New Fluorinated Stannic Compounds as Precursors of F-Doped SnO$_2$ Materials Prepared by the Sol−Gel Route

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Dialkoxydi(β-diketonate)tin(IV) compounds react either with difluorodi(β-diketonate)tin(IV) or with butanoyl fluoride to yield novel tin complexes Sn(OR^1)F(R^{2}COCHCOR^2)$_2$ **1** (R^1 = *tert*-amyl, isopropyl, ethyl; R^2 = methyl, *tert*-butyl). Multinuclear ^{1}H, ^{13}C, ^{19}F, and ^{119}Sn NMR spectroscopic characterization showed that complexes **1** are octahedral in solution with a cis configuration for the fluorine and the alkoxide group. Kinetics of configurational rearrangements were studied by variable-temperature ^{13}C NMR spectroscopy. The hydrolytic behavior of **1** was determined for different hydrolysis ratios h = [H$_2$O]/[**1**]. For R^1 = *tert*-amyl, a dimeric fluorinated species was mainly obtained for h = 0.5, and addition of 2 mol equiv of water led to a fluorinated stannic oxopolymer soluble in CH$_3$CN. In the latter case, the powder obtained after solvent elimination and treatment in air at 550 °C consisted of crystalline SnO$_2$ cassiterite particles containing the required amount (3 mol %) of doping fluorine and exhibiting electronic conductivity comparable to that of Sn-doped In$_2$O$_3$. Complexes **1** are the first precursors of F-doped SnO$_2$ materials prepared by the sol−gel route.

Introduction

Doped tin dioxide films are transparent conductors exhibiting high chemical and mechanical stabilities even at high temperature.[1] They therefore find widespread applications in the field of modern optoelectronic devices such as electrochromic displays and solar cells. Fluorine is usually preferred to antimony as a dopant because it gives films with the highest transparency and conductivity.[1,2]

Fluorine-doped tin dioxide (SnO$_2$:F) thin films have been prepared by a number of techniques such as spray pyrolysis,[3] reactive rf sputtering,[4] and chemical vapor deposition (CVD).[5] These routes, however, require drastic experimental conditions such as high temperature or low pressure and often use two separate precursors as sources of tin and fluorine, leading to an increase of the parameters to control. In addition, the wide use of stannic chloride derivatives as a tin source sometimes alters the conductivity properties due to pollution by chlorine.[2]

To circumvent the previous drawbacks, the sol−gel method seems to be promising, although new troubles such as shrinkage and cracking due to elimination of the organics may appear.

Sol−gel processes involve mild conditions and are based on hydrolysis and condensation reactions of metalloorganic compounds, such as metal alkoxides M(OR)$_n$, preforming an oxide network in solution named "sol". Deposition of the latter by dip-coating and thermal pretreatment at moderate temperature could then allow, at low cost, films of good quality to be obtained on large areas. Although examples concerning undoped[6] and antimony-doped[7] tin dioxide films have already been described in the literature, to our knowledge, this method has never been investigated to prepare F-doped SnO$_2$ materials due to the lack of a suitable precursor. Several requirements must be filled by such a molecule: it should include tin, fluorine, and moieties cleaved by water with fluorine retention, and give stable sols after hydrolysis−condensation reactions. Single precursors such as Sn(OOCCF$_3$)$_2$,[5b] Sn(OCH(CF$_3$)$_2$)$_2$(HNMe$_2$),[8] and Sn(OCH(CF$_3$)$_4$(HNMe$_2$)$_2$,[5c] which have been reported for the CVD technique, cannot be presently used since the fluorine atoms are located on groups removed upon hydrolysis.

In this work, our aim was to design new precursors that have the potential to yield fluorine-doped tin dioxide materials by the sol−gel route. We have chosen to create a covalent bond between tin and fluorine since the Sn−F bond is very strong[9] and to introduce different moisture-sensitive groups in the coordination sphere of tin to vary the hydrolysis kinetics. It is well-known that tin can easily expand its coordination sphere up to 8, which makes hydrolysis of tin alkoxides very fast.[10] To avoid precipitation even at low water content, a convenient

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strategy is to use hydroxylated strong complexing agents such as β-diketones which lower hydrolysis rates of metal alkoxides and give sols for the deposition by the sol−gel technique.[11] Consequently, we herein report the synthesis, the structure in solution, and the hydrolytic behavior of new molecular precursors $SnF(OR^1)(R^2COCHCOR^2)_2$ **1** of F-doped SnO_2 materials.

Experimental Section

General Procedures and Starting Materials. All reactants and products were manipulated under a nitrogen atmosphere by using standard Schlenk techniques and a glovebox, or in a vacuum, with exclusion of moisture and air. THF and diethyl ether were distilled from sodium benzophenone ketyl prior to use. Acetonitrile, chloroform, dichloromethane, and *n*-hexane were distilled over CaH_2. Ethyl, isopropyl, and *tert*-amyl alcohols were distilled over magnesium. All solvents were stored over activated 4 Å molecular sieves under an atmosphere of nitrogen in a glass storage vessel fitted with a high-vacuum PTFE stopcock. Tin(II) difluoride (Acros) was used as purchased. Pentane-2,4-dione (Aldrich) was distilled just before use. 2,2,6,6-Tetramethylheptane-3,5-dione[12] and butanoyl fluoride[13] were prepared according to the literature methods. Tetra(*tert*-amyloxy)tin-(IV) was synthesized according to Thomas's procedure.[14] Trans-alcoholysis of the latter compound gave tetra(isopropoxy)tin(IV) and tetra(ethoxy)tin(IV) according to previously reported results.[15]

Instrumentation. NMR solution analyses were performed on a Bruker AC-250 spectrometer or a Bruker DPX-200 spectrometer. ^{1}H NMR spectra were recorded at 250 MHz (solvent $CDCl_3$), while ^{13}C NMR spectra were obtained at 62.9 MHz (solvent $CDCl_3$). Chemical shifts were referenced using the *protio* impurities of the deuterated solvent. ^{119}Sn NMR spectra were recorded at 74.6 MHz (solvent $CDCl_3$, internal reference Me_4Sn) and ^{19}F NMR spectra at 188.3 MHz (solvent $CDCl_3$, internal reference $CFCl_3$). For NMR data, the multiplicity, coupling constants (Hz), and integration are given in parentheses. Tin−hydrogen and tin−carbon coupling constants (Hz) are given in brackets. As far as the assignments of NMR resonances are concerned, *chel* and *al* stand for β-diketonate and alkoxide groups, respectively. Mass spectrometry data were collected with a VG Autospec-Q working in the electronic impact mode. Elemental analyses were performed at the Center of Chemical Analysis of the CNRS (Vernaison, France).

Bis(2-methylbutan-2-oxy)di(pentane-2,4-dionato)tin(IV) (2a). In a Schlenk tube, 3.96 g (39.5 mmol) of pentane-2,4-dione was slowly added to 9.24 g (19.7 mmol) of $Sn(O^tAm)_4$. The mixture was stirred at room temperature for 30 min, and the released *tert*-amyl alcohol was removed under reduced pressure at 50 °C. The crude oil was purified by distillation ($E_b^{0.001} = 140$ °C) to give an orange solid (6.97 g, 14.2 mmol, yield 72%). ^{1}H NMR ($CDCl_3$): δ 5.34 (s, 2H, CH(chel)), 1.93 (s, 6H, CH_3(chel)), 1.81 (s, 6H, CH_3(chel)), 1.37 (q, 7, 4H, CH_2(al)), 1.06 (s, 12H, C(C$H_3)_2$(al)), 0.72 (t, 7, 6H, CH_2CH_3(al)). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 193.6 ([30], CO(chel)), 193.3 ([33], CO(chel)), 100.8 ([64], CH(chel)), 73.2 ([51], C($CH_3)_2$(al)), 37.6 ([45], CH$_2CH_3$(al)), 29.8 ([26], C(C$H_3)_2$(al)), 29.4 ([28], C(C$H_3)_2$(al)), 27.3 and 27.1 ([23], CH$_3$(chel)),

8.7 ($CH_2C$$H_3$(al)). MS-EI: m/z 405 [$M^+ - (C_5H_{11}O)$]; 364 [$M^+ - (CH_3$-$COCHCOCH_3) - (C_2H_5)$]; 335 [$M^+ - (CH_3COCHCOCH_3) - (C_2H_5)$ − (CH_3)].

Di(pentane-2,4-dionato)di(propan-2-oxy)tin(IV) (2b). Procedure A. The same procedure as for **2a** was followed with 4.19 g (42 mmol) of pentane-2,4-dione and 7.51 g (21 mmol) of $Sn(O^iPr)_4$. The crude oil was purified by distillation ($E_b^{0.003} = 110$ °C) to give a yellow solid (2.75 g, 6.3 mmol, yield 30%). **Procedure B.** In a Schlenk tube, an excess of isopropyl alcohol (10 mL) was added to 4.01 g (8.2 mmol) of **2a**. The mixture was stirred at room temperature for 3 h, and the released *tert*-amyl alcohol was removed under reduced pressure at 50 °C to give 3.46 g (7.9 mmol, yield 96%) of crude product which was purified as previously described. ^{1}H NMR ($CDCl_3$): δ 5.38 (s, 2H, CH(chel)), 4.11 (septet, 6, 6H, CH(al)), 1.95 (s, 6H, CH_3(chel)), 1.84 (s, 6H, CH_3(chel)), 1.01 (d, 6, 6H, CH_3(al)), 0.99 (d, 6, 6H, CH_3(al)). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 194.7 ([32], CO(chel)), 194.5 ([29], CO-(chel)), 101.3 ([61], CH(chel)), 64.6 ([38], CH(al)), 27.2 ([21], CH$_3$-(chel)), 26.3 (CH$_3$(al)). (MS-EI: (m/z) 377 [$M^+ - (C_3H_7O)$]; 219 [M^+ − 2F − ($CH_3COCHCOCH_3$)].

Di(ethanoxy)di(pentane-2,4-dionato)tin(IV) (2c). Procedure A. In a Schlenk tube, 1.40 g (4.68 mmol) of $Sn(OEt)_4$ was dissolved in 2 mL of $CHCl_3$. Then, 0.94 g (9.36 mmol) of pentane-2,4-dione was added slowly, and the mixture was stirred at room temperature for 30 min. The released ethyl alcohol was removed under reduced pressure at 50 °C, leading to an oil which could be used without further purification (1.75 g, 4.3 mmol, yield 92%). **Procedure B.** The same procedure as for **2b** was followed with 1.34 g (2.73 mmol) of **2a** and 0.4 g (8.7 mmol) of ethyl alcohol. After removal of the volatile compounds, 1.09 g (2.67 mmol, yield 98%) of an oil was obtained and used without further purification. ^{1}H NMR ($CDCl_3$): δ 5.35 (s, 2H, CH(chel)), 3.72 (q, 7, 4H, CH_2(al)), 1.92 (s, 6H, CH_3(chel)), 1.82 (s, 6H, CH_3(chel), 0.99 (t, 7, 6H, CH_3(al)). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 194.8 ([32], CO(chel)), 194.7 ([30], CO(chel)), 101.4 ([61], CH(chel)), 59.7 ([38], CH$_2$(al)), 27.1 ([22], CH$_3$(chel)), 19.3 ([37], CH$_3$(al)).

Bis(2-methylbutan-2-oxy)bis(2,2,6,6-tetramethylheptane-3,5-di-onato)tin(IV) (2d). In a Schlenk tube, 3 g (6.4 mmol) of $Sn(O^tAm)_4$ was dissolved in 6 mL of CH_2Cl_2. After cooling at 0 °C, 2.36 g (12.8 mmol) of 2,2,6,6-tetramethylheptane-3,5-dione was slowly added, and the mixture was then stirred at room temperature for 1 h. The solvent and the released *tert*-amyl alcohol were removed under vacuum at 70 °C, leading to a white powder. Recrystallization at −30 °C after dissolution in 4 mL of boiling diethyl ether gave colorless needles (2.3 g, 3.5 mmol, yield 55%). ^{1}H NMR ($CDCl_3$): δ 5.71 (s, [6], 2H, CH(chel)), 1.45 (q, 7, 4H, CH_2(al)), 1.18 (s, 30H, CH_3(chel) and C(C$H_3)_2$(al)), 1.04 (s, 18H, CH_3(chel)), 0.85 (t, 7, 6H, CH$_2C$$H_3$(al)). [13]C{[1]H} NMR ($CDCl_3$): δ 203.3 ([40], CO(chel)), 202.9 ([36], CO-(chel)), 91.2 ([62], CH(chel)), 72.8 ([52], C($CH_3)_2$(al)), 41.6 and 41.5 ([20], C($CH_3)_3$(chel)), 38.1 ([51], CH$_2CH_3$(al)), 30.0 ([23], C(CH$_3)_2$-(al)), 29.9 ([25], C(CH$_3)_2$(al)), 28.1 and 27.9 ([not resolved], C(CH$_3)_3$-(chel)), 9.1 ($CH_2C$$H_3$(al)). MS-EI: m/z 573 [$MH^+ - OC_5H_{11}$]; 303 [$MH^+ - 2(OC_5H_{11}) - ((CH_3)_3CCOCHCOC(CH_3)_3)$]. Anal. Calcd for $C_{32}H_{60}O_6Sn$: C, 58.28; H, 9.17; Sn, 19.00. Found: C, 57.85; H, 8.90; Sn, 19.80.

Difluorodi(pentane-2,4-dionato)tin(IV) (3a). In a Schlenk tube, a suspension of 6.1 g (38.8 mmol) of SnF_2 in 87.75 g (876 mmol) of pentane-2,4-dione was heated at 90 °C. Oxygen was then bubbled through the mixture for 6 h. Chloroform (40 mL) was immediately added, and the warm mixture was filtrated over Celite to remove the unreacted SnF_2. The resulting solution was concentrated under reduced pressure, and addition of *n*-hexane induced precipitation of a white powder purified by successive washings (5 × 40 mL) with *n*-hexane. After drying in a vacuum, 12.15 g (34.1 mmol, yield 88%) of **3a** was obtained. (mp 227 °C). ^{1}H NMR ($CDCl_3$): δ 5.70 (s, 2H, CH(chel)), 2.18 (s, 6H, CH_3(chel)), 2.10 (s, 6H, CH_3(chel). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 197.4 and 197.3 ([34], CO(chel)), 103.0 ([77], CH(chel)), 28.0 ([33], CH$_3$(chel)). MS-EI: m/z 356 [M^+]; 336 [$MH^+ - F$]; 279 [$MH^+ - F - (CH_3COCH_3)$]; 257 [$M^+ - (CH_3COCHCOCH_3)$]; 238 [$M^+ - F - (CH_3COCHCOCH_3)$]; 219 [$M^+ - 2F - (CH_3$-$COCHCOCH_3)$].

Difluorobis(2,2,6,6-tetramethylheptane-3,5-dionato)tin(IV) (3b). In a Schlenk tube, a suspension of 3.45 g (22 mmol) of SnF_2 in 32 g

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(174 mmol) of 2,2,6,6-tetramethylheptane-3,5-dione was heated at 90 °C. Oxygen was then bubbled through the mixture for 6 h. After cooling, hot chloroform (60 mL) was added, and unreacted SnF₂ was removed by filtration over Celite. The resulting solution was concentrated under vacuum to give a yellow paste. Addition of *n*-hexane induced crystallization of a white powder purified by five washings (40 mL) with *n*-hexane. After the powder was dried in a vacuum, 7.79 g (14.9 mmol, yield 68%) of **3b** was obtained. Recrystallization from boiling diethyl ether yielded colorless plates (mp 122−123 °C). ^{1}H NMR (CDCl₃): δ 5.91 (s, [7.9], 2H, C*H*(chel)), 1.21 (s, 18H, C*H₃*(chel)), 1.07 (s, 6H, C*H₃*(chel). ^{13}C{^{1}H} NMR (CDCl₃): δ 207.3 and 206.6 ([32], *C*O(chel)), 93.2 ([76], *C*H(chel)), 42.4 and 42.3 ([not resolved], *C*(CH₃)₃(chel)), 27.8 and 27.7 ([not resolved], C(*C*H₃)₃(chel)). MS-EI: *m/z* 524 [M⁺]; 505 [M⁺ − F]; 487 [MH⁺ − 2F]; 467 [M⁺ − C(CH₃)₃]; 341 [M⁺ − ((CH₃)₃CCOCHCOC(CH₃)₃)]; 303 [M⁺ − F − ((CH₃)₃-CCOCHCOC(CH₃)₃)]. Anal. Calcd for C₂₂H₃₈F₂O₄Sn: C, 50.50; H, 7.32; F, 7.26; Sn, 22.69. Found: C, 49.85; H, 7.30; F, 7.13; Sn, 23.12.

Fluoro(2-methylbutan-2-oxy)bis(pentane-2,4-dionato)tin(IV) (1a). Procedure A. In a Schlenk tube, 1.16 g (2.37 mmol) of **2a** in 2 mL of *tert*-amyl alcohol was added to a suspension of 0.84 g (2.37 mmol) of **3a** in 2 mL of *tert*-amyl alcohol. The resulting mixture was heated at 80 °C for 15 min to obtain a clear solution. Removal of the solvent under reduced pressure at 50 °C yielded 2 g of a brown oil containing 90 mol % **1a**. **Procedure B.** In a Schlenk tube, 1.75 g (3.6 mmol) of **2a** was dissolved in 10 mL of freshly distilled THF. Under vigorous stirring, 0.321 g (3.6 mmol) of butanoyl fluoride was slowly added with a syringe. The mixture was then refluxed overnight. Evaporation of the solvent and of the released ester under vacuum at 50 °C gave 1.5 g of an orange oil containing 86 mol % **1a**. ^{1}H NMR (CDCl₃): δ 5.55 (s, 1H, C*H*(chel)), 5.52 (s, 1H, C*H*(chel)), 2.09 (s, 3H, C*H₃*(chel)), 2.07 (s, 3H, C*H₃*(chel)), 2.01 (s, 3H, C*H₃*(chel)), 2.00 (s, 3H, C*H₃*(chel)), 1.44 (q, 7, 2H, C*H₂*(al)), 1.14 (s, 6H, C(C*H₃*)(al)), 0.80 (t, 7, 3H, CH₂C*H₃*(al)). ^{13}C{^{1}H} NMR (CDCl₃): δ 195.7 ([32], *C*O(chel)), 195.0 ([30], *C*O(chel)), 194.7 and 194.6 [not resolved], *C*O(chel)), 101.5 ([65], *C*H(chel)), 101.3 ([65], *C*H(chel)), 73.2 (d, $J(^{13}$C−^{19}F) = 2, [46], *C*(CH₃)₂(al)), 37.1 (d, $J(^{13}$C−^{19}F) = 1, [45], C*H₂*CH₃(al)), 29.6 and 29.2 ([32], C*H₃*(chel)), 27.1 and 27.0 ([24], C(*C*H₃)₂(al)), 8.4 (CH₂*C*H₃(al)).

Fluorodi(pentane-2,4-dionato)(propan-2-oxy)tin(IV) (1b). Procedure A. The same procedure as for **1a** was followed with 0.89 g (1.97 mmol) of **2b**, 0.70 g (1.97 mmol) of **3a**, and 8 mL of isopropyl alcohol (heating time at 90 °C, 1.5 h). Removal of the solvent under reduced pressure at 50 °C yielded 1.55 g of a brown oil containing 65 mol % **1b**. **Procedure B.** The same procedure as for **1a** was followed with 3.43 g (7.88 mmol) of **2b**, 0.71 g (7.88 mmol) of butanoyl fluoride, and 6 mL of THF. The mixture was refluxed overnight. Evaporation of the solvent and of the released ester under vacuum at 50 °C gave 3 g of an orange oil containing 70 mol % of **1a**. ^{1}H NMR (CDCl₃): δ 5.56 (s, 2H, C*H*(chel)), 4.26 (septet, 6, 1H, C*H*(al)), 2.09 (s, 3H, C*H₃*(chel)), 2.07 (s, 3H, C*H₃*(chel)), 1.99 (s, 3H, C*H₃*(chel)), 1.97 (s, 3H, C*H₃*(chel)), 1.06 (d, 6, 3H, C*H₃*(al)), 1.02 (d, 6, 3H, C*H₃*(al)). ^{13}C{^{1}H} NMR (CDCl₃): δ 197.1 ([33], *C*O(chel)), 196.2, 195.9 and 195.7 ([not resolved], *C*O(chel)), 102.1 ([67], *C*H(chel)), 65.8 ([40], *C*H(al)), 27.5 (C*H₃*(chel)), 26.4 ([38], C*H₃*(al)).
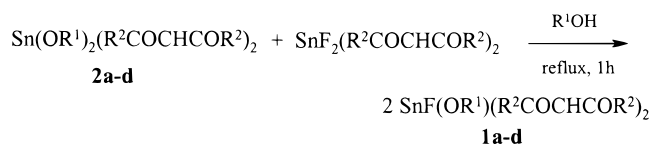
Ethoxyfluorobis(pentane-2,4-dionato)tin(IV) (1c). Procedure A. The same procedure as for **1a** was followed with 1.09 g (2.67 mmol) of **2c**, 0.95 g (2.67 mmol) of **3a**, and 8 mL of ethyl alcohol (heating time at 90 °C, 1.5 h). Removal of the solvent under reduced pressure at 50 °C gave 2 g of a brown oil containing 70 mol % **1c**. ^{1}H NMR (CDCl₃): δ 5.52 (s, 2H, C*H*(chel)), 3.84 (q, 7, 2H, C*H₂*(al)), 2.02 (s, 6H, C*H₃*(chel)), 1.94 (s, 6H, C*H₃*(chel), 1.08 (t, 7, 3H, C*H₃*(al)). ^{13}C{^{1}H} NMR (CDCl₃): δ 196.3, 196.1, 195.9 and 195.8 ([not resolved], *C*O(chel)), 102.1 ([70], *C*H(chel)), 60.4 (d, $J(^{13}$C−^{19}F) = 2, [42], C*H₂*-(al)), 27.4 (C*H₃*(chel)), 19.4 ([39], C*H₃*(al)).
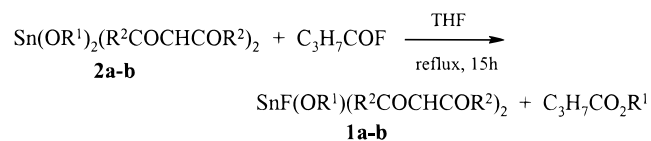
Fluoro(2-methylbutan-2-oxy)bis(2,2,6,6-tetramethylheptane-3,5-dionato)tin(IV) (1d). Procedure A. The same procedure as for **1a** was followed with 1.16 g (1.76 mmol) of **2d**, 0.91 g (1.75 mmol) of **3b**, and 15 mL of *tert*-amyl alcohol (heating time at 90 °C, 1.5 h). Removal of the solvent under reduced pressure at 50 °C yielded 2.06 g of an orange oil containing 80 mol % **1d**. ^{1}H NMR (CDCl₃): δ 5.74 (s, [7], 1H, C*H*(chel)), 5.72 (s, [7], 1H, C*H*(chel)), 1.40 (q, 7, 2H, C*H₂*(al)),

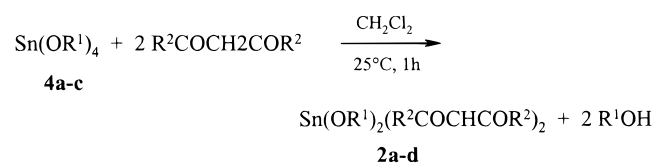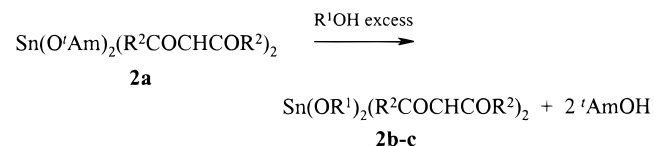**Scheme 1.** Synthetic Pathway toward Alkoxyfluorobis(β-diketonate)tin(IV) **1**^{a}

Route A:

$$\text{Sn(OR}^1)_2(\text{R}^2\text{COCHCOR}^2)_2 \ + \ \text{SnF}_2(\text{R}^2\text{COCHCOR}^2)_2 \xrightarrow[\text{reflux, 1h}]{\text{R}^1\text{OH}}$$

2a–d

$$2 \ \text{SnF(OR}^1)(\text{R}^2\text{COCHCOR}^2)_2$$

1a–d

Route B :

$$\text{Sn(OR}^1)_2(\text{R}^2\text{COCHCOR}^2)_2 \ + \ \text{C}_3\text{H}_7\text{COF} \xrightarrow[\text{reflux, 15h}]{\text{THF}}$$

2a–b

$$\text{SnF(OR}^1)(\text{R}^2\text{COCHCOR}^2)_2 \ + \ \text{C}_3\text{H}_7\text{CO}_2\text{R}^1$$

1a–b

^{a} **1a**, **2a**: R^1 = *t*-Am, R^2 = Me. **1b**, **2b**: R^1 = *i*-Pr, R^2 = Me. **1c**, **2c**: R^1 = Et, R^2 = Me. **1d**, **2d**: R^1 = *t*-Am, R^2 = *t*-Bu.

1.13 (s, 6H, C(C*H₃*)(al)), 1.12, 1.11, 0.98 and 0.97 (s, 36H, C*H₃*(chel)), 0.77 (t, 7, 3H, CH₂C*H₃*(al)). ^{1}H NMR (C₇D₈): δ 5.76 (s, 1H, C*H*(chel)), 5.74 (s, 1H, C*H*(chel)), 1.65 (q, 7, 2H, C*H₂*(al)), 1.43 and 1.42 (s, 6H, C(C*H₃*)(al)), 1.11, 1.10, 0.97 and 0.96 (s, 36H, C*H₃*(chel)), 1.06 (t, 7, 3H, CH₂C*H₃*(al)). ^{13}C{^{1}H} NMR (CDCl₃): δ 205.2, 205.1, 204.8, 204.2 ([not resolved], *C*O(chel)), 92.1 and 91.9 ([78], *C*H(chel)), 73.1 ([49], *C*(CH₃)₂(al)), 41.8, 41.7 and 41.6 [not resolved], *C*(CH₃)₃(chel)), 37.6 ([45], C*H₂*CH₃(al)), 30.0 and 29.9 ([not resolved], C(*C*H₃)₂(al)), 27.9, 27.7, and 27.6 [not resolved], C(*C*H₃)₃(chel)), 8.8 (CH₂*C*H₃(al)).

Hydrolysis Experiments. To a stirred solution of **1** in CH₃CN was added slowly a mixture of water and CH₃CN. The molar ratio between CH₃CN and **1** was maintained at 50:1, and the hydrolysis ratio h = [H₂O]/[**1**] was varied from 0.5 to 10. After the mixture was dried for 1 h at room temperature, sols, gels, or precipitates were obtained depending on the precursor **1** used and on the h value. In each case, the solvent and volatile compounds were removed under vacuo at 50 °C to yield white or yellow powders. For $h \leq 2$, the xerosols or xerogels were completely soluble in CDCl₃ or *d₆*-DMSO and analyzed by multinuclear (^{1}H, ^{13}C, ^{19}F, ^{119}Sn) NMR spectroscopy. Two xerosols (**1a**, h = 0.5, and **1a**, h = 2), labeled X₁ and X₂, respectively, were particularly studied and prepared as follows. (X₁) **1a**, 3.2 g, 7.56 mmol; H₂O, 0.064 g, 3.55 mmol; CH₃CN, 15.41 mL. After drying, 2.6 g of a yellow powder was recovered. Elemental analysis: (exptl) wt % Sn = 35.39, wt % F = 6.18, wt % C = 29.33, wt % H = 3.45. (X₂) **1a**, 2.83 g, 6.68 mmol; H₂O, 0.24 g, 13.33 mmol; CH₃CN, 13.62 mL. After drying, 2 g of a yellow powder was obtained. Elemental analysis: (exptl) wt % Sn = 44.70, wt % F = 7.25, wt % C = 21.00, wt % H = 3.00. The volatile organics removed during the drying of xerosol X₂ were recovered with two successive liquid nitrogen cold traps. The obtained residues were analyzed by ^{1}H NMR spectroscopy, allowing the determination of the relative amount of alkoxide and β-diketonate groups hydrolyzed.

Thermolysis Experiments. Thermolysis of xerosol X₂ was carried out by first drying the powder at 50 °C, followed by pressing (5 ton·cm⁻²) the resulting material (400 mg) as a pellet which was then treated in air for 30 min at various temperatures ranging between 150 and 550 °C. Crystallinity of the resulting powder was determined by powder X-ray diffraction using a Philips θ-2θ PW1820 diffractometer. The sample resistivity was estimated by compacting under pressure (10 tons) a given amount of powder (200 mg) between two stainless steel cylinders. The resistance R_s of the as-pelletized materials (13 mm diameter, 0.42 mm thickness) was measured with a Metrix ITT MX50 multimeter. The measurements were performed under pressure (0.5 ton) using the previous cylinders as contacts. The sample resistivity ρ_s was deduced from R_s by the simple formula $\rho_s = SR_s/e$ where S and e are the surface and the thickness of the sample, respectively. The resistivity of the materials prepared in this study was compared to that of tin-doped indium oxide (ITO) powder (purchased from Samsung Electronics (Korea); tin content 10 mol %) determined in the same experimental conditions.
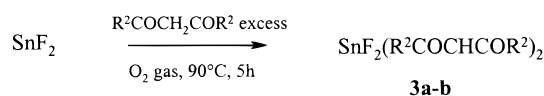
Scheme 2. Synthetic Pathway toward Dialkoxybis(β-diketonate)tin(IV) **2**[a]

Route A:

$$Sn(OR^1)_4 + 2\ R^2COCH2COR^2 \xrightarrow[\text{25°C, 1h}]{CH_2Cl_2}$$

4a-c

$$Sn(OR^1)_2(R^2COCHCOR^2)_2 + 2\ R^1OH$$

2a-d

Route B :

$$Sn(O^tAm)_2(R^2COCHCOR^2)_2 \xrightarrow{R^1OH\ excess}$$

2a

$$Sn(OR^1)_2(R^2COCHCOR^2)_2 + 2\ {}^tAmOH$$

2b-c

[a] **2a**, **4a**: R^1 = t-Am, R^2 = Me. **2b**, **4b**: R^1 = i-Pr, R^2 = Me. **2c**, **4c**: R^1 = Et, R^2 = Me. **2d**: R^1 = t-Am, R^2 = t-Bu.

Results and Discussion

Synthetic Aspects. Two main chemical pathways can be contemplated to reach complexes **1** (Scheme 1). The first path (route A) uses a Kocheshkov-like redistribution[16] between a dialkoxytin(IV), **2**, and a difluorotin(IV), **3**, derivative, the latter being obtained from commercially available SnF_4[17] or SnF_2.[18] The second way (route B) consists of a direct fluorination of a dialkoxytin(IV) compound, **2**, with a carboxylic acid fluoride. To our knowledge, very few examples of these two routes have been previously described in the literature. The latter has been developed with success on dialkoxydiorganotin compounds,[19] whereas the former was reported on difluoro- and dialkoxydiorganotin derivatives.[20]

In both cases, the preparation of dialkoxytin(IV) complexes **2** is required. Since the pioneering works of Mehrotra,[21] who described the preparation of mixed complexes $Sn(OR)_{4-n}(\beta$-diketonate)$_n$ (n = 1, 2) from tin tetraalkoxides **4** and pentane-2,4-dione, few detailed studies on related compounds have appeared. Chandler et al. obtained both 3:1 and 2:2 complexes with primary and secondary alkoxides,[22] whereas it was recently reported that only 2:2 pure complexes can be isolated with tertiary alkoxides.[11b] In the first step, we quantitatively obtained compounds **2** by adding 2 equiv of β-diketones to tin tetraalkoxides **4** as described by Armelao et al.[11b] (Scheme 2). Analytically pure products were obtained by distillation but with a significant decrease in yield. Primary and, to a lesser extent, secondary tin tetraalkoxides are rather difficult to handle and isolate in good yields due to their higher moisture sensitivity and their high molecular complexity.[23] It was therefore more efficient to use alcohol interchange reactions to obtain **2b,c** from the more easily available **2a**. It must be noted that two opposite trends rule trans alcoholysis. It is indeed well-known that, on one hand, the facility for interchange increases when the steric hindrance of the removed alkoxy group decreases in the order OC_2H_5 > $OCH(CH_3)_2$ > $OC(CH_3)_2C_2H_5$[24] and, on the other hand, this

Scheme 3. Synthesis of Difluorobis(β-diketonate)tin(IV) **3**[a]

$$SnF_2 \xrightarrow[\text{O}_2\ \text{gas, 90°C, 5h}]{R^2COCH_2COR^2\ excess} SnF_2(R^2COCHCOR^2)_2$$

3a-b

[a] **3a**: R^2 = Me. **3b**: R^2 = t-Bu.

reaction is favored when the pK_a of the alcohol added is lower than that of the alcohol being liberated,[22] the acidity order in solution being H_2O > C_2H_5OH > $(CH_3)_2CHOH$ > $C_2H_5(CH_3)_2$-COH.[25] To drive the reaction in the desired direction, a large excess of alcohol was used and allowed to quantitatively convert **2a** into **2b,c**.

Besides, route A (Scheme 1) necessitates the preliminary synthesis of stabilized difluorotin(IV) complexes **3**. Analytically pure (pentane-2,4-dionato)$_2$SnF$_2$ (**3a**) has already been synthesized by the nucleophilic substitution of tin tetrafluoride with pentane-2,4-dione.[17] Because of handling difficulties and the cost of SnF_4, we decided to generalize a method proposed by Stepanov[18] to reach the difluorotin derivatives **3**. This route consists of the oxidative addition of β-diketones to tin difluoride in the presence of gaseous oxygen (Scheme 3). The reaction conditions have been improved by increasing the β-diketone excess and the reaction time, permitting the synthesis of large amounts of **3** in good yield (68−88%).

Redistribution (Scheme 1, route A) between **2** and **3** yielded **1** in a 65−90 mol % conversion rate, determined by ^{1}H NMR analysis, depending on the nature of the alkoxide group. Purification of **1** by distillation led to **2**. Several features must be underlined: (i) 5−10 mol % of each starting material was always recovered; (ii) primary and secondary alkoxides **2c,d** always led to small amounts of hydrolysis products; (iii) higher conversion rates were observed for the bulky alkoxides **2a** and **2d**. These results may be rationalized as follows. An equilibrium among compounds **2**, **3**, and **1** likely takes place, preventing the complete conversion into **1**. In addition, hydrolysis kinetics of primary and secondary alkoxides being faster than that of tertiary analogues, complexes **1b,c** were obtained in lower yields.

Direct fluorination of stabilized dialkoxytin(IV) compounds **2a,b** was investigated to shorten the synthetic pathway (Scheme 1, route B). Butanoyl fluoride was preferred to acetyl fluoride because it is easier to manipulate and forms a volatile ester simple to remove with *tert*-amyl alcohol. The use of a stoichiometric amount of the fluoride and a reaction time of 12 h allowed 85 and 70 mol % conversion to **1a** and **1b**, respectively, to be reached. Special attention must be paid to the removal conditions of the ester formed. Temperatures higher than 60 °C indeed induce a degradation of the monofluorinated compounds **1**. However, compound **3a** was also found as a byproduct. It must be noted that experiments driven in the presence of 2 equiv of the carboxylic acid fluoride yield stepwise the monofluoro **1** (after 1 h) and then the difluoro **3** (overnight) derivatives.

Characterization of $Sn(OR^1)_2(R^2COCHCOR^2)_2$ 2. Studies have already been devoted to the structure in solution of tin-(IV) alkoxides stabilized by β-diketones.[11b,22,23] However, the nature of the compounds obtained remains uncertain in the case of the less bulky alkoxides[22] and was reinvestigated.

Complexes **2** were characterized by a single ^{119}Sn NMR resonance in solution between −690 ppm and −725 ppm, a

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Table 1. ^{119}Sn and ^{19}F NMR Data of Compounds **1**, **2**, and **3**[a]

	^{119}Sn NMR		^{19}F NMR	
	δ (ppm)	$^1J(^{119}\text{Sn}-^{19}\text{F})$ (Hz)	δ (ppm)	$^1J(^{19}\text{F}-^{119}\text{Sn})$ (Hz)
2a	−725 (s)			
2b	−698 (s)			
2c	−693 (s)			
2d	−720 (s)			
3a	−763 (t)	2130	−168 (s)	2130
3b	−760 (t)	2090	−170 (s)	2090
1a	−736 (d)	2565	−149 (s)	2565
1b	−730 (d)	2440	−165.5 (s)	2435
1c	−728 (d)	2420	−168.5 (s)	2420
1d	−737 (d)	2425	−154 (s)	2425

^{a} s = singlet, d = doublet, t = triplet.

more shielded signal being obtained when the alkoxide is bulky (Table 1). The other noteworthy feature of this spectrum is the absence of any ^{119}Sn−$^{117/119}$Sn coupling. This is consistent with a monomeric species containing a single six-coordinate tin according to the correlation between ^{119}Sn chemical shift values and tin coordination numbers previously proposed.[26] Besides, ^{1}H and ^{13}C spectra show that the tin atom is linked both to two alkoxide groups and to two β-diketonate ligands. The tin environment therefore results from two chelating β-diketonate ligands and two monodentate alkoxide groups. The mass spectral data obtained in the EI (electronic impact) mode are in agreement with the proposed molecular structure in solution. Strong changes therefore occurred in the coordination sphere of the tin atom compared to the starting tetraalkoxides **4** prepared from tin tetrachloride.[14] Thus, a shielding of about 350 ppm was recorded from Sn(O^{t}Am)$_4$ (δ = −370 ppm) to complex **2a**, indicating a coordination number change from 4 to 6 as described by Armelao et al.[11b] In the isopropoxide series, the room temperature ^{119}Sn NMR spectrum of the starting compound **4b** exhibits a peak at −595 ppm indicative of a single type of environment. One set of satellites ($J(^{119}$Sn−^{117}Sn = 223 Hz) corresponding to approximately 15% of the total signal intensity was obtained. The intensity and coupling constant are therefore in agreement with the values expected for two-bond ^{119}Sn−O−^{117}Sn coupling constants[27] and established that all tin sites are equivalent and linked to two other tin atoms. In addition, ^{1}H and ^{13}C spectra show the absence of the isopropyl alcohol molecule in the structure. At this stage, it must be remembered that a trimeric structure of Sn(O^{i}Pr)$_4$ was inferred from mass measurements carried out after removal of isopropyl alcohol.[28] Consequently, these data confirm the cyclic trimeric structure for **4b**. It must be noted that this structure is quite different from that described in the presence of isopropyl alcohol, which is a dinuclear species [Sn(O^{i}Pr)$_4$,HO^{i}Pr)]$_2$ in solution characterized by a resonance at −652 ppm.[15b,23,29] Consequently, addition of β-diketone to **4b** induced both a 100 ppm shielding of the signal and the disappearance of tin satellites. This indicates the formation of a 6-fold-coordinated monomeric species **2b** in solution. The changes are even more pronounced with a primary alkoxide. For instance, in the case of ethoxide substituents, the ^{119}Sn NMR spectrum of the tetraalkoxytin(IV) **4c** in CDCl$_3$ at room temperature shows more than eight broad signals between −600 and −650 ppm, indicating a mixture of oligomeric species in rapid equilibrium on the NMR time scale and a complex behavior. The reaction

with pentane-2,4-dione spectacularly simplified the spectrum to give a single peak at −693 ppm. The synthetic methods proposed to obtain **2c** are more specific than that reported by Chandler et al. since they described two resonances at −689 and −656 ppm in a 12:5 ratio for Sn(OMe)$_2$(CH$_3$-COCHCOCH$_3$)$_2$.[22]

Moreover, NMR spectra allowed the determination of the stereochemistry of **2**. Proton NMR spectra indeed show two discrete and equivalent resonances assigned to the CH$_3$ groups in **2a−c** and to the C(CH$_3$)$_3$ groups in **2d** of β-diketonate ligands. In addition, ^{13}C NMR spectra exhibit a concomitant splitting of the expected peaks for CH$_3$, CO in **2a−c** and C(CH$_3$)$_3$, CO in **2d** of the chelating ligands. As already proposed by Chandler et al.,[22] these spectroscopic data may be attributed to a configuration of the metallic center where the alkoxide groups are cis to each other. A variable-temperature NMR study was also carried out on **2d**. ^{13}C NMR spectroscopy was preferred over ^{1}H NMR spectroscopy because ^{13}C resonances of alkoxide and β-diketonate do not overlap. Heating the solution of **2d** in C$_7$D$_8$ led to the progressive coalescence of all splitted signals in the ^{13}C NMR spectra. The coalescence temperature was found at 83 °C for the CH$_3$(^{t}Bu) resonances ($\Delta\nu$ = 14 Hz at 22 °C) of the acetylacetonato moieties. As stereochemical flexibility is a known characteristic feature of octahedral metal complexes,[30] the temperature-dependent changes described above could be due to the variations of the exchange rate of the β-diketonate ligands with temperature. The corresponding exchange rates k_c and free energies of activation $\Delta G_c^{\ddagger}$ at the coalescence temperature may be calculated in the usual way from the spectral parameters using the Eyring rate equation.[31] Accordingly, the exchange rate k_c was estimated to be 31.7 s^{-1} for CH$_3$(chel), and the free enthalpy of activation $\Delta G_c^{\ddagger}$ at the coalescence temperature was 77.5 ± 0.3 kJ·mol^{-1} for **2d**. These data also indicate that the low-temperature spectrum (22 °C) corresponds to a unique species of cis configuration.

Characterization of SnF$_2$(R^{2}COCHCOR^2)$_2$ 3. Some ^{1}H and ^{19}F NMR data have already been reported for compound **3a**,[17] but neither ^{119}Sn NMR nor mass spectral data. As expected, complexes **3** are characterized in ^{119}Sn NMR spectroscopy by a well-defined 1:2:1 triplet around −760 ppm with a coupling constant $J(^{119}$Sn−F) of about 2100 Hz (Table 1). The ^{19}F NMR spectra exhibit a signal around −170 ppm with two sets of $^{117/119}$Sn satellites with $J(^{119}$Sn−F) = 2100 Hz, slightly higher than the data previously described.[17] The multiplicity of the NMR signals and the large values of the $J(^{119}$Sn−F) coupling constants are consistent with a direct bonding of tin with two chemically equivalent fluorine atoms. Besides, ^{13}C NMR spectra show splittings similar to those for complexes **2**, which is in favor of a cis configuration of the two fluorine atoms in **3**, as proposed by Jones et al.[17] The mass spectral data obtained in the EI (electronic impact) mode revealed the SnF$_2$(R$_2$-COCHCOR$_2$)$_2$$^+$ molecular ions, reinforcing the molecular structure in solution proposed.

Characterization of SnF(OR^1)(R^{2}COCHCOR^2)$_2$ 1. Compounds **1** are characterized in ^{119}Sn NMR spectroscopy by well-defined 1:1 doublets around −730 ppm (Figure 1A) with coupling constants $J(^{119}$Sn−F) of 2400−2500 Hz (Table 1). The ^{19}F NMR spectrum exhibits a signal in the range −145 to −170 ppm (Figure 1B, Table 1) with two sets of $^{117/119}$Sn satellites, $J(^{119}$Sn−F) = 2400−2500 Hz. The multiplicity of the NMR

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(31) Spectral data were independent from the concentration. The kinetics can be considered as first order. Consequently, $k_c = 2.22\Delta\gamma$ and $\Delta G_c^{\ddagger} = 19.14T_c (10.32 + \log T_c)$ J·mol^{-1}.
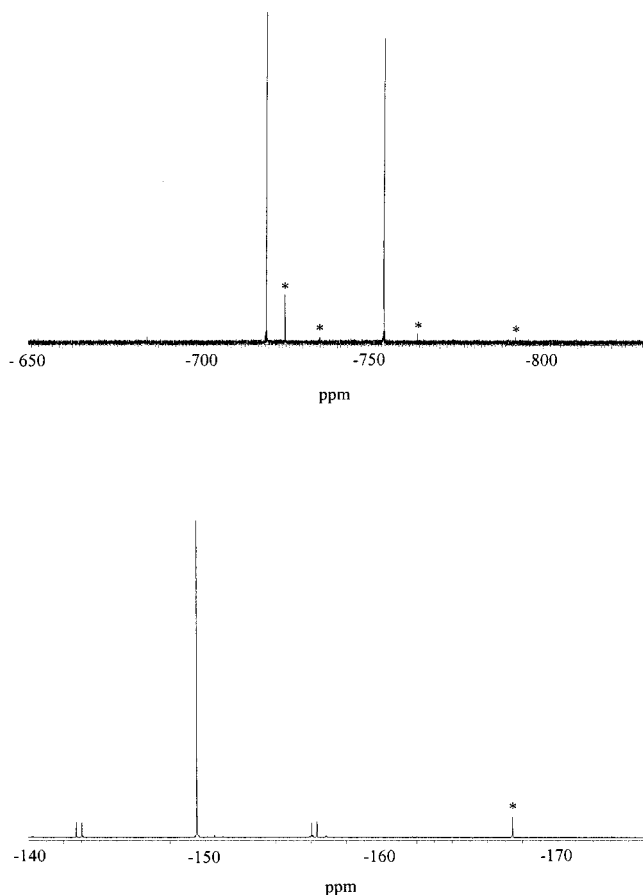
Figure 1. ^{119}Sn (A) and ^{19}F (B) NMR spectra of **1a** recorded in CDCl$_3$ at room temperature. The asterisks indicate peaks of impurities.

resonances and the large values of $J(^{117/119}\text{Sn}-\text{F})$ indicate a direct bonding of tin with a single fluorine atom. The absence of any $^{119}\text{Sn}-^{117/119}\text{Sn}$ coupling is in favor of a monomeric species. Proton NMR spectra reveal characteristic CH peaks of the β-diketonate ligand in the narrow range 5.4−5.8 ppm and show a 2:1 ratio between ketoenolate moieties and the alkoxide group. The local tin environment is therefore constituted of two β-diketonate ligands, an alkoxide group, and a fluorine atom, arranged in an octahedral manner.

Complexes **1** may exist as different stereoisomers which can be counted according to Bailar's method.[32] This leaves a total of two diastereoisomers (I and II), one of which has enantiomers (Figure 2). The very low symmetry of form I induces, respectively, two (a, b) and four (1, 2, 3, 4) different sites for the CH and the O=CR^2 groups of the β-diketonate moieties. The ^{1}H and ^{13}C nuclei of these groups should therefore be anisochronous by NMR spectroscopy. Conversely, the more symmetric form II exhibits a unique environment for the CH (a) and the O=CR^2 (1) groups, respectively. Multinuclear (^{1}H, ^{13}C) NMR data allowed forms I and II to be distinguished. ^{1}H NMR spectra of complexes **1a** and **1d** reveal two resonances for the CH(chel) group and four peaks for the CH$_3$(chel) groups of the β-diketonate ligands (Table 2). The ^{13}C NMR spectra of **1a** and **1d** recorded at room temperature (Table 3) exhibit four resonances in the range 195−205 ppm (CO(chel)) and two resonances in the domain 90−92 ppm (CH(chel)) for the β-diketonate ligands. These spectroscopic data strongly suggest that **1** exists in solution as the enantiomer pair (I) in which the
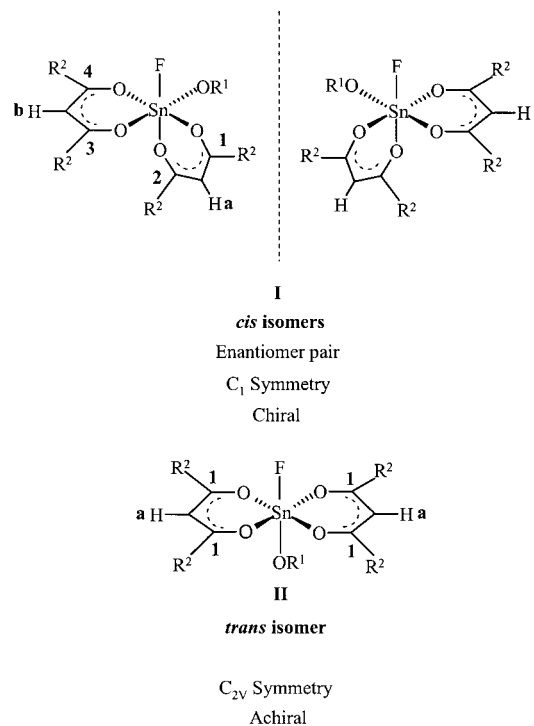
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Figure 2. Schematic representation of the different possible stereoisomers of complexes **1**.

Table 2. ^{1}H NMR Chemical Shifts (δ) in CDCl$_3$ for Complexes **1a** and **1d** at Room Temperature^a

	CH$_3$(chel)	CH(chel)	C(CH$_3$)(al)	CH$_2$(al)	CH$_3$(al)
1a	2.09	5.55	1.14	1.44	0.80
	2.07	5.52			
	2.01				
	2.00				
1d	1.12	5.74	b	1.40	0.77
	1.11	5.72			
	0.98				
	0.97				

^{a} chel = β-diketonate ligands; al = alkoxide. ^{b} Hidden by CH$_3$(chel) resonances.

fluorine atom and the alkoxide groups are arranged in cis configuration. To our knowledge, complexes **1** are the first stannic fluorides of C_1 symmetry, a similar structure in solution only being reported for stannic chlorides RSnCl(CH$_3$-COCHCOCH$_3$)$_2$.[33]

As for **2**, the kinetics of configurational rearrangements have been studied on complexes **1a** and **1d** by variable-temperature ^{13}C NMR spectroscopy. C$_7$D$_8$, which did not noticeably influence the room temperature spectrum, was chosen as a solvent. A progressive broadening and collapse of the CH(chel) and CO-(chel) ^{13}C resonances into a single, sharp line at 100 °C were observed for **1d** (Figure 3).[34] These changes are ascribed to a configurational rearrangement process in the β-diketonate rings which exchanges chelate ring carbons (CH(chel) and CO(chel)) between the two and four, respectively, nonequivalent sites in the cis stereoisomers (I). The exchange rate k_c and the free energy of activation $\Delta G_c^{\ddagger}$ at the coalescence temperature have been calculated as previously done for **2d**.[28] The exchange rate was estimated to be 40.2 s^{-1} ($T_c = 70$ °C) for CH(chel), and the free enthalpy of activation $\Delta G_c^{\ddagger}$ at the coalescence tem-

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(34) **1a** behaves similarly.

Table 3. ^{13}C NMR Chemical Shifts (δ) for Complexes **1** at Room Temperature[a]

	CO(chel)	CH(chel)	C$_q$(chel)	C(CH$_3$)(chel)	C$_q$(al)	C(CH$_3$)(al)	CH(al)	CH$_2$(al)	CH$_3$(al)
1a	195.7	101.5		27.1	73.2	29.6		37.1	8.4
	195.0	101.3		27.0		29.2			
	194.7								
	194.6								
1b	197.1	102.1		27.5			65.8		26.4
	196.2								
	195.9								
	195.7								
1c	196.3	102.1		27.4				60.4	19.4
	196.1								
	195.9								
	195.8								
1d	205.2	92.1	41.8	27.9	73.1	30.0		37.6	8.8
	205.1	91.9	41.7	27.7		29.9			
	204.8		41.6[b]	27.6[b]					
	204.2								

[a] C$_q$ = quaternary carbon; chel = β-diketonate ligands; al = alkoxide. [b] Double intensity.
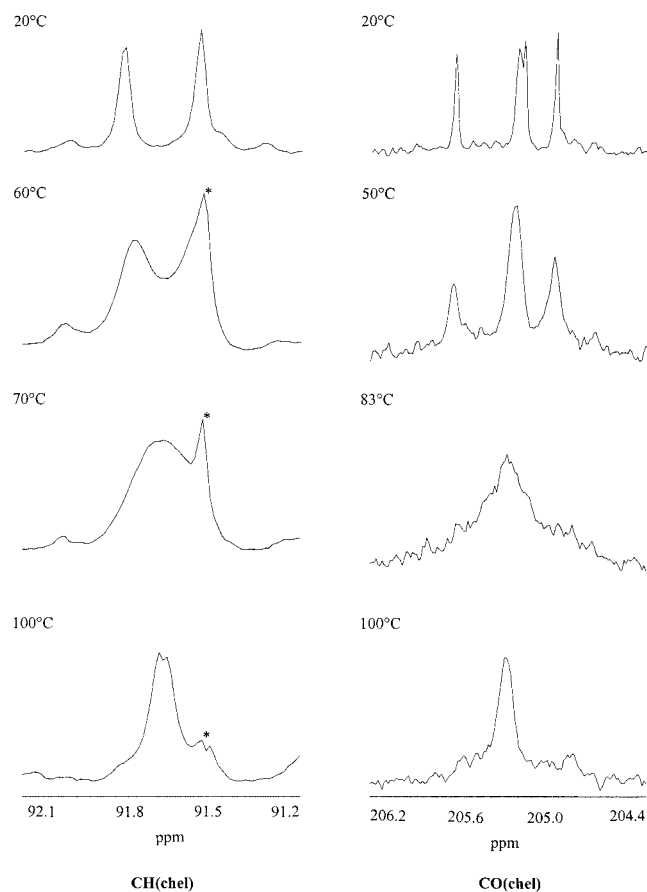

Figure 3. ^{13}C NMR spectra in C$_7$D$_8$ for the β-diketonate CO and CH regions as a function of temperature for **1d**. The resonance of the hydrolysis product is indicated by an asterisk.

perature was 73.9 ± 0.3 kJ·mol^{-1} for **1d**. The corresponding values for CH(chel) in **1a** are k_c = 27.5 s^{-1} (T_c = 60 °C) and $\Delta G_c^{\ddagger}$ = 72.7 ± 0.3 kJ·mol^{-1}. The exchange phenomenon therefore seems to be slightly easier with the less bulky diketonate ligands.

Different mechanisms for configurational rearrangements of dihalo-[17] and monohaloorganobis(β-diketonato)tin(IV)[33b] complexes have been described in the literature. They include (i) an intermolecular path via complete dissociation of some ligands and (ii) intramolecular paths via either partial dissociation of ligand or twisting motions. Several authors proposed strong evidence against the intermolecular mechanisms.[17,33,35] Thus, Jones and Fay have noticed that ^{1}H$-^{119}$Sn coupling in Sn(CH$_3$-

Table 4. Hydrolytic Behavior of Compounds **1** Dissolved in CH$_3$CN[a]

	h = 0.5	h = 1	h = 2	h = 3	h = 10
1a	S	S	S	G	G
1b	S	S			
1c	S				
1d	S	S	S	G	S + P

[a] S = sol, G = gel, P = precipitate.

COCHCOCH$_3$)$_2$X$_2$ (X = F, Cl, Br, I) is observed before, during, and after coalescence of the methyl resonances.[17] This is also the case for complex **1d** where the ^{1}H$-^{119}$Sn coupling constant in the CH(chel) group was found equal to 7 and 7.5 Hz in the slow (room temperature) and fast-exchange (80 °C) limits, respectively. Existence of ^{1}H$-^{119}$Sn coupling at high temperature implies that a given β-diketonate ligand remains linked to the same tin atom during a long time period compared to the time scale of the ketoenolate ligand exchange. Moreover, Serpone et al. have proposed in the case of CH$_3$SnCl(CH$_3$-COCHCOCH$_3$)$_2$ a configurational rearrangement proceeding via twist motions through the trigonal-prismatic transition state.[33b] Accordingly, it is likely that the configurational rearrangement in complexes **1** is purely intramolecular.

Hydrolytic Behavior. Contrary to tin tetraalkoxides **4**, it has been recently shown that the dialkoxy derivative **2a** led to stable sols only in very polar solvents such as formamide or dimethyl sulfoxide.[11b] They indeed prevent aggregation and precipitation of the colloidal oxide particles created by the hydrolysis–condensation step. However, such high boiling solvents are not suitable for the film deposition by the sol–gel method. Acetonitrile was therefore preferred to perform hydrolysis experiments on **1**. Qualitative data for different hydrolysis ratios h are listed in Table 4. Stable sols in CH$_3$CN were obtained for h up to 2 in the case of **1a** and **1d**. This hydrolytic behavior is near that reported for **2a** in the same solvent.[11b]

As the powders obtained after evaporation of the solvent and the volatile hydrolysis products were soluble, NMR spectroscopy allowed the study of the species formed after hydrolysis. Thus, the ^{19}F and ^{119}Sn NMR spectra of xerosol X$_1$ (h = 0.5) in d_6-DMSO show a nearly complete disappearance of the starting precursor **1a** with the concomitant formation of new fluorinated stannic compounds. The main species S$_1$ (>70 mol %) is characterized (i) in ^{119}Sn NMR by two doublets of equivalent intensity at −729.4 ppm ($J(^{119}$Sn$-^{19}$F) = 2272 Hz) and at

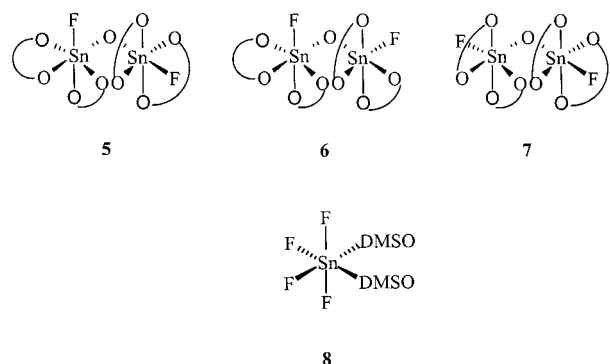(35) Faller, J. W.; Davisen, A. *Inorg. Chem.* **1967**, *6*, 182.
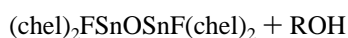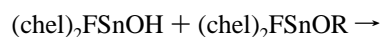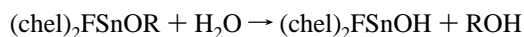
Figure 4. Structures of the different products formed by hydrolysis of **1a** with $h = 0.5$.

−729.7 ppm ($J(^{119}\mathrm{Sn}-^{19}\mathrm{F}) = 2269$ Hz), (ii) in $^{19}\mathrm{F}$ NMR by two singlets of equivalent intensity at −150.0 and −150.2 ppm, each singlet possessing two sets of $^{117/119}\mathrm{Sn}$ satellites such as $J(^{19}\mathrm{F}-^{119}\mathrm{Sn}) = 2269$ and 2273 Hz, respectively, and (iii) in $^{1}\mathrm{H}$ and $^{13}\mathrm{C}$ NMR by resonances indicating the presence of chelating β-diketonate ligands and no signal characteristic of the alkoxide groups. Moreover, the molar ratios F/Sn (1.09) and C/Sn (8.2) determined by elemental analysis are consistent with the presence of approximately one fluorine and two chelating ligands per tin atom. A minor species S_2 (<15 mol %) has also been formed upon hydrolysis. It is characterized (i) in $^{119}\mathrm{Sn}$ NMR by a triplet of triplets (part X of an A_2M_2X spin system) at −778 ppm with two different $J(^{119}\mathrm{Sn}-^{19}\mathrm{F})$ values (1835 and 1885 Hz) and (ii) in $^{19}\mathrm{F}$ NMR by two triplets (A_2M_2 spin system) at −148.6 and −163.1 ppm with the same $J(^{19}\mathrm{F}-^{19}\mathrm{F})$ = 48 Hz, each triplet showing two sets of $^{119/117}\mathrm{Sn}$ satellites (part A_2M_2 of an A_2M_2X spin system) such as $J(^{19}\mathrm{F}-^{119}\mathrm{Sn})$ = 1835 and 1885 Hz, respectively. Similar species were obtained upon hydrolysis of **1d** with 0.5 mol equiv of $\mathrm{H_2O}$, which shows the reproducibility of this hydrolytic behavior.

According to the NMR spectroscopic data, species S_1 includes two chemically nonequivalent six- or seven-coordinated tins, each linked to a single terminal fluorine atom since the coupling constant is higher than 2000 Hz.[36] Tin atoms are thus bounded via an oxygen bridge resulting from the hydrolysis of the alkoxide group of **1a**, the other coordination sites of each tin being occupied by β-diketonate ligands and a fluorine atom. Possible structures for species S_1 could therefore be a dimeric form **5** or a mixture of equimolar amounts of **6** and **7** (Figure 4). It is likely that such species are associated through intermolecular tin−oxygen coordination bonds as in distannoxanes.[37] As reported by Sita et al. for $\mathrm{Sn_6}(\mu\text{-O})_4(\mu_3\text{-OSiMe}_3)_4$, no $^{119}\mathrm{Sn}-^{117/119}\mathrm{Sn}$ satellites in the $^{119}\mathrm{Sn}$ NMR spectrum could be detected.[38] It can be concluded that 0.5 mol equiv of $\mathrm{H_2O}$ is sufficient to consume all the alkoxide group due to the hydrolysis−condensation process as experimentally found:

$$(\mathrm{chel})_2\mathrm{FSnOR} + \mathrm{H_2O} \rightarrow (\mathrm{chel})_2\mathrm{FSnOH} + \mathrm{ROH}$$

$$(\mathrm{chel})_2\mathrm{FSnOH} + (\mathrm{chel})_2\mathrm{FSnOR} \rightarrow$$
$$(\mathrm{chel})_2\mathrm{FSnOSnF}(\mathrm{chel})_2 + \mathrm{ROH}$$

(36) (a) Beckmann, J.; Biesemans, M.; Hassler, K.; Jurkschat, K.; Martins, J. C.; Schürmann, M.; Willem, R. *Inorg. Chem.* **1998**, *37*, 4891. (b) Beckmann, J.; Mahieu, B.; Nigge, W.; Schollmeyer, D.; Schürmann, M.; Jurkschat, K. *Organometallics* **1998**, *17*, 5697. (c) Altmann, R.; Jurkschat, K.; Schürmann, M.; Dakternieks, D.; Duthie, A. *Organometallics* **1998**, *17*, 5858.
(37) (a) Gross, D. C. *Inorg. Chem.* **1989**, *28*, 2355. (b) Primel, O.; Llauro, M.-F.; Pétiaud, R.; Michel, A. *J. Organomet. Chem.* **1998**, *558*, 19.
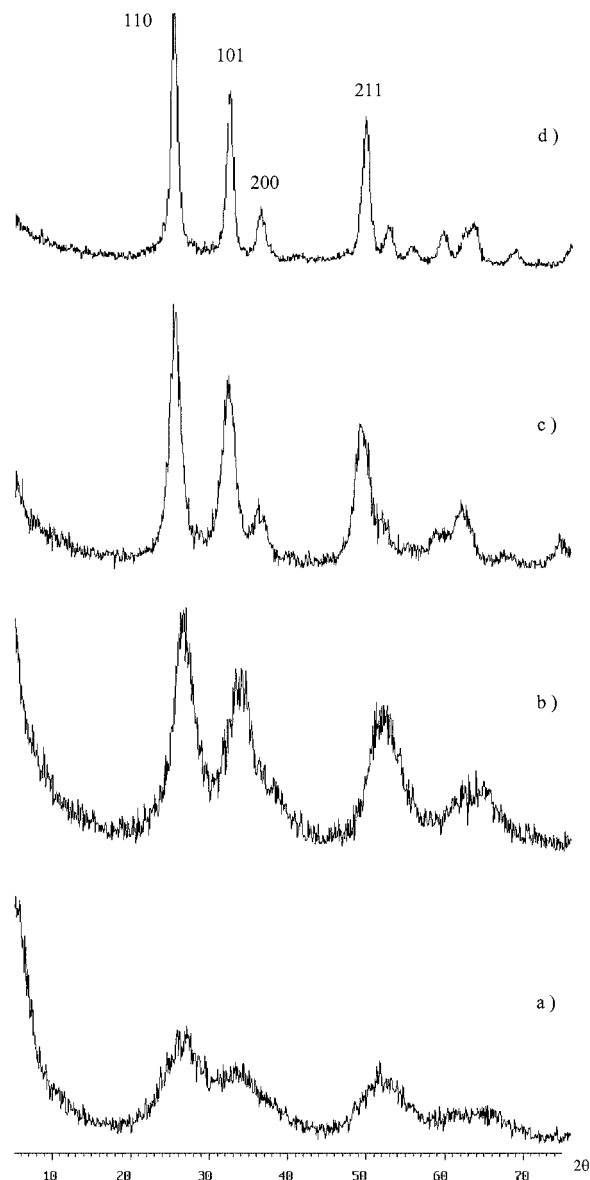

Figure 5. X-ray diffraction pattern of xerosol X_2 after different thermal pretreatments: (a) 150 °C; (b) 350 °C; (c) 450 °C; (d) 550 °C.

As far as S_2 is concerned, the tin atom is directly bonded to two groups of two magnetically equivalent $^{19}\mathrm{F}$ nuclei and should be linked to two solvent molecules, i.e., DMSO, acting as Lewis base, to explain the six-coordination deduced from the chemical shift found. In addition, the only structure consistent with the spectra is an octahedral model **8** (Figure 3) in which the solvent molecules occupy positions cis to each other. In this structure, two axial F^a and equatorial F^e fluorine atoms can be distinguished, and the $J(^{19}\mathrm{F}-^{19}\mathrm{F})$ = 48 Hz measured falls in the domain of the $^{19}\mathrm{F}^a-\mathrm{Sn}-^{19}\mathrm{F}^e$ coupling constant reported in octahedral species.[39] It must also be noted that this stucture is in agreement with those described for different metal tetrafluorides.[40] However, the origin of the species S_2 remains unclear. It may result from complete hydrolysis of **1a** followed by disproportionation of the resulting mixed tin oxofluoride.

Xerosol X_2 was also characterized. Elemental analysis clearly indicates that tin, fluorine, and organic ligands were present.

(38) Sita, L. R.; Xi, R.; Yap, G. P. A.; Liable-Sands, L. M.; Rheingold, A. L. *J. Am. Chem. Soc.* **1997**, *119*, 756.
(39) Berger, S.; Braun, S.; Kalinowski, H.-O. *NMR Spectroscopy of the Nonmetallic Elements*; John-Wiley & Sons: New York, 1997; p 639.
(40) Muetterties, E. L. *J. Am. Chem. Soc.* **1960**, *82*, 1082.

The molar ratios F/Sn (1.01) and C/Sn (4.7) were found. The presence of chelating β-diketonate ligands on tin nuclei and the lack of alkoxide groups in X_2 were pointed out by ^{1}H and ^{13}C NMR spectra. The quantitative analysis of the organics removed by hydrolysis, carried out by ^{1}H NMR spectroscopy, shows the departure of both one alkoxide group and one β-diketonate ligand per **1a**. These amounts are in agreement with the experimental weight loss (40%) observed after hydrolysis and the remaining carbon content determined by elemental analysis. The ^{19}F NMR spectrum exhibits an intense broad ($\sim$30 ppm) resonance centered at $-$130 ppm, with the weak triplet of triplets characteristic of a small amount of S_2. In addition, solution ^{119}Sn NMR analyses were tentatively made, but the species formed gave no resonance. This is probably due to the formation of large and ill-defined stannic oxopolymeric species which are known to be NMR silent.[41] It can therefore be concluded that xerosol X_2 mainly contains a stannic fluorinated oxopolymer with a F/Sn ratio near unity and one β-diketonate ligand per tin atom.

Characterization of the Thermolyzed Xerosol X₂. To check that xerosol X_2 can lead to F-doped SnO_2 materials, it was thermolyzed at various temperatures. Figure 5 shows the typical XRD patterns recorded for xerosol X_2 treated in air between 150 and 550 °C. After X_2 was dried at 150 °C, the obtained materials were poorly crystallized but showed an X-ray diffraction pattern which accounted for the cassiterite structure of tin dioxide. It is, as expected, more obvious when the temperature is increased to 350 °C, and the pattern recorded after treatment at 550 °C is clearly characteristic of crystalline particles of SnO_2 cassiterite,[42] the size of which size was estimated to be 8 nm by using the conventional Laue−Scherrer formula.[43] The remaining fluorine content in this powder heated at 550 °C was determined by elemental analysis: a molar F/Sn

ratio of 0.03 was found. At this stage, one has to emphasize that this value is in the range of the best doping rate of SnO_2 thin films, leading to the highest conductivity and transparency.[44] The doping effect of fluorine in the powder prepared in this study was confirmed by electrical measurements. Indeed, xerosol X_2 treated at 550 °C in air exhibits resistivity as low as 6 Ω·cm under pressure (0.5 ton). The real resistivity of the materials is lower than what is deduced here because of an unnegligible drop of the carrier mobility, and therefore of the conductivity at the grain boundary. In fact, only comparison of the resistivity of samples measured using similar experimental conditions is meaningful. Thus, the value of 6 Ω·cm herein found is noticeably lower than that measured in the same conditions for the ITO powder (30 Ω·cm) purchased from Samsung Electronics. These results show that complex **1a** is a suitable precursor for conductive F-doped SnO_2 materials.

Conclusion

New alkoxyfluoro(β-diketonate)tin(IV) compounds have been synthesized by fluorine transfer from carboxylic acid fluorides and characterized by multinuclear NMR spectroscopy. The cis configuration of F and the OR group has been demonstrated in solution by variable-temperature ^{1}H and ^{13}C NMR spectroscopy. Hydrolysis of $SnF(O^tAm)(MeCOCHCOMe)_2$ for $h = 2$ has led to a fluorinated stannic oxopolymer soluble in CH_3CN. After solvent removal, the resulting powders treated at 550 °C consist of crystalline particles of SnO_2 cassiterite containing the required amount of doping fluorine and show electronic conductivity comparable to that of ITO powders. $SnF(O^tAm)(MeCOCHCOMe)_2$ is thus the first precursor of conductive F-doped SnO_2 materials prepared by the sol−gel route.

Work is in progress to prepare SnO_2:F thin films by the sol−gel route from previous sols. The corresponding results and the detailed properties of the F-doped powders will be published shortly.

(41) (a) Banse, F. Ph.D. Thesis, University of Paris VI, 1994. (b) Eychenne-Baron, C.; Ribot, F.; Sanchez, C. *J. Organomet. Chem.* **1998**, *567*, 137.
(42) Powder Diffraction File; JCPDS International Center for Diffraction Data: Swarthmore, PA, 1997; no. 41-1445.
(43) The mean particle size is given by the Laue−Scherrer relation $t = (\lambda/\epsilon \cos \theta)$, with $\epsilon = (\epsilon_m^2 - \epsilon_0^2)^{1/2}$ where θ is the Bragg angle for the chosen *hkl* reflection and ϵ_m and ϵ_0 are the angular half-widths of the *hkl* peak for the studied sample and well-crystallized SnO_2 without size effect, respectively. See: Eberhardt, J. P. *Structural and Chemical Analysis of Materials*; John-Wiley & Sons: New York, 1991; p 203.

(44) The best doping amount is between 1 and 8 atom % F per Sn atom. See refs 2 and 3b.