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Journal of Organometallic Chemistry 567 (1998) 137–142

Journal of Organo metallic Chemistry

New synthesis of the nanobuilding block $\{(BuSn)_{12}O_{14}(OH)_6\}^{2+}$ and exchange properties of $\{(BuSn)_{12}O_{14}(OH)_6\}(O_3SC_6H_4CH_3)_2$

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Received 8 October 1997; received in revised form 14 January 1998

Abstract

This paper deals with a new and easy way to synthesize the macrocation $\{(BuSn)_{12}O_{14}(OH)_6\}^{2+}$ from BuSnO(OH) and *p*-toluene sulfonic acid. It was isolated by crystallization as $\{(BuSn)_{12}O_{14}(OH)_6\}(O_3SC_6H_4CH_3)_2C_4H_8O_2$. Exchange properties of sulfonates with different anions have been studied in several solvents by using ^{119}Sn- and ^{1}H-NMR. Sulfonate anions can be exchange in isopropanol by acetate or hydroxyl groups by reaction with sodium acetate or tetramethylammonium hydroxide, respectively. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Nano-building blocks; Oxo-hydroxo organotin clusters; ^{119}Sn-NMR

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1. Introduction

The combination at the nanosize level of inorganic and organic components in a single material makes accessible an immense new area of materials science that has extraordinary implications for developing novel multi-functional materials exhibiting a wide range of properties [1]. Among soft chemistry processes, sol-gel chemistry [2] offers a versatile access to chemically designed new hybrid organic-inorganic materials. However, sol-gel derived hybrid materials are very often amorphous and the organic and inorganic nanodomains could exhibit polydispersity both in size and in composition [1,2]. Chemists' skills play a major role in the elaboration and comprehension of such materials. However, the understanding and optimization of the structure–properties relationship needs the synthesis of 'model' hybrid materials in which the structure of the organic and inorganic domains, together with those of their interface, are perfectly defined.

Tin is a very interesting element because the $Sn-C_{sp^3}$ bond is stable, especially towards nucleophilic agents such as water. This last characteristic allows to chemically link organic moieties to the tin oxo polymers/oligomers, usually obtained by hydrolysis of organotin precursors. Moreover, this non-hydrolysable bond reduces the inorganic functionality of tin and therefore favors the formation of oxo-clusters [3,4], such as the macrocation $\{(RSn)_{12}(\mu_3\text{-}O)_{14}(\mu_2\text{-}OH)_6\}^{2+}$ [5–8]. These tin oxo-clusters are stable in many media, can crystallized, and their structure can be determined by single crystal X-ray diffraction. Moreover, they can be easily characterized in the solution and solid state by ^{119}Sn-NMR which provides an efficient probe of the structure of the cluster all over the polymerization or crosslinking reactions needed to transform this discrete species into an hybrid material. As a consequence $\{(RSn)_{12}O_{14}(OH)_6\}^{2+}$ clusters are good nanobuilding blocks for the synthesis of well defined tin-oxo based hybrid materials. These clusters exhibit a high versatility to design hybrids. Indeed, $\{(RSn)_{12}O_{14}(OH)_6\}X_2$ species can be assembled through organic networks by using the covalent interface provided by the $Sn-C_{sp3}$ bonds or by using the ionic interface associated to the

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PII S0022-328X(98)00676-7

charge compensating anions X^- or even by using both interfaces [8–11]. This article reports a direct and cheap synthesis of the nanobuilding block $\{(BuSn)_{12}(O)_{14}(OH)_6\}(O_3SC_6H_4CH_3)_2$ from butyltin hydroxide oxide BuSnO(OH). Some possibilities to exchange the sulfonate anions have also been studied.

2. Characterization techniques

2.1. NMR spectroscopy

Routine ^1H and proton decoupled ^{119}Sn solution NMR experiments were performed on a Bruker AC300 spectrometer (300.13 MHz for ^1H, 111.92 MHz for ^{119}Sn). $^{119}Sn\{^1H\}$ spectra were obtained with a composite pulse decoupling sequence (CPD). CD_2Cl_2 or $CDCl_3$ were used as internal deuterated solvents. ^{119}Sn chemical shifts are quoted relative to external tetramethyltin ($\delta = 0$ ppm). ^1H chemical shifts are quoted to TMS using the protonated impurities of the deuterated solvents as secondary internal reference (CD_2Cl_2: 5.33 ppm, $CHCl_3$: 7.25 ppm). Quantitative $^{119}Sn\{^1H\}$ experiments were also performed on a Bruker AM250 spectrometer (93.27 MHz for ^{119}Sn). To avoid the loss of quantitativity causes by nuclear Overhauser effect, an inverse gated decoupling sequence [12] was used, where the ^1H decoupler is turned on only during acquisition and turned off during a recycling delay set to 20 s. For these experiments, a coaxial geometry consisting of a 5 mm NMR tube inside a 10 mm NMR tube was chosen. A known amount of product to analyze (ca. 500 mg) was placed with 1.5 ml of toluene in the 10 mm tube. A known amount of $[BuSnO(O_2CCH_3)]_6$ [4,6,10,13] (ca. 100mg) was placed in the 5 mm tube with 500 µl of CD_2Cl_2, this compound giving a single ^{119}Sn resonance at -484 ppm [6,10]. Comparison of the areas of the ^{119}Sn-NMR signals allow to determine the quantity of $\{(BuSn)_{12}(O)_{14}(OH)_6\}(O_3SC_6H_4CH_3)_2$. This method was checked with crystalline $\{(BuSn)_{12}O_{14}(OH)_6\}(O_3SC_6H_4CH_3)_2C_4H_8O_2$ as the product to analyze, and the error was estimated to less than 5%.

3. Synthesis

3.1. Compound **1·Diox**: $\{(BuSn)_{12}O_{14}(OH)_6\}(O_3SC_6H_4CH_3)_2C_4H_8O_2$

Twenty grams of BuSnO(OH) (95%, Strem Chemicals) and 5.77 g of *p*-toluene sulfonic acid ($HO_3SC_6H_4CH_3 \cdot H_2O$, Fluka) (Sn/S = 3) were mixed with 500 ml of toluene in a 1 l round-bottom flask equipped with a Dean-Starck and a condenser. The mixture was refluxed for 48 h. To remove unreacted solid materials the mixture was filtered on a glass frit no. 4 (average porosity: 10–16 µm). The clear solution obtained was then evaporated under reduced pressure to yield around 23 g of white solid. Chem. Anal.: Sn = 47.9%; S = 3.3% (Sn/S = 3.9).

This crude solid was dissolved upon heating (around 85°C) in 1,4-dioxane containing 0.5 wt% of water. About 11 g (50% yield) of crystals were obtained after few days at room temperature. Chem. Anal.: Sn = 50.7% (49.7), S = 2.3% (2.3), C = 26.9% (27.6) and H = 4.6% (4.7), theoretical percentages for **1·Diox** are given between parentheses.

3.2. Reaction with acetic acid

A 10 wt% solution of **1·Diox** in $CDCl_3$ was mixed, under strong magnetic stirring, with a 10 wt% solution of acetic acid in $CDCl_3$ (AcOH/'$BuSn_{12}$' = 2). A clear solution was obtained and directly studied by ^{119}Sn and ^1H-NMR.

3.3. Reaction with sodium acetate

First, dioxane was removed from **1·Diox** by drying at 100°C overnight. Its complete removal and the preservation of the cluster was checked by ^1H- and ^{119}Sn-NMR. Dioxane free $\{(BuSn)_{12}O_{14}(OH)_6\}(O_3SC_6H_4CH_3)_2$ was preferred for this experiment because of its better solubility in isopropanol. Secondly, a 25 wt% solution of **1** in isopropanol was mixed with 151 mg of $CH_3CO_2Na \cdot 3H_2O$ (CH_3CO_2Na/'$BuSn_{12}$' = 2).

A precipitate formed readily was removed by filtration on a glass frit no. 4 to leave a clear solution. After a couple of days at −20°C, this clear solution yielded a white precipitate which was isolated by filtration and studied.

3.4. Reactions with tetramethylammonium hydroxyde (TAMOH)

The TAMOH was used as a 1 M aqueous solution. Different solvents were tested.

A 25 wt% solution of **1** in *N*,*N*-dimethyl formamide (DMF) was mixed, under strong stirring, with a solution of aqueous TAMOH in DMF (20 wt%, OH/'$BuSn_{12}$' = 2) yielding a light precipitate removed by filtration on a glass frit no. 4. The obtained clear solution gave well shaped millimetric crystals after 24 h at −20°C.

A 20 wt% solution of **1** in isopropanol was mixed, under strong stirring, with a solution of aqueous TAMOH in isopropanol (65 wt%, OH/'$BuSn_{12}$' = 2.3). After 30 min a tenuous precipitate was observed but left in suspension. Good quality needle shaped crystals formed (90% yield) after one night at −20°C.

4. Results and discussion

4.1. Structure of *1·Diox*

The structure of $\{(BuSn)_{12}O_{14}(OH)_6\}(O_3SC_6H_4CH_3)_2C_4H_8O_2$ was solved by single crystal X-ray diffraction [14]. It is based on a centrosymmetric macrocation $\{(BuSn)_{12}O_{14}(OH)_6\}^{2+}$ (Fig. 1), the molecular structure of which have been previously reported [5–7]. This macrocation is composed of twelve tin atoms linked by μ_3-O and μ_2-OH bridges. Each tin of this closo type structure bears a butyl chain which points toward the outside of the cage. Six tin atoms are five-coordinate and exhibit a square pyramidal environment. The other six tin atoms are six-coordinate and exhibit a distorded octahedral geometry. The bridging hydroxy groups (μ_2-OH) are only present in the environment of six-coordinate tin atoms. This oxo-hydroxo butyltin structure can be described as made from three subunits. Two are trimers '$\{(BuSn)(\mu_2\text{-OH})\}_3(\mu_3\text{-O})$' and contain only six-coordinate tin atoms. The other one is a hexameric cycle '$(BuSn)_6(\mu_3\text{-O})_{12}$' where tin atoms are only five-coordinate. The cage is obtained by capping each side of the hexameric cycle by a trimeric unit. One positive charge is located at each pole (trimeric sub-units containing hydroxylated six-coordinate tin atoms). The charge balance is given by the sulfonate groups. A framework of hydrogen bonds, characterized by an average O–O distance of 2.75 Å, involving the three oxygen atoms of each sulfonate moieties and the six bridging hydroxy groups of each macrocation, links the clusters into chains [14]. A 1,4-dioxane molecule is also involved in the structure. Each of its oxygen atoms interacts weakly (d(Sn–O) = 3.3 Å) with two five-coordinate tin atoms, thus connecting the chains into planes [14].

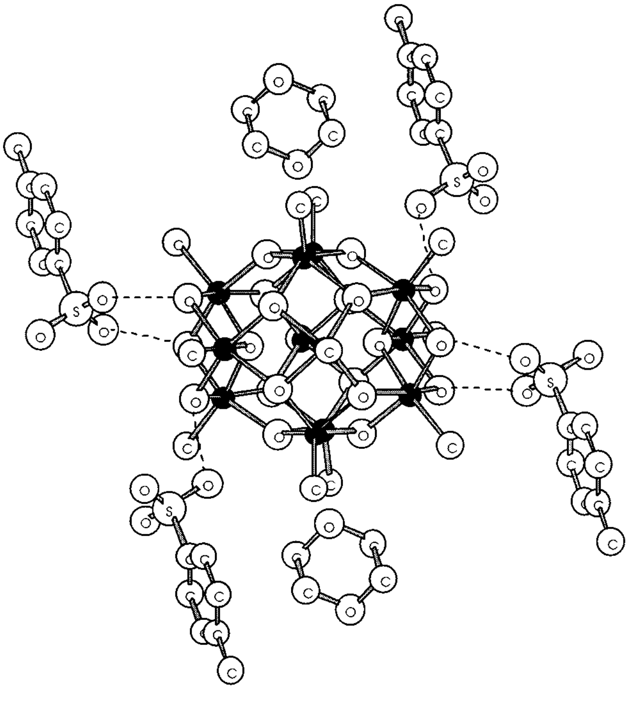

Fig. 1. Molecular structure of $\{(BuSn)_{12}O_{14}(OH)_6\}(O_3SC_6H_4CH_3)_2(C_4H_8O_2)$. Only the first carbon of each butyl chain has been drawn for clarity.

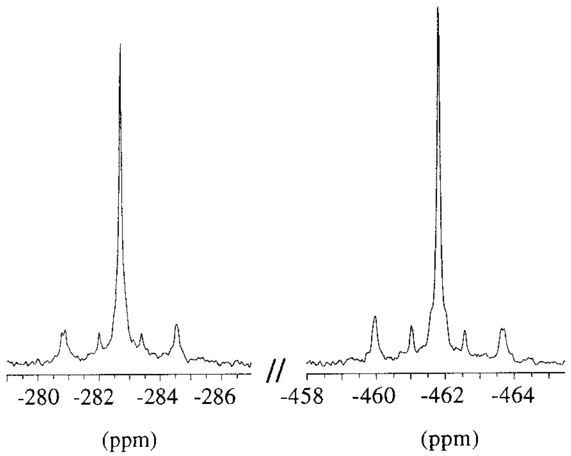

Fig. 2. $^{119}Sn\{^1H\}$ spectrum of **1·Diox** in CD_2Cl_2.

4.2. ^{119}Sn-NMR of $\{(BuSn)_{12}O_{14}(OH)_6\}(O_3SC_6H_4CH_3)_2\cdot C_4H_8O_2$

The $^{119}Sn\{^1H\}$ spectra of **1·Diox** (Fig. 2) or **1** in CD_2Cl_2 exhibit two resonances at -282.8 and -461.8 ppm corresponding to five- and six-coordinate tin atoms, respectively [6,7,10,15]. Each resonance also exhibits several satellites due to $^{119}Sn-^{119}Sn$ and/or $^{119}Sn-^{117}Sn$ two bonds scalar coupling [6,7,10,15]. Previous works have shown the same type of spectra for compounds based on $\{(BuSn)_{12}O_{14}(OH)_6\}^{2+}$ and different anions [6,7,10,15]. The main difference when the anions change is observed on the chemical shift related to six-coordinate tin atoms (δ_o); $\delta_o(OH^-) = -448.9$ ppm, $\delta_o(AcO^-) = -460.9$ ppm, $\delta_o(Cl^-) = -463.7$ ppm (in CD_2Cl_2). The positive charges of the macrocation being located at each pole, which contains only six-coordinate tin atoms, and the solvent having a low dielectric constant, this chemical shift effect was explained by the absence of ionic dissociation for $\{(BuSn)_{12}O_{14}(OH)_6\}X_2$ [7,10,15]. Therefore, the $^{119}Sn\{^1H\}$-NMR spectrum presented in Fig. 2 characterizes the ion triplet $\{(BuSn)_{12}O_{14}(OH)_6\}(O_3SC_6H_4CH_3)_2$ in CD_2Cl_2.

The $^{119}Sn\{^1H\}$-NMR spectrum of the crude material (before crystallization in 1,4-dioxane) in CD_2Cl_2 is identical to the one of **1**, displaying two resonances of equal intensity (quantitative conditions). No other resonance is observed, but quantitative $^{119}Sn\{^1H\}$-NMR experiments have indicated that these resonances represent only 50% of the tin introduced in the NMR tube. This result is in good agreement with the crystallization yield in 1,4-dioxane. The other 50% of tin likely constitute large and ill-defined oxo-polymeric species which are not observed by solution ^{119}Sn-NMR because of their longer reorientation times.

4.3. Reactivity of 1·Diox with acetic acid

In order to form hybrid materials, the nanobuilding blocks $\{(BuSn)_{12}O_{14}(OH)_6\}^{2+}$ need to be connected. This can be done by connecting the macrocations through dianionic species and was recently achieved by reacting $\{(BuSn)_{12}O_{14}(OH)_6\}(OH)_2$ with di-carboxylic acids such as adipic or terephthalic acids [10], or carboxymethyl terminated poly(ethylene glycol) [8]. In this reaction, the charge compensating hydroxyl anions are replaced by carboxylates and water is eliminated. Compound **1·Diox** being much easier to prepare than $\{(BuSn)_{12}O_{14}(OH)_6\}(OH)_2$, exchange in solution of the sulfonate anions of **1** by carboxylates was attempted, using acetic acid as a simple model.

Just after mixing the reagents (see Section 3.2), the ^{119}Sn{^{1}H} spectrum displays two resonances at −282.4 and −462.7 ppm corresponding to the five- and six-coordinate tin atoms of $\{(BuSn)_{12}O_{14}(OH)_6\}X_2$, respectively. Some other resonances of lower intensity are also observed between −484 and −508 ppm and correspond to one, or several, unidentified species containing only six-coordinate tin atoms. The ^{1}H-NMR spectrum shows four peaks around 2.0 ppm. These resonances have been attributed to acetate moieties covalently bond to tin atoms by comparison with the value of 2.05 ppm found for the acetate of $[BuSnO(O_2CCH_3)]_6$ (vide infra). On the contrary, no ^{1}H-NMR resonance is observed around 1.8 ppm which could have been assigned to ionic acetate, by comparison with the value of 1.85 ppm found for $\{(BuSn)_{12}O_{14}(OH)_6\}(O_2CCH_3)_2$. After 20 days, only three resonances, at −282.2, −461.7 and −484.1 ppm with relative intensities of 5/5/2, remain in the ^{119}Sn{^{1}H} spectrum. The two first correspond to the five- and six-coordinate tin atoms of **1**, respectively. The third one is unambiguously assigned to the six-coordinate tin atoms of the hexameric butyltin oxo-carboxylate cluster, $[BuSnO(O_2CCH_3)]_6$, in which each carboxylate bridge two tin atoms [4,6,10,13]. The relative intensity of each peak indicates that all the acetate groups introduced initially are involved in the cluster $[BuSnO(O_2CCH_3)]_6$. This point is confirmed by ^{1}H-NMR, which exhibits only one type of acetate, at 2.05 ppm.

Therefore, and unlike $\{(BuSn)_{12}O_{14}(OH)_6\}(OH)_2$, **1** does not exchange its charge compensating anions for carboxylates when reacted with two equivalents of carboxylic acid. Instead, **1** is partially destroyed into other species which slowly yield $[BuSnO(O_2CCH_3)]_6$. After 20 days, the overall reaction can be written:

$$\begin{aligned}&\{(BuSn)_{12}O_{14}(OH)_6\}(O_3SC_6H_4CH_3)_2 + 2CH_3CO_2H\\ &\rightarrow 5/6\{(BuSn)_{12}O_{14}(OH)_6\}(O_3SC_6H_4CH_3)_2\\ &\quad + 1/3[BuSnO(O_2CCH_3)]_6 + 1/3HO_3SC_6H_4CH_3\\ &\quad + 4/3H_2O\end{aligned}$$

The interconversion of $\{(BuSn)_{12}O_{14}(OH)_6\}(OH)_2$ into $[BuSnO(O_2CCH_3)]_6$ was also observed, but only when more than two equivalents of carboxylic acid were used [10]. These different behaviors likely arise from the different acidities of $CH_3C_6H_4SO_3H$, CH_3CO_2H, and H_2O.

4.4. Reactivity of 1 with sodium acetate

The white precipitate formed at −20°C was analyzed by solution ^{119}Sn{^{1}H}-NMR in CD_2Cl_2. Only two resonances were observed at −282.1 and −463.6 ppm, corresponding, respectively, to the five- and six-coordinate tin atoms of a species based on $\{(BuSn)_{12}O_{14}(OH)_6\}^{2+}$.

The low frequency ^{119}Sn resonance appeared very slightly shielded compared to **1** (−461.8 ppm) and $\{(BuSn)_{12}O_{14}(OH)_6\}(OAc)_2$ (−460.9 ppm). The ^{1}H-NMR spectrum of this precipitate exhibits, in addition to the resonances related to the two types of butyl chains found in $\{(BuSn)_{12}O_{14}(OH)_6\}^{2+}$ [7,15], a singlet at 1.82 ppm which is attributed to ionic acetate, as well as some weak resonances corresponding to *p*-toluene sulfonate groups (2.37 ppm, s; 7.20 ppm, d; 7.69 ppm, d). Therefore, the sulfonate anions of **1** can be exchanged by carboxylate without destroying the butyltin oxo-framework when sodium carboxylate is used. This point shows that the acidity is indeed a key factor. Yet, under the conditions used the exchange appeared incomplete, the final solid corresponding to the average formula $\{(BuSn)_{12}O_{14}(OH)_6\}(O_3SC_6H_4CH_3)_{0.4}(OAc)_{1.6}$ (from ^{1}H-NMR integration). No attempts to optimize the exchange process were carried out because it might not be easily transposed to other acid sodium salts.

4.5. Reactivity of 1 with tetramethylammonium hydroxyde

Transformation of **1** into $\{(BuSn)_{12}O_{14}(OH)_6\}(OH)_2$ was attempted in different solvents. Indeed, $\{(BuSn)_{12}O_{14}(OH)_6\}(OH)_2$ appears as a more versatile starting material for further exchange of the charge compensating ions [8,10,11,15].

4.5.1. DMF

The ^{119}Sn{^{1}H}-NMR spectrum of the crystals formed in DMF (see Section 3.4) shows two resonances located at −281.7 and −461.1 ppm (in CD_2Cl_2). They correspond to the five- and six-coordinate tin atoms of a compound based on $\{(BuSn)_{12}O_{14}(OH)_6\}^{2+}$. Yet, this compound cannot be $\{(BuSn)_{12}O_{14}(OH)_6\}(OH)_2$ for which the high field ^{119}Sn resonance is found at −448.9 ppm [7]. The ^{1}H-NMR spectrum (in CD_2Cl_2) does not show any resonance around 7 ppm, thus indicating the absence of *p*-toluene sulfonate groups, but exhibits a ^{1}H resonance at 8.4 ppm. This last resonance is quite characteristic of the hydrogen of a formiate ($\underline{H}COO^-$). The area of this peak versus the total area of the resonances of the butyl chains is consistent with a stoichiometry of two formiate molecules per macrocation and suggests the formation of $\{(BuSn)_{12}O_{14}(OH)_6\}(HCOO)_2$. This hypothesis was confirmed by preparing directly $\{(BuSn)_{12}O_{14}(OH)_6\}(HCOO)_2$ from $\{(BuSn)_{12}O_{14}(OH)_6\}(OH)_2$ and two equivalents of formic acid [10]. With this latter synthesis, ^{119}Sn{^{1}H}-NMR shows chemical shifts of −281.9 and −461.2 ppm (in CD_2Cl_2) and ^{1}H-NMR shows chemical shift of 8.4 ppm for the hydrogen of the formiate, which match perfectly those for the exchange in DMF.

The formation of formiate, which exchanges the sulfonate and yields $\{(BuSn)_{12}O_{14}(OH)_6\}(HCOO)_2$, can be easily explained by the base (TAMOH) hydrolysis of DMF, this reaction being likely catalyzed by $\{(BuSn)_{12}O_{14}(OH)_6\}^{2+}$.

$$(CH_3)_2NCOH + OH^- \rightarrow (CH_3)_2NH + HCOO^-$$

No attempt has been made, so far, to extend this type of exchange to other amides than DMF. It could be a new way to prepare $\{(BuSn)_{12}O_{14}(OH)_6\}(O_2CR)_2$, using **1** instead of $\{(BuSn)_{12}O_{14}(OH)_6\}(OH)_2$. Yet, this synthesis might strongly depend on the ability of $\{(BuSn)_{12}O_{14}(OH)_6\}(O_2CR)_2$ to crystallize, what probably push the exchange toward completion.

4.5.2. Isopropanol

The ^{119}Sn{^{1}H}-NMR spectrum (CD_2Cl_2) of the needle crystals formed in isopropanol (see Section 3.4) presents two resonances at −282.4 and −451.1 ppm. ^{1}H-NMR indicates the absence of *p*-toluene sulfonate groups, but the presence of isopropanol molecules. Even though not in perfect agreement with the ^{119}Sn chemical shifts previously reported, the crystals formed correspond likely to $\{(BuSn)_{12}O_{14}(OH)_6\}(OH)_2(HOPr^i)_4$ [7]. Surprisingly, a slight excess of TAMOH is needed. With two equivalents of TAMOH the yield of $\{(BuSn)_{12}O_{14}(OH)_6\}(OH)_2(HOPr^i)_4$ is around 10%, while with 2.3 equivalents the yield reaches almost 90%. Therefore, exchange of the sulfonate groups by OH^- groups appears possible. The slight shielding of both ^{119}Sn resonances for this synthesis from **1** likely arises from a small quantity of anionic impurities which rapidly exchange, on the NMR time scale, with the hydroxyl anions at the cluster poles.

4.5.3. Acetonitrile or dimethyl sulfoxyde

Reaction between **1** and TAMOH was tried in both solvents, but no evidence for any exchange of the sulfonates was obtained, i.e. the ^{119}Sn-NMR chemical shifts remain identical to those of **1**.

As the nature of the solvent used for the exchange appeared to be a key factor, the ^{119}Sn{^{1}H}-NMR spectrum of **1** alone has been recorded in different solvents without any ‘lock solvent’. No broadening, compared to a standard acquisition with CD_2Cl_2 or $CDCl_3$, was observed for both resonances, as expected from magnetic field stability and signals exhibiting natural width of about 20 Hz. Results are gathered in Table 1.

The ^{119}Sn chemical shift of the six-coordinate tin atoms appears strongly dependent on the nature of solvent. As its dielectric constant increases, this chemical shift moved toward high field (shielding). A possible explanation is the modification of the electrostatic interaction between the macrocation and the sulfonate due to the modification of the dielectric constant (i.e. change in the average distance between the three μ_2-OH of a cluster pole and the three oxygen atoms of the sulfonate anion) [15]. It is well known that ion pairs are more or less associated depending on the nature of the solvent. This phenomenon might, indeed, directly influence the ease to exchange the sulfonates by other charge compensating anions. However, the nucleophilic characteristic of the solvent is a parameter that cannot be fully excluded. Conductivity experiments are currently in progress to shed some light on a possible ionic dissociation of **1** in solvents with relatively high dielectric constant (i.e. DMSO).

5. Conclusion

This paper has described a new and easy way to synthesize the macrocation $\{(BuSn)_{12}O_{14}(OH)_6\}^{2+}$, which was isolated by crystallization as $\{(BuSn)_{12}O_{14}(OH)_6\}(O_3SC_6H_4CH_3)_2(C_4H_8O_2)$. This new synthetic route has been extended to other sulfonic acids (sulfanilic acid, 2-acrylamido-2-methyl-1-propanesulfonic acid, (1R)-(-)-10-camphorsulfonic acid, 4-morpholinepropanesulfonic acid, 4,4′-biphenyldisulfonic

Table 1
^{119}Sn chemical shifts for $\{(BuSn)_{12}O_{14}(OH)_6\}(O_3SC_6H_4CH_3)_2$ in various solvents (subscript p or o refer to the five- or six-coordinate tin atoms)

Solvent (ε)[a]	$\delta(Sn_p)$ (ppm)	$\delta(Sn_o)$ (ppm)
DMSO (48.9)	−285.4	−473.5
DMF (37.8)	−286.7	−471.4
Isopropanol (18.3)	−283.9	−471.0
THF (7.6)	−282.5	−460.9

[a] Dielectric constant.

acid) affording various $\{(BuSn)_{12}O_{14}(OH)_6\}X_2$ compounds. Their purification by crystallization has not been possible so far.

Exchange of the charge compensating sulfonate anions of $\{(BuSn)_{12}O_{14}(OH)_6\}(O_3SC_6H_4CH_3)_2$ by carboxylates has appeared impossible when carboxylic acid was used. Moreover, destruction of the macrocation was observed. Yet, some achievements for this exchange have been obtained with sodium acetate and also with the in situ generation of formiate through the base hydrolysis of DMF. Exchange of the sulfonate groups by hydroxyl, to yield the more versatile $\{(BuSn)_{12}O_{14}(OH)_6\}(OH)_2$, was achieved with a high yield by reaction with tetramethylammonium hydroxide in isopropanol.

The elaboration of materials from these nanobuilding blocks requires an assembling step which can be achieved by reacting $\{(BuSn)_{12}O_{14}(OH)_6\}(OH)_2$ with molecules or polymers bearing at least two anionic anchoring groups (carboxylate, sulfonate, ...) [8,10,11].

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