH) + 6\,R'CO_2H \longrightarrow \{RSnO(O_2CR')\}_6 \qquad (7)$$

$$\{(RSn)_{12}O_{14}(OH)_6\}X_2 + 12\,R'CO_2H \longrightarrow 2\,\{RSnO(O_2CR')\}_6 + 10\,H_2O + 2HX \qquad (8)$$
$$X = OH^-, Cl^-, R''SO_3^-$$

The first reaction is usually performed at the reflux of a non-polar solvent for several hours, while the second takes place within few minutes at room temperature. This difference is likely not related to the oxolation degree which is equal to 1 in RSnO(OH) and $\{RSnO(O_2CR')\}_6$ and to 6/7 in the "Tin-12" clusters but to the much higher solubility of these latter compared to organostannonic acids.

In reaction 8, when the anions are chlorides or hydroxyls the by-products (HCl and/or H_2O) are easily eliminated allowing one to recover quantitatively the "Tin-6" cluster. Yet, in some cases, such as R = Bu, $X = OH^-$ and $R' = C(CH_3)=CH_2$ or $4-(CH_2=CH)C_6H_4$, this reaction produces only an insoluble compound which exhibits the same chemical composition but is characterized by a single ^{119}Sn isotropic chemical shift of -515 ppm. The structure of this compound is so far unknown nor what orients the outcome of reaction 8.[27]

"Tin-6" clusters represent an other type of nanobuilding blocks, in which the carboxylate groups could be used to provide the assembling functions (*vide infra*).

STRATEGIES TO ASSEMBLE THE NBB

Several strategies can be considered to assemble monoorganotin oxo-clusters into hybrid materials. This variety illustrates the versatility of tin in such an approach. They will be presented according to the way the assembling functions can be bound to the nanobuilding blocks.

Sn-C Bond

As for silicon, the stability of the Sn-C(sp^3) bonds offers a direct access to class II hybrid materials. Yet, for the nanobuilding blocks approach, the organic moiety bound to tin should exhibit an assembling function which can be subsequently triggered to chemically connect the NBB with themselves or through additional spacers. Unfortunately, very few functional monoorganotin compounds are known so far.[26,33]

Such a case was partially achieved with a 3-butenyltin (BySn) functionalized NBB, $\{By_xBu_{12-x}Sn_{12}O_{14}(OH)_6\}X_2$, prepared by co-hydrolysing $BySn(OAm')_3$ and $BuSn(OAm')_3$.[34] Yet, and contrary to what was previously reported, no sign of homopolymerization was clearly evidenced under free radical initiation. This result is likely due to the poor reactivity of alkenes under such conditions. More efficient polymerization processes for alkenes, such as a Ziegler-Natta type catalysis, might however be incompatible with the chemical nature of "Tin-12" clusters.

Assembling these 3-butenyl functionalized "Tin-12" clusters by hydrosylilation with a poly(methylhydrosiloxane) spacer was also unsuccessful as side reactions between Si-H and Sn-O-Sn or Sn-OH-Sn results in the destruction of the "Tin-12" based-nanobuilding blocks.[35]

This strategy remains very attractive but requires more reactive assembling functions. "Tin-12", "Tin-6" or any other monoorganotin based nanobuilding blocks deriving from $4\text{-}(H_2C{=}CH)C_6H_4(CH_2)_nSn{\equiv}$ or $CH_3HC{=}CHCO_2(CH_2)_nSn{\equiv}$ moieties should meet these criteria.[26,33]

Complexing Ligand

The good affinity of tin for various complexing ligands provides an other possible organic/inorganic interface. This type of connections is typically achieved in "Tin-6" clusters.[12]

$\{BuSnO(O_2CC_6H_4NH_2)\}_6$ can be prepared by using p-aminobenzoic acid in reaction 7 or 8.[27] This "Tin-6" cluster exhibits on its periphery 6 amino functions amenable to subsequent reactions. For further functionalization or connection of the clusters, one possible choice is the clean and efficient formation of a urea bridge upon reaction with an isocyanate (eq. 9).[36] This reaction was shown perfectly compatible with the cluster.[27]

$$\{BuSn(O_2CC_6H_4NH_2)\}_6 + 6\,O=C=N\text{-}R \xrightarrow{THF/Reflux} \{BuSn(O_2CC_6H_4NHCONHR)\}_6 \qquad (9)$$

The reaction with $OCN(CH_2)_3Si(OEt)_3$ affords in quantitative yield a "Tin-6" oxo core with 18 peripheral ethoxy functions amenable hydrolysis-condensation.[27] This functionalized nanobuilding block could be used to prepared, by sol-gel process, silica based materials in which the pore size could be controlled by a templating effect.[14,37]

Assembling was also evidenced by the formation of insoluble systems, within a few hours, upon reacting $\{BuSnO(O_2CC_6H_4NH_2)\}_6$ with commercial diisocyanates, $1,4\text{-}(OCN)_2C_6H_4$ or $OCN(CH_2)_6NCO$.[27] The resulting urea bridges were clearly evidenced by ^{13}C CP MAS and ^{119}Sn MAS NMR (Fig. 4) shows that the "Tin-6" oxo-cores are fully preserved in the solid. The hexa functionality of the nanobuilding blocks results in an important cross-linking, likely responsible of the insolubility, even though some amino groups might have not reacted because of steric constraints.

The simultaneous synthesis and assembling of "Tin-6" oxo-cores was also attempted, unsuccessfully, using a poly(ethyleneglycol) bis(carboxymethyl) ether, $HO_2CCH_2(OCH_2CH_2)_nOCH_2CO_2H$ ($<n>\approx 2.75$; $M_n \approx 250$ g/mol) in reaction 8.[38] The addition of 6 equivalents ($-CO_2H/Sn=1$) of diacid on $\{(BuSn)_{12}O_{14}(OH)_6\}(OH)_2$ yielded an insoluble system, but "Tin-6" oxo-cores were not evidenced by ^{119}Sn MAS NMR. Instead, the unknown species characterized by an isotropic chemical shift of -515 ppm was observed (*vide supra*). This result likely arose from the impossibility of the "Tin-6" oxo-cores to be formed when telechelic complexing ligands reduce the mobility of the species. Moreover, it illustrates the need of a step by step process in the nanobuilding blocks approach.

Cation-Anion Interaction

In addition to a possible use of the organic groups covalently bound to tin (*vide supra*), the charged cage-poles in "Tin-12" clusters represent two intrinsic assembling or functionalization points. Indeed in solution, its charge compensating anions remain in contact with the cluster (*vide supra*) and should allow one to develop hybrid systems with an organic/inorganic interface based on electrostatic interactions.

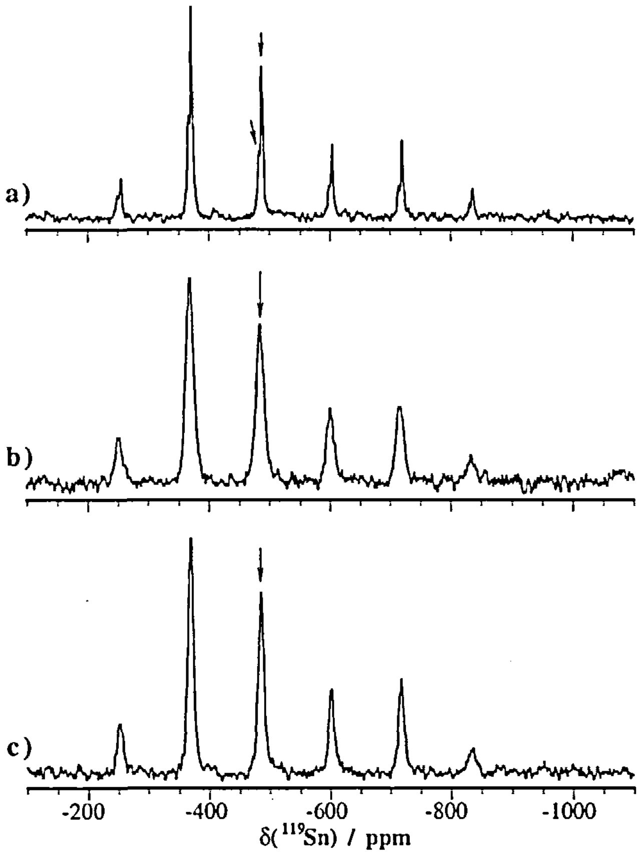

FIGURE 4 - ^{119}Sn MAS NMR spectra of (a) $\{BuSnO(O_2CC_6H_4NH_2)\}_6$, (b) after reaction with 3 equivalents of $1,4\text{-}(OCN)_2C_6H_4$ and (c) after reaction with 3 equivalents of $OCN(CH_2)_6NCO$ (at 111.9 MHz and ν_{MAS} = 13 kHz, isotropic resonances are pointed with arrows).

This strategy was used to functionalize $\{(BuSn)_{12}O_{14}(OH)_6\}^{2+}$ with polymerizable anions : methacrylates (Mc) [39,40] or 2-acrylamido-2-methyl-1-propanesulfonate (AAMPS).[28] $\{(BuSn)_{12}O_{14}(OH)_6\}(Mc)_2$ does not homopolymerize with free radical initiation, but can be co-polymerized with methylmethacrylate. This latter case yields soluble products indicative of a substantial absence of cross-linking originated from the difunctional hybrid comonomer. Spectroscopic characterizations seem to indicate that termination of the growing poly(MMA) chains occurs upon the addition of a $\{(BuSn)_{12}O_{14}(OH)_6\}(Mc)_2$ unit. Thus, linear polymers containing only one cluster and two poly(MMA) chains are preferentially formed.[40]

On the contrary, $\{(BuSn)_{12}O_{14}(OH)_6\}(AAMPS)_2$, in which the polymerizable functions are more remote from the oxo-core, homopolymerizes under free radical initiation.[28] The characterizations performed on the insoluble part allow one to describe this hybrid system as made of short poly(AAMPS) chains cross-linked by "Tin-12" clusters via electrostatic interactions.

This cation-anion interaction can also be used to directly assemble "Tin-12" dications with polyanionic spacers. Such an approach has been exemplified by reacting, in THF, $\{(BuSn)_{12}O_{14}(OH)_6\}(OH)_2$ with only one equivalent of a α,ω-dicarboxylic acid (eq. 4).[25,38] Elimination of the water upon drying results in hybrid co-polymers which correspond to the formula $[\{(BuSn)_{12}O_{14}(OH)_6\}(O_2C\text{-}R\text{-}CO_2)]_n$ and exhibit a beads structure. Depending on the nature of the spacer, insoluble (R : $(CH_2)_4$, $(CH_2)_{10}$, 1,4-C_6H_4) or soluble (R : $CH_2(OCH_2CH_2)_nOCH_2$ with $\langle n \rangle \approx 2.75$ or 11.3) systems were obtained. The soluble ones present a definite advantage for materials processing and thin films were obtained by classical deposition techniques such as spin-coating. From the solid state ^{119}Sn MAS NMR and IR spectra of these systems, and by comparison with the crystalline structure of $\{[BuSn(OH)(O_2PPh_2)]_3O\}^+(O_2PPh_2^-)$,[41] whose cationic trimeric unit is almost identical to a "Tin-12" cage pole, a geometry was proposed for the interaction taking place between the "Tin-12" clusters and the carboxylates : one oxygen of the carboxylate interacts with one bridging hydroxy, while the other oxygen interacts with the two other bridging hydroxy present at the cage pole.[25]

CONCLUSION

Several functionalization and assembling strategies have been illustrated with two monoorganotin oxo-clusters, a "Tin-12" and a "Tin-6". These different examples likely show the versatility of tin clusters to prepare, by the nanobuilding blocks approach, model hybrid materials with various organic/inorganic interfaces : iono-covalent (Sn-C or Sn-Carboxylate) and purely ionic ($cluster^+ \leftrightarrow anion$).

Work remains to be done to indeed make materials out of these systems and study their properties. Moreover, the polyfunctional nature of these clusters generally leads to highly cross-linked systems which can be difficult to process. Preparative routes in which the functionality of the clusters could be perfectly adjusted, while avoiding the mixture of several species, represent a future challenge.

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