DOI: 10.1002/ejic.200500570

Carboxylate-Containing Tin(IV) Isopropoxides: Synthesis and Characterization of $[Sn(O\textit{i}Pr)_2(O_2CR)_2]_2$ [R = $(CH_3)CCH_2$, C_6H_5, CH_3]

Eugenia Martinez-Ferrero,[a] Kamal Boubekeur,[b] and François Ribot*[a]

Keywords: Carboxylate ligands / Organic–inorganic hybrid composites / NMR spectroscopy / Sol–gel processes / Tin

Tin(IV) isopropoxide solvate has been modified by treatment with methacrylic, benzoic and acetic acid. For carboxylate to tin ratios ranging from 1.4 to 2, a dimer, namely $[Sn(\mu_2\text{-O}\textit{i}Pr)(O\textit{i}Pr)(O_2CR)_2]_2$ [R = $(CH_3)CCH_2$, C_6H_5, CH_3], is isolated. Its structure, as determined by X-ray diffraction on the methacrylate derivative, is based on two seven-coordinate tin atoms, terminal and bridging isopropoxy ligands, and purely chelating carboxylates. These compounds have also been characterized by ^{119}Sn, ^{1}H, and ^{13}C solution NMR and ^{119}Sn CP-MAS NMR spectroscopy. The possible use of this dimer as a precursor for carboxylate-modified tin–oxo clusters has been tested.

Introduction

Hybrid organic–inorganic materials are excellent candidates for the design of new functional materials.[1] One approach to them relies on the chemical modification of metal alkoxides by suitable organic ligands,[2] which, in addition to providing a chemical link between the organic and inorganic components, control the reactivity of these precursors during the sol–gel process. The reaction of metal alkoxides with carboxylic acids, β-diketones, or related compounds is also often the first step in the synthesis of metal–oxo clusters of well-defined structure that can be used as versatile building blocks in the preparation of hybrid organic–inorganic materials.[3] Among the various modifying carboxylates used in the area of hybrid materials, the most extensively studied are probably methacrylate and acrylate, as they can be easily polymerized. A large number of modified transition metal–oxo clusters have been reported with these ligands[4–6] and polymerized with various co-monomers (e.g. methacrylic acid, methyl methacrylate) to yield materials with enhanced properties compared to those of the parent polymers.[7]

Methacrylic acid modified tin(IV) alkoxides have already been used to prepare tin dioxide thin films (with or without antimony doping).[8] The films were obtained by UV-induced free radical polymerization of the organic modifiers and the results showed that the direct photo-patterning process increases the conductivity of the films. The photo-patterned organo–metal polymer structures could, furthermore, be thermally decomposed into the corresponding metal oxides at elevated temperatures. However, these previous studies did not give any information about the structure of the methacrylate-modified tin(IV) alkoxides. Moreover, if compounds containing C–Sn bonds are excluded, there are only a few reports of tin(IV)–alkoxo clusters.[9] All this prompted us to look at the compounds formed by treating tin(IV) isopropoxide solvate with different carboxylic acids.

The work presented here reports the modification of tin(IV) isopropoxide solvate by methacrylic, benzoic, and acetic acids. The compounds $[Sn(O\textit{i}Pr)_2(O_2CR)_2]_2$ [R = $(CH_3)CCH_2$, C_6H_5, CH_3] were characterized by NMR spectroscopy (^{119}Sn, ^{1}H, and ^{13}C) and the X-ray structure of the methacrylate derivative was determined. The possibility of obtaining defined oxo clusters from this modified alkoxide was also tested.

Results and Discussion

Crystals of $[Sn(O\textit{i}Pr)_2(OMc)_2]_2$ (**1**) were obtained with carboxylate to tin ratios ranging from 1.4 to 2 (see Experimental Section). According to previously reported data on the influence of the solvent in the preparation of mixed metal–oxo clusters,[9c,10] two different solvents, i.e. toluene and THF, were tested. No influence was found, and the same compounds were obtained with both solvents.

The structure of this complex was elucidated by single-crystal X-ray diffraction (Figure 1 and Table 1). The molecular unit corresponds to a centrosymmetric dimer containing two bridging isopropoxy groups. Each tin atom is also coordinated by two chelating carboxylate molecules. The remaining isopropoxy groups are terminal, resulting in an overall coordination number of seven for tin. The geometry around each tin atom is well described by a pentagonal

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[a] Chimie de la Matière Condensée de Paris (UMR, 7574), Université Pierre et Marie Curie,
4 Place Jussieu, 75252 Paris cedex 05, France
E-mail: fri@ccr.jussieu.fr
[b] Chimie Inorganique et Matériaux Moléculaires (UMR, 7071), Université Pierre et Marie Curie,
4 Place Jussieu, 75252 Paris cedex 05, France

bipyramid, where O5 and O6 occupy the apical positions. The Sn–O bond lengths of the isopropoxy ligands are similar to those found in $[Sn(OiPr)_4{\cdot}HOiPr]_2$,[11a] and $[Sn(OiPr)_3(acac)]_2$,[11b] and are longer for the bridging groups [2.0601(5) and 2.0939(12) Å] than for the terminal ones [1.9549(16) Å]. The bridging isopropoxy ligands are planar, the sum of the angles about O6 being 360.0°. The angle at the oxygen atom of the in-plane terminal alkoxy is smaller in compound **1** [Sn1–O5–C9 = 119.21(12)°] than in $[Sn(OiPr)_4{\cdot}HOiPr]_2$ (139° and 160°)[11a] but similar to the ones observed in $[Sn(OiPr)_3(acac)]_2$ (122.0° and 124.4°)[11b] and $[Sn(OtBu)_4]$ (124.1° and 125.0°).[11a] These values of around 120° are expected for alkoxy ligands not involved in π-donation to the metal center. The carboxylate ligands are purely chelating and fairly symmetrical, with Sn–O bond lengths ranging from 2.1764(14) to 2.2465(15) Å. The charge of each carboxylate moiety is equally delocalized over the two oxygen atoms as the C–O bond lengths are almost identical [from 1.260(2) to 1.275(3) Å].

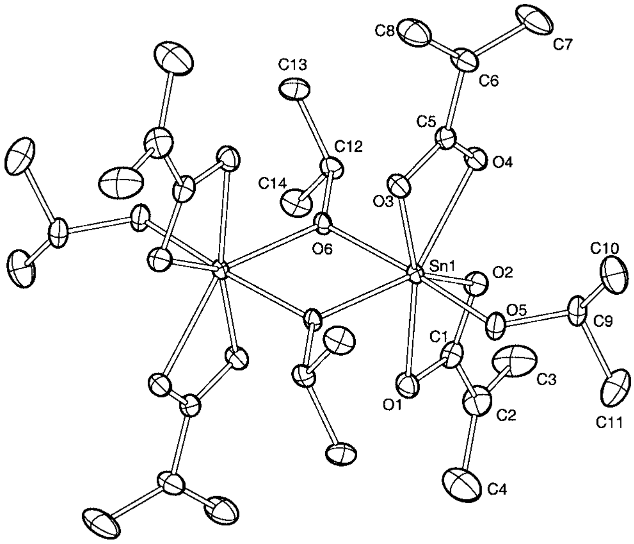

Figure 1. DIAMOND drawing of $[Sn(\mu_2\text{-}OiPr)(OiPr)(OMc)_2]_2$ showing the atom-labeling scheme. Atomic thermal ellipsoids are drawn at 50% probability and H atoms have been omitted for clarity.

Table 1. Selected interatomic distances [Å] and angles [°] for compound **1**.

Sn1–O1	2.2465(15)	Sn1–O5	1.9549(16)
Sn1–O2	2.1764(14)	Sn1–O6	2.0601(15)
Sn1–O3	2.2113(15)	Sn1–O6[a]	2.0939(12)
Sn1–O4	2.1987(14)	Sn1···Sn1[a]	3.3370(3)
O5–Sn1–O6	174.11(5)	O5–Sn1–O4	94.89(5)
O1–Sn1–O2	58.87(5)	O5–Sn1–O6[a]	101.06(6)
O2–Sn1–O4	79.83(5)	O6–Sn1–O1	91.79(5)
O3–Sn1–O4	59.12(5)	O6–Sn1–O2	88.25(5)
O3–Sn1–O6[a]	81.21(5)	O6–Sn1–O3	88.86(5)
O1–Sn1–O6[a]	82.00(5)	O6–Sn1–O4	89.01(5)
O5–Sn1–O1	88.20(6)	O6–Sn1–O6[a]	73.11(6)
O5–Sn1–O2	96.78(6)	Sn1–O6–Sn1[a]	106.89(6)
O5–Sn1–O3	89.35(6)		

[a] Symmetry operation: –*x*, –*y*, –*z*.

To assess the purity of the crystalline precipitate the ^{119}Sn solid-state NMR (CP-MAS) spectrum of compound **1** was recorded (Figure 2). It displays a single, sharp, isotropic resonance, at δ = –759 ppm, with an anisotropy (ζ) and asymmetry (η) equal to 325 ppm and 0, respectively. The observation of a single resonance is in agreement with the presence of a unique tin environment in the crystal structure. Moreover, the axial (or nearly axial)[12] character of the chemical shielding tensor is in line with the pentagonal bipyramid coordination polyhedron.

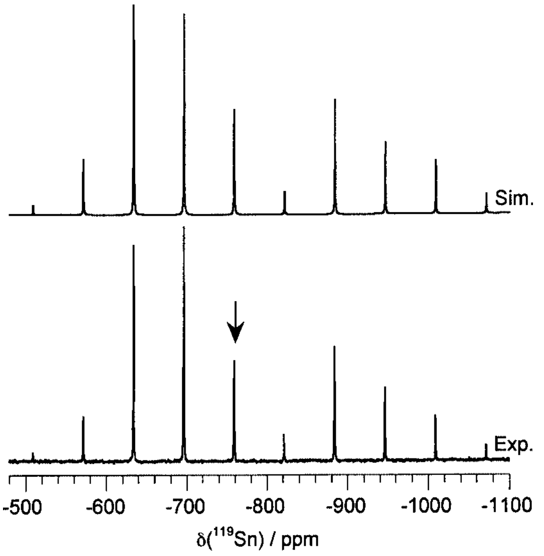

Figure 2. ^{119}Sn CP-MAS NMR spectrum (111.9 MHz, ν_{MAS} = 7000 Hz) of $[Sn(OiPr)_2(OMc)_2]_2$ with its simulation (the arrow points to the isotropic chemical shift).

To the best of our knowledge there are very few reports of crystalline compounds in which a tin atom exhibits a sevenfold coordination based only on oxygen atoms (SnO_7 environment),[13] and no ^{119}Sn NMR spectroscopic data have been reported for these compounds. For comparison, the ^{119}Sn solid-state NMR (CP-MAS) spectrum of $[Sn(OiPr)_4{\cdot}HOiPr]_2$ was also recorded. It exhibits an isotropic chemical shift of δ = –654 ppm (ζ = 103 ppm and η = 0.65) for its unique SnO_6 environment. The ^{119}Sn NMR isotropic chemical shift of tin dioxide, in which tin is also six-coordinate, has been reported to be δ = –603 ppm.[14] For SnO_8 environments, there is a series of tin tetracarboxylates, the ^{119}Sn NMR chemical shifts of which have been reported to lie in the range δ = –840 to –860 ppm,[15] and two tetrakis(*N*,*N*-dialkylcarbamato-*O*,*O'*)tin(IV) complexes, with ^{119}Sn NMR chemical shifts of around δ = –925 ppm.[16] In conclusion, according to the general rules whereby an increase of one oxygen atom at tin causes a low-frequency shift of about 100 to 150 ppm,[17] the ^{119}Sn NMR isotropic chemical shift observed for compound **1**, i.e. δ = –759 ppm, indeed falls in the expected range for a seven-coordinate tin atom surrounded only by oxygen atoms.

The ^{119}Sn solution NMR spectrum of compound **1** shows a single narrow line at δ = –754.7 ppm, in very good agreement with the solid-state isotropic chemical shift and the heptacoordinate nature of tin. Moreover, this line exhibits a set of satellites the intensity and magnitude of which are consistent with a dimer and a two-bond ^{119}Sn-^{117}Sn

coupling constant. All these features indicate unambiguously that the molecular structure observed for compound **1** in the solid state is maintained in solution.

The ^{1}H and ^{13}C solution NMR spectra of compound **1**, at room temperature, indicate the presence of one type of methacrylate and two types of isopropoxy groups (2:1:1 ratio), in perfect agreement with the dimeric structure. The intensities of the ^{13}C-$^{119/117}$Sn coupling satellites for the methyne carbon of the isopropoxy groups account for about 19 and 35% of the resonances located at δ = 66.8 and 74.1 ppm, respectively. As a bridging alkoxy sees two tin atoms and a terminal alkoxy only one, the ^{13}C resonance at δ = 66.8 ppm can be assigned to the terminal isopropoxy groups while the one at δ = 74.1 ppm is assigned to the bridging ligands. This result shows that in compound **1**, the magnitudes of the $^{2}J_{^{13}\mathrm{C}\text{-}^{119}\mathrm{Sn}}$ coupling constants follow the rule observed for tin(IV) tetraalkoxide, i.e. they are larger for terminal alkoxides (ca. 40 Hz) than for doubly bridging alkoxides (ca. 20 Hz).[18] With these first assignments and with the help of 2D NMR experiments (^{1}H-^{1}H COSY and ^{1}H-^{13}C HMQC), the ^{1}H and ^{13}C resonances of compound **1** have been fully attributed (Table 2). The $^{3}J_{^{1}\mathrm{H}\text{-}^{119}\mathrm{Sn}}$ coupling constants of the isopropoxy ligands appear to follow the same order as $^{2}J_{^{13}\mathrm{C}\text{-}^{119}\mathrm{Sn}}$ in that they are larger for a terminal than for a bridging alkoxy. These features likely arise from the longer Sn–O bond of a bridging alkoxy compared to a terminal one. The observation of several $^{n}J_{^{1}\mathrm{H}\text{-}^{119}\mathrm{Sn}}$ and $^{n}J_{^{13}\mathrm{C}\text{-}^{119}\mathrm{Sn}}$ scalar couplings, which, moreover, are different for the terminal and bridging isopropoxy groups, indicates that the exchange of ligands (isopropoxy or methacrylate) between different dimers and the exchange of terminal and bridging isopropoxy groups within the same dimer is either absent or very slow (slower than 1/J).

Table 2. ^{1}H and ^{13}C NMR spectroscopic data for $[\mathrm{Sn}(\mathrm{O}i\mathrm{Pr})_2(\mathrm{OMc})_2]_2$.[a]

$\delta(^{1}\mathrm{H})$/mult./integr./[$^{n}J_{^{1}\mathrm{H}\text{-}^{119}\mathrm{Sn}}$]	$\delta(^{13}\mathrm{C})$ [$^{n}J_{^{13}\mathrm{C}\text{-}^{119}\mathrm{Sn}}$]	Assignment
1.35/d/12 H	27.4 [48][b]	$\mathrm{OCH}(CH_3)_2$
1.63/d/12 H	24.2	$\mu_2\text{-}\mathrm{OCH}(CH_3)_2$
1.92/s/12 H	18.7	$\mathrm{O_2CC}(CH_3)\text{=}\mathrm{CH_2}$
4.49/sept/2 H/[90][b]	66.8 [52][c]	$\mathrm{O}CH(\mathrm{CH_3})_2$
5.27/sept/2 H/[70][b]	74.1 [16][c]	$\mu_2\text{-}\mathrm{O}CH(\mathrm{CH_3})_2$
5.29[d]/d/4 H and 6.37[e]/d/4 H	128.1	$\mathrm{O_2CC}(\mathrm{CH_3})\text{=}CH_2$
–	135.0 [32][b]	$\mathrm{O_2C}C(\mathrm{CH_3})\text{=}\mathrm{CH_2}$
–	179.0 [25][c]	$\mathrm{O_2}C\mathrm{C}(\mathrm{CH_3})\text{=}\mathrm{CH_2}$

[a] δ in ppm, J in Hz. [b] n = 3. [c] n = 2. [d] *cis*-CH$_3$. [e] *trans*-CH$_3$.

Syntheses were also performed with acetic or benzoic acid instead of methacrylic acid under the same conditions as for compound **1** (see Experimental Section). Transparent crystals were obtained with both acids and characterized by multinuclear NMR spectroscopy. Solution NMR (^{119}Sn, ^{1}H, and ^{13}C) clearly indicated that the same dimer is formed $[\mathrm{Sn}(\mu_2\text{-O}i\mathrm{Pr})(\mathrm{O}i\mathrm{Pr})(\mathrm{O_2CR})_2]_2$ (R = CH$_3$ or C$_6$H$_5$). Solid-state ^{119}Sn NMR (CP-MAS) spectra were also recorded for the benzoate (compound **2**) and acetate (compound **3**) derivatives. The spectra exhibit a single, sharp, isotropic resonance (δ = –757.3 and –759.5 ppm for **2** and **3**, respectively) very similar to the one reported for compound **1** and assigned to seven-coordinate tin atoms. Analysis of the spinning side-band manifolds for both compounds yields the same results, i.e. ζ = 280 ppm and η = 0.0. As for compound **1**, the unique tin site of compounds **2** and **3** exhibits an axial environment. The tin shielding anisotropy is slightly smaller for compounds **2** and **3** than for **1**. This feature likely indicates that the tin environment in the acetate and benzoate derivatives is less distorted than in the methacrylate derivative.

Experiments with a carboxylate to tin ratio of 1 were also performed with acetic and benzoic acid. Clear solutions were obtained in toluene or THF and characterized by ^{119}Sn NMR spectroscopy (Figure 3). For benzoic acid (in THF), the ^{119}Sn NMR spectrum shows two main resonances of equal intensity (46% for each) at δ = –662.7 and –683.4 ppm, both with coupling satellites, the magnitude (180 Hz) and the intensity (17%)[19] of which are consistent with two nonequivalent tin atoms bridged by two alkoxy groups. The spectrum also shows minor resonances between δ = –632 and –654 ppm (8% for all). For acetic acid (in toluene), there are also two main resonances of equal intensity (δ = –664.9 and –687.5 ppm, 48% each), but their width prevented us from measuring the tin–tin scalar coupling which, however, could exist. The remaining 4% of tin atoms are located in a single minor resonance at δ = –645.3 ppm that could be assigned to tin isopropoxide solvate.[18] Bearing in mind that the tin starting material and the compound formed with two carboxylates per tin atoms are both dimers, it is reasonable to hypothesize that the major species formed with only one carboxylate per tin is also a dimer. Such a dimer has to be made of two nonequivalent six-coordinate tin atoms. Such a feature could arise from a molecular structure based on two edge-sharing octahedra {as in $[\mathrm{Sn}(\mathrm{O}i\mathrm{Pr})\cdot\mathrm{HO}i\mathrm{Pr}]_2$}[11a] with a chelating carboxylate on each tin (carboxylate/Sn = 1) but without any symmetry operation between the two carboxylates. Another possibility would be a dimer built by chelation, through two bridging isopropoxy ligands, of $[\mathrm{Sn}(\mathrm{O}i\mathrm{Pr})_4]$ by $[\mathrm{Sn}(\mathrm{O}i\mathrm{Pr})_2(\mathrm{O_2CR})_2]$. One tin atom would be coordinated by four terminal and two bridging isopropoxy groups, while the other would be coordinated by two chelating carboxylates and two bridging isopropoxy ligands. At this stage, there is no reason to prefer one possibility over the other.

Attempts were made to isolate the major compound by crystallization at low temperature or solvent evaporation and recrystallization. None of them were successful, but the ^{119}Sn NMR spectrum (CDCl$_3$) of the dried benzoate sample indicates a modification of the tin speciation. The peaks at δ = –662.8 and –683.2 ppm, assigned to a dimer, now account for only around 36% each, while two of the minor peaks, located at δ = –643.9 and –655.1 ppm increase to about 22 and 6%, respectively. The ^{1}H and ^{13}C spectra of the same sample reveal complex patterns made up of many different benzoates (at least six from the ^{13}C carbonyl signals at around δ = 172 ppm) and isopropoxy groups (at least ten from the ^{13}C methyne signals between δ = 77 and 65 ppm).

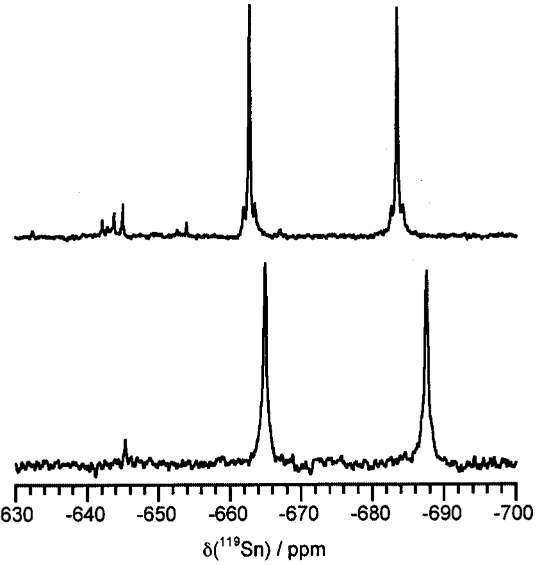

Figure 3. ^{119}Sn NMR spectra (111.9 MHz) of [Sn(O*i*Pr)$_4$·HO*i*Pr]$_2$ with 2 equiv. of benzoic acid in THF (top) and 2 equiv. of acetic acid in toluene (bottom).

Crystals of compounds **1**, **2**, and **3**, which exhibit a carboxylate to tin ratio of 2, can be precipitated for initial ratios smaller than 2. Therefore, some tin-containing species must remain in solution. Their nature was studied in the case of the benzoate derivative only. Compound **2** was prepared, in toluene, with a benzoic acid to tin ratio of 1.5 and the ^{119}Sn NMR spectrum was recorded for the solution once the crystals of **2** had been removed. The spectrum exhibits the same resonances as those described for an experiment with a benzoic acid to tin ratio of 1.0. It also shows a small peak at around $\delta = -751$ ppm that can be assigned to compound **2**. In conclusion, the tin-containing species that remain in solution correspond mainly to the dimer made of two nonequivalent tin atoms and discussed above.

The formation of carboxylate-modified metal–oxo clusters upon treatment of metal alkoxides with carboxylic acids generally results from esterification reactions[20,21] that can take place between free acid and released alcohol molecules, which results in the slow generation of water in situ for the controlled hydrolysis and condensation of the remaining alkoxy groups, or between a bonded carboxylate and a bonded alkoxy group, which yields an M–O–M link and an ester directly. Studies performed on titanium oxo-acetate clusters have demonstrated that a very small increase of the AcOH/Ti ratio favors the formation of more condensed species. However, extreme conditions (e.g. solvothermal synthesis) might be needed in order to force the esterification process.[22] For instance, [SnO(O*t*Bu)(OAc)]$_6$, a tin(IV) carboxylate oxo cluster, can only be obtained by refluxing [Sn(O*t*Bu)$_4$] and [Sn(OAc)$_4$] in toluene, a noncoordinating solvent.[9c] We tried several approaches to the possible formation of well-defined methacrylate-modified tin–oxo clusters with compound **1** as precursor. Solvothermal treatment or refluxing compound **1** in different solvents (THF, DMF, toluene) gave gels or clear solutions. The ^{119}Sn NMR spectra of the latter did not indicate any new resonance that could be associated with the formation of new, well-defined molecular species. Direct addition of various amounts of water to compound **1** always yielded transparent gels that are insoluble in organic solvents or turbid solutions that did not show any significant signals in the solution NMR spectra that could be linked back to a well-defined methacrylate-modified tin–oxo clusters.

In an alternative approach to prepare well-defined, methacrylate-modified tin–oxo clusters, syntheses were performed with higher McOH/Sn molar ratios, i.e. 5 and 10. In both cases a white precipitate was obtained. These precipitates are soluble in CDCl$_3$ but their ^{119}Sn NMR spectra are silent and their ^{1}H NMR spectra show only the presence of methacrylate ligands. The absence of any well-defined ^{119}Sn NMR resonance might be attributed to the formation of ill-defined oxo polymers,[23] either by esterification or parasitic hydrolysis, but in any case indicates clearly that this alternative approach is not more successful for preparing well-defined, methacrylate-modified tin–oxo clusters.

Conclusions

The behavior of tin(IV) isopropoxide towards the addition of different carboxylic acids (methacrylic, benzoic, and acetic) has been studied. The nature of the carboxylic acid does not affect the final result. Moreover, the solvent (i.e. toluene or tetrahydrofuran) does not seem to play any major role either. Thus, the main parameter is the carboxylate to metal molar ratio. For a ratio of 1, a dimer based on hexacoordinate tin atoms is likely formed but its exact structure remain unknown. For ratios between 1.4 and 2 the compound [Sn(μ$_2$-O*i*Pr)(O*i*Pr)(O$_2$CR)$_2$]$_2$ [R = (CH$_3$)CCH$_2$, C$_6$H$_5$, and CH$_3$], based on heptacoordinate tin atoms, is isolated. Ratios higher than 2 do not seem to yield well-defined oxo species, as for titanium or zirconium,[21] but probably result in the formation of ill-defined polymeric species.

Studies with other tin(IV) alkoxides are in progress to check the influence of the nature of the alkoxide ligand on the carboxylate substitution reactions.

Experimental Section

Synthesis: All the reactions were carried under inert atmosphere using Schlenk tubes and vacuum-line techniques. The compound [Sn(O*i*Pr)$_4$·HO*i*Pr]$_2$ was prepared by isopropanolysis of [Sn(O*t*Bu)$_4$], which was obtained according to literature methods and purified by vacuum distillation.[24] The reactions between tin(IV) isopropoxide solvate and carboxylic acids were performed in toluene or tetrahydrofuran (THF) as tin(IV) isopropoxide solvate shows little solubility in its parent alcohol (2-propanol).

[Sn(O*i*Pr)$_2$(OMc)$_2$]$_2$ (OMc = methacrylate) (1): A solution of methacrylic acid (1.22 g, 14.2 mmol) in THF (4.6 mL) was added to [Sn(O*i*Pr)$_4$·HO*i*Pr]$_2$ (3.03 g, 3.7 mmol, McOH/Sn = 1.94). The resulting clear solution was kept at –18 °C after stirring. Crystals of **1** were obtained after one week. For ^{1}H and ^{13}C NMR (C$_6$D$_6$, 25 °C) data see Table 2. ^{119}Sn NMR (C_6D_6, 25 °C): δ = –754.7 ppm ($^{2}J_{^{119}\text{Sn},^{117}\text{Sn}}$ = 190 Hz, with satellites corresponding to 7.3% of the total intensity). Yield: 76.7% (2.28 g). Compound **1** is highly soluble in chloroform, dichloromethane, and benzene. It is poorly soluble in acetonitrile, DMSO, and 2-propanol.

[Sn(O*i*Pr)$_2$(O$_2$CC$_6$H$_5$)$_2$]$_2$ (2): A similar compound was obtained by replacing methacrylic acid with benzoic acid. A solution of benzoic acid (0.91 g, 7.5 mmol) in THF (6 mL) was added to [Sn(O*i*Pr)$_4$·HO*i*Pr]$_2$ (2.00 g, 2.4 mmol, $C_6H_5CO_2H$/Sn = 1.55). ^{1}H NMR ($CDCl_3$, 25 °C): δ = 8.22 (d, 8 H, *o*-C$_6$*H*$_5$CO$_2$), 7.67 (m, 4 H, *p*-C$_6$*H*$_5$CO$_2$), 7.49 (m, 8 H, *m*-C$_6$*H*$_5$CO$_2$), 5.10 [sept, $^3J_{^1\text{H}-^{119/117}\text{Sn}}$ = 70 Hz, 2 H, OC*H*(CH$_3$)$_2$], 4.18 [sept, $^3J_{^1\text{H}-^{119/117}\text{Sn}}$ = 90 Hz, 2 H, OC*H*(CH$_3$)$_2$], 1.37 [d, 12 H, OCH(C*H*$_3$)$_2$], 1.08 [d, 12 H, OCH(C*H*$_3$)$_2$] ppm. ^{13}C NMR ($CDCl_3$, 25 °C): δ = 178.0 [$^2J_{^{13}\text{C}-^{119/117}\text{Sn}}$ = 26 Hz, C$_6$H$_5$*C*O$_2$], 134.0 (*p*-*C*$_6$H$_5$CO$_2$), 131.5 (*o*-*C*$_6$H$_5$CO$_2$), 128.5 (*m*-*C*$_6$H$_5$CO$_2$), 127.9 ($^3J_{^{13}\text{C}-^{119/117}\text{Sn}}$ = 33 Hz, *i*-*C*$_6$H$_5$CO$_2$), 74.2 [$^2J_{^{13}\text{C}-^{119/117}\text{Sn}}$ = 17 Hz, μ_2-O*C*H(CH$_3$)$_2$], 66.5 [$^2J_{^{13}\text{C}-^{119/117}\text{Sn}}$ = 54 Hz, O*C*H(CH$_3$)$_2$], 27.0 [$^3J_{^{13}\text{C}-^{119/117}\text{Sn}}$ = 48 Hz, OCH(*C*H$_3$)$_2$], 24.0 [μ_2-OCH(*C*H$_3$)$_2$] ppm. ^{119}Sn NMR ($CDCl_3$, 25 °C): δ = –751.3 ppm ($^{2}J_{^{119}\text{Sn},^{117}\text{Sn}}$ = 180 Hz, with satellites corresponding to 8.7% of the total intensity). Yield: 58.9% (1.354 g).[25] Compound **2** is highly soluble in chloroform, dichloromethane, and benzene. It is poorly soluble in acetonitrile, DMSO, and 2-propanol.

[Sn(O*i*Pr)$_2$(O$_2$CCH$_3$)$_2$]$_2$ (3): A similar compound was obtained by replacing methacrylic acid by acetic acid. A solution of acetic acid (0.44 g, 7.4 mmol) in toluene (3 mL) was added to [Sn(O*i*Pr)$_4$·HO*i*Pr]$_2$ (2.00 g, 2.4 mmol, CH_3CO_2H/Sn = 1.53). ^{1}H NMR ($CDCl_3$, 25 °C): δ = 4.72 [sept, $^3J_{^1\text{H}-^{119/117}\text{Sn}}$ = 70 Hz, 2 H, OC*H*(CH$_3$)$_2$], 4.10 [sept, $^3J_{^1\text{H}-^{119/117}\text{Sn}}$ = 90 Hz, 2 H, OC*H*(CH$_3$)$_2$], 2.18 (s, 12 H, O$_2$CC*H*$_3$) 1.35 [d, 12 H, OCH(C*H*$_3$)$_2$], 1.14 [d, 12 H, OCH(C*H*$_3$)$_2$] ppm. ^{13}C NMR ($CDCl_3$, 25 °C): δ = 183.6 ($^2J_{^{13}\text{C}-^{119/117}\text{Sn}}$ = 26 Hz, CH$_3$*C*O$_2$), 73.8 [$^2J_{^{13}\text{C}-^{119/117}\text{Sn}}$ = 16 Hz, μ_2-O*C*H(CH$_3$)$_2$], 66.4 [$^2J_{^{13}\text{C}-^{119/117}\text{Sn}}$ = 52 Hz, O*C*H(CH$_3$)$_2$], 27.0 [$^3J_{^{13}\text{C}-^{119/117}\text{Sn}}$ = 47 Hz, OCH(*C*H$_3$)$_2$], 24.0 [μ_2-OCH(*C*H$_3$)$_2$], 18.3 ($^3J_{^{13}\text{C}-^{119/117}\text{Sn}}$ = 32 Hz, *C*H$_3$CO$_2$) ppm. ^{119}Sn NMR ($CDCl_3$, 25 °C): δ = –748.4 ppm ($^{2}J_{^{119}\text{Sn},^{117}\text{Sn}}$ = 190 Hz, with satellites corresponding to about 8% of the total intensity). Yield: 24.4% (0.418 g).[25] Compound **3** is highly soluble in chloroform, dichloromethane, benzene and poorly soluble in acetonitrile, DMSO, and 2-propanol.

Chemical Analyses: Despite numerous attempts, including sampling under inert atmosphere, chemical analyses matching reasonably well the expected results could not be obtained due to a too high sensitivity of the sample to moisture. However, the ^{119}Sn solid-state and solution NMR (^{119}Sn, ^{1}H, and ^{13}C) spectra indicate that the samples are pure.

NMR Spectroscopy: ^{1}H, ^{13}C, and ^{119}Sn solution NMR experiments were performed on a Bruker AC300 spectrometer (300.13, 75.47, and 111.92 MHz for ^{1}H, ^{13}C, and ^{119}Sn, respectively). $CDCl_3$ and C_6D_6 were used as solvent and internal lock. ^{1}H and ^{13}C chemical shifts are quoted relative to TMS, using the solvent or its protonated impurities as secondary internal reference (^{1}H: δ = 7.26 and 7.16 ppm for $CHCl_3$ and C_6HD_5, respectively; ^{13}C: δ = 77.16 and 128.06 ppm for $CDCl_3$ and C_6D_6, respectively).[26] The ^{119}Sn chemical shifts are quoted relative to external tetramethyltin (δ = 0 ppm). To avoid the loss of quantitativity that can arise from the Nuclear Overhauser effect, ^{119}Sn-{^{1}H} spectra were obtained with an inverse gated decoupling sequence (pulse of about 30°, recycling delay set to 2 s for an acquisition/decoupling time of 0.18 s). ^{1}H-^{1}H COSY and ^{1}H-^{13}C HMQC experiments were performed on a Bruker Avance 400 spectrometer (400.13 and 100.61 MHz for ^{1}H and ^{13}C, respectively).

^{119}Sn solid-state NMR (CP-MAS) spectra were recorded at room temperature on a Bruker Avance 300 spectrometer (111.92 MHz for ^{119}Sn) equipped with a 4-mm locked Bruker probe. The chemical shifts are quoted relative to tetramethyltin (δ = 0 ppm) using tetracyclohexyltin (δ = –97.35 ppm) as a secondary external reference. At least two different MAS speeds were used to locate the isotropic chemical shifts unambiguously. The contact time was 3 ms and the recycling delay 3 s. The chemical shielding tensor analyses were performed according to Herzfeld and Berger[27] using the software "dm2004".[28] The results are reported as the isotropic chemical shift (δ_{iso}), the anisotropy ($\zeta = \sigma_{33} - \sigma_{\text{iso}}$), and the asymmetry ($\eta = |\sigma_{22} - \sigma_{11}|/|\zeta|$), with $\delta_{\text{iso}} = -(\sigma_{11} + \sigma_{22} + \sigma_{33})/3 = -\sigma_{\text{iso}}$ and the principal components of the tensor labeled according to $|\sigma_{33} - \sigma_{\text{iso}}| > |\sigma_{11} - \sigma_{\text{iso}}| > |\sigma_{22} - \sigma_{\text{iso}}|$.

Crystal Structure Determination: A single crystal of the moisture-sensitive compound **1** was selected, rapidly mounted on a glass fiber, and transferred into a cold nitrogen gas stream. Diffraction data were collected on a Nonius KappaCCD diffractometer at 123 K. Unit-cell parameters determination, data collection, and integration were carried out with the Nonius EVAL-14 suite of programs.[29] The data were corrected for absorption by a multi-scan method.[30] The structure was solved by direct methods with SHELXS-86,[31] refined by full-matrix least-squares on F^2 and completed with SHELXL-97.[32] Graphics were produced with DIAMOND.[33] All non-H atoms were refined with anisotropic displacement parameters and H atoms were simply introduced at calculated positions (riding model).

$C_{28}H_{48}O_{12}Sn_2$, M = 814.04, monoclinic, a = 11.1180(10), b = 11.1316(10), c = 14.3234(13) Å, β = 101.36°, V = 1737.9(3) Å^3, T = 123(2) K, $P2_1/n$, Z = 2, $d_{\text{calcd.}}$ = 1.556 g cm^{-3}, λ(Mo-K_α) = 0.71073, μ(Mo-K_α) = 1.492 mm^{-1}, 28539 reflections measured, 6040 unique (R_{int} = 0.0791) which were used in all calculations. The final $wR(F)^2$ was 0.0770 (all data).

CCDC-256335 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments

This work was supported in part by the European Community's Human Potential Program under contract HPRN-CT-2002-00306 (NBB Hybrids). E.M.-F. thanks the European Community for financial support [HPRN-CT-2002-00306 (NBB Hybrids)]. Ms. Marie-Nöelle Rager is gratefully acknowledged for her kind and valuable help in recording and processing the 2D NMR spectra.

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Received: June 27, 2005