3924 *Inorg. Chem.* **2000,** *39,* 3924−3927

Notes

The First Mixed-Valence Fluorotin Alkoxides: New Sol−Gel Precursors of Fluorine-Doped Tin Oxide Materials

D. Boegeat,[†] B. Jousseaume,[†] T. Toupance,*,[†]
G. Campet,[‡] and L. Fournès[‡]

Laboratoire de Chimie Organique et Organométallique,
UMR 5802 CNRS, Université Bordeaux I,
351 Cours de la Libération, F-33405 Talence Cedex, France,
and Institut de Chimie de la Matière Condensée de
Bordeaux, UPR 9048 CNRS, Château Brivazac,
Avenue du Docteur A. Schweitzer,
F-33608 Pessac Cedex, France

Received February 3, 2000

Introduction

Doped and undoped nanocrystalline tin dioxide has many potential or demonstrated applications in various fields including solar energy conversion,[1] catalysis,[2] gas sensors,[3] antistatic coatings,[4] and transparent electrode preparation.[5] Fluorine is the most efficient doping agent of tin dioxide materials used to reach the highest electronic conductivity and IR reflectivity.[6] Preparation of nanostructured SnO_2 has already been reported,[7] but to our knowledge, no study has been devoted to the preparation of similar F-doped tin dioxide materials, despite its huge practical interest. The sol−gel process, based on the hydrolysis−condensation reactions of molecular precursors (usually metal alkoxides), allows the preparation of oxide materials of various shapes.[8] In addition, the wealth of the metal alkoxide chemistry permits the design of molecular precursors including each atomic component of the desired material. This strategy has led to metal oxides of high chemical homogeneity and has been widely investigated in the study of heteropolymetallic precursors.[9] Until recently, the concept of a single molecular precursor of F-doped SnO_2 prepared by the sol−gel route had never been investigated. We have recently reported the first stabilized fluoroalkoxytin complexes giving conductive F-doped SnO_2 nanocrystalline powders.[10] The synthesis of these precursors requires three synthetic steps; we have searched for a faster synthesis of F-doped SnO_2 sol−gel materials from tin(II) difluoride, which is cheap and easily handled. We describe here the one-step synthesis and the characterization of the first mixed-valence fluoroalkoxytin molecules leading to the preparation of novel fluorine-doped tin dioxide nanoparticles by the sol−gel process.

Experimental Section

General Procedures. Tin(II) difluoride (Acros) was dried under vacuum at 120 °C for 4 h before use. Tetraalkoxides were synthesized according to previously reported procedures.[11] All experiments were carried out under nitrogen atmosphere by using standard Schlenk techniques. 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 $CDCl_3$). ^{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 $CFCl_3$). Infrared spectra (KBr pellets or plates) were recorded using a FTIR Perkin-Elmer spectrophotometer. Elemental analyses were performed in the Center of Chemical Analysis of the CNRS (Vernaison, France). The water content was determined by the Karl Fischer method with short time contact to avoid the titration of surface hydroxyl functions. The Mössbauer resonance spectra were obtained with a constant-acceleration Halder-type spectrometer with a room-temperature $CaSnO_3$ source in a transmission geometry. The spectra were fitted to the sum of Lorentzians by least-squares refinements. All isomeric shifts given refer to $CaSnO_3$ at 293 K. The abbreviations O^tBu and O^tAm correspond to 2-methylpropan-2-oxy and 2-methylbutan-2-oxy groups, respectively.

SnF_2.Sn(O^tBu)$_4$ (1a). A mixture of SnF_2 (1.29 g, 8.2 mmol) and Sn(O^tBu)$_4$ (3.27 g, 7.95 mmol) was heated at 90 °C under dry nitrogen. The tin(II) difluoride was progressively dissolved in the melted tin(IV) alkoxide, and the heating was continued for 1.5 h. The volatile compounds were evaporated under vacuum, then the residue was dissolved in dry chloroform, and the solution was filtered on dry Celite to remove nonsoluble impurities. The filtrate was concentrated, and the obtained solids were washed four times with dry acetonitrile to yield 4.3 g (95%) of a white powder. Mp: 95−100 °C. ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 1.21$ (s, 27H, CH_3), 1.12 (s, 9H, CH_3). $^{13}C\{^{1}H\}$ NMR (62.9 MHz, $CDCl_3$): $\delta = 78.1$ (br, $C(CH_3)_3$), 73.7 ($^{2}J(Sn,C) = 50$ Hz, $C(CH_3)_3$), 33.7 ($C(CH_3)_3$), 33.5($C(CH_3)_3$). $^{119}Sn\{^{1}H\}$ NMR (74.6 MHz, $CDCl_3$): $\delta = -388$ (s, $^{2}J(Sn,Sn) = 438$ Hz), −669 (t, $^{1}J(Sn,F) = 2797$ Hz, $^{2}J(Sn,Sn) = 438$ Hz). ^{19}F NMR (188.6 MHz, $CDCl_3$): $\delta = -120$ (s, $^{1}J(Sn,F) = 2797$ Hz). IR (KBr plates): ν (cm^{-1}) = 2976, 2920, 1465, 1365, 1245, 1190, 1050, 935, 780, 600, 550. Anal. Calcd

---

* To whom correspondence should be addressed. E-mail: t.toupance@lcoo.u-bordeaux.fr.

[†] UMR 5802.

[‡] UPR 9048.

(1) (a) Bedja, T.; Hotchandani, S.; Kamat, P. V. *J. Phys. Chem.* **1994**, *98*, 4133. (b) Ferrere, S.; Zaban, A.; Gregg, B. A. *J. Phys. Chem. B* **1997**, *101*, 4490. (c) Ford, W. E.; Wessls, J. M.; Rodgers, M. A. J. *J. Phys. Chem. B* **1997**, *101*, 7435. (d) Li, W.; Osora, H.; Otero, L.; Duncan, D. D.; Fox, M. A. *J. Phys. Chem. A* **1998**, *102*, 5333.

(2) Cebolla, V. C.; Bacaud, R.; Besson, M.; Cagniant, D.; Charcosset, H.; Oberson, M. *Bull. Soc. Chim. Fr.* **1987**, 935.

(3) (a) Harrison, P. G.; Willett, M. J. *Nature* **1988**, *332*, 337. (b) Kaciulis, S.; Mattogno, G.; Galdikas, A.; Mironas, A.; Setkus, A. *J. Vac. Sci. Technol., A* **1996**, *14*, 3164. (c) Ansari, S. G.; Boroojerdian, P.; Sainkar, S. R.; Karekar, R. N.; Aiyer, R. C.; Kulkarni, S. K. *Thin Solids Films* **1997**, *295*, 271.

(4) (a) Sonoda, N.; Shimotsuma, W.; Tsubusaki, S. US Patent 4246143, 1981. (b) Robert, J. C. US Patent 5494652, 1996.

(5) (a) Goebbert, C.; Aegerter, M. A.; Burgard, D.; Nass, R.; Schmidt, H. *J. Mater. Chem.* **1999**, *9*, 253. (b) Cao, L.; Huo, L.; Ping, G.; Wang, D.; Zeng, G.; Xi, S. *Thin Solids Films* **1999**, *347*, 258. (c) Goebbert, C.; Nonninger, R.; Aegerter, M. A.; Schmidt, H. *Thin Solids Films* **1999**, *351*, 79.

(6) (a) Chopra, K. L.; Major, S.; Pandya, D. K. *Thin Solids Films* **1983**, *102*, 1. (b) Proscia, J.; Gordon, R. G. *Thin Solids Films* **1992**, *214*, 175.

(7) (a) Ocana, M.; Matijevic, E. *J. Mater. Res.* **1990**, *5*, 1083. (b) Nayral, C.; Ould-Ely, T.; Maisonnat, A.; Chaudret, B.; Fau, P.; Lescouzères, L.; Peyre-Lavigne, A. *Adv. Mater.* **1999**, *11*, 61. (c) Texter, J.; Lelental, M. *Langmuir* **1999**, *15*, 654.

(8) Brinker, C. J.; Scherer, G. W. *Sol-Gel Science*; Academic Press: San Diego, 1990.

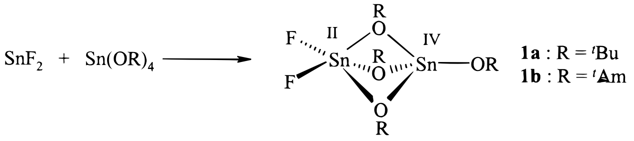
(9) (a) Mehrotra, R. C. *J. Non-Cryst. Solids* **1990**, *121*, 1. (b) Hubert-Pfalzgraf, L. G. *New J. Chem.* **1987**, *11*, 662. (c) Chandler, C. D.; Roger, C.; Hampden-Smith, M. J. *Chem. Rev.* **1993**, *93*, 1205.

(10) Gamard, A.; Jousseaume, B.; Toupance, T.; Campet, G. *Inorg. Chem.* **1999**, *38*, 4671.

(11) Thomas, I. M. U.S. Patent 3946056, 1976.

10.1021/ic000111z CCC: $19.00

Scheme 1



for $C_{16}H_{36}F_2O_4Sn_2$: C, 33.84; H, 6.39; Sn, 41.80; F, 6.70. Found: C, 32.1; H, 5.90; Sn, 42.81; F, 6.89.

SnF_2.Sn(O^{t}Am)$_4$ (1b). The same procedure as for **1a** was used with SnF_2 (2.1 g, 13.4 mmol) and Sn(O^{t}Am)$_4$ (6.07 g, 13 mmol). An orange oil was isolated (7.87 g, yield 97%). ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 1.68$ (q, 6H, ^3J(H,H) = 7.5 Hz, CH_2), 1.49 (q, 2H, ^3J(H,H) = 7.3 Hz, CH_2), 1.36 (s, 18H, C(CH_3)$_2$), 1.22 (s, 6H, C(CH_3)$_2$), 0.86 (t, 9H, ^3J(H,H) = 7.5 Hz, CH_3), 0.80 (t, 3H, ^3J(H,H) = 7.3 Hz, CH_3). ^{13}C{^{1}H} NMR (62.9 MHz, $CDCl_3$): $\delta = 80.6$ (br, *C*(CH_3)$_2$), 75.6 (^2J(Sn,C) = 55 Hz, *C*(CH_3)$_2$), 39.0 and 38.6 (*C*H_2), 30.4 and 29.8 (C(*C*H_3)$_2$), 9.4 and 8.4 (*C*H_3). ^{119}Sn{^{1}H} NMR (74.6 MHz, $CDCl_3$): $\delta = -397$ (s, ^2J(Sn,Sn) = 426 Hz), -668 (t, ^1J(Sn,F) = 2805 Hz, ^2J(Sn,Sn) = 426 Hz). ^{19}F NMR (188.6 MHz, $CDCl_3$): $\delta = -117$ (s, ^1J(Sn,F) = 2805 Hz). IR (KBr plates): ν (cm^{-1}) = 2976, 2957, 2926, 2880, 1463, 1385, 1367, 1162, 1144, 1060, 963, 929, 875, 738, 590, 560.

1a/THF/4. In a Schlenk tube under a nitrogen atmosphere, a mixture of water (0.467 g, 25.9 mmol) and dry tetrahydrofuran (1.6 mL) was added slowly to a stirred solution of **1a** (3.68 g, 6.48 mmol) dissolved in dry THF (24.4 mL). After the resulting solution was stirred at room temperature overnight, a white precipitate appeared. The solution was removed after centrifugation, and the resulting powder was washed with dry *n*-pentane and dried under vacuum at 50 °C. A white powder (2.3 g) was obtained. Anal. Calcd for $F_2O_{1.9}Sn_2{\cdot}(OC_4H_9)_{0.2}{\cdot}(H_2O)_{0.8}$: C, 2.87; H, 1.02; Sn, 70.90; F, 11.34; H_2O, 4.30. Found: C, 2.43; H, 1.09; Sn, 69.95; F, 10.89; H_2O, 3.86.

Electrical Measurement. Thermolysis and X-ray characterization procedures have been already described.[10] 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 Rhopoint M210 Milli-ohmeter. 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 area and the thickness of the sample, respectively.

Results and Discussion

Only a very few mixed-valence tin compounds, with moisture-sensitive ligands, have been described, and none have been employed as tin oxide precursor.[12−14] To introduce the fluorine to such compounds, a Lewis acid−base reaction between an equimolar amount of tin difluoride and tin tetraalkoxide without solvent was used to give the new mixed-valence adducts $Sn^{II}Sn^{IV}F_2(OR)_4$ (R = *tert*-butyl, *tert*-amyl) **1**. This reaction path leads to defined compounds only with tertiary alkoxides (Scheme 1).

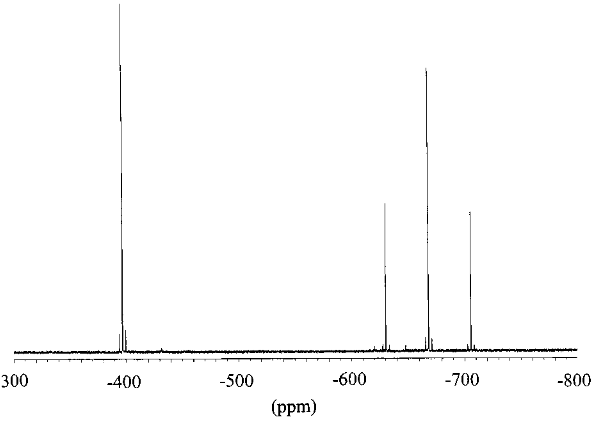


Figure 1. ^{119}Sn {^{1}H} NMR spectrum of **1b** recorded in $CDCl_3$.

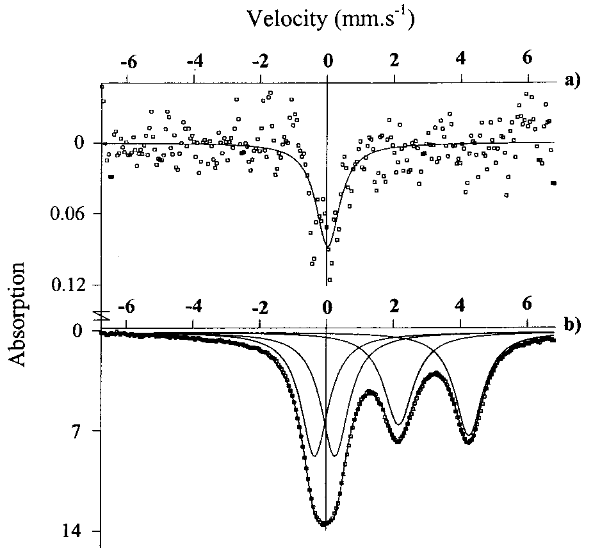


Figure 2. Experimental and fitted Mössbauer spectra of **1a** recorded at (a) 293 K and (b) 77 K.

The resonances of the room-temperature ^{119}Sn NMR spectrum (Figure 1) of **1** are located at −390 ppm (singlet) and at −670 ppm (triplet) in a 1:1 ratio. According to the correlation in ^{119}Sn NMR between the chemical shift and the coordination number of Sn,[15] the less shielded signal, close to that of the starting alkoxides,[16] can be assigned to a four-coordinated Sn, whereas the more shielded resonance, strongly different from that of SnF_2,[17] may be attributed to a five-coordinated Sn bearing two equivalent fluorines. The latter signal shows a well-resolved coupling (~2800 Hz) which falls into the range of direct ^{119}Sn−F coupling with terminal fluorine atoms.[18] Both components possess doublet satellites arising from strong ^2J(^{119}Sn−X−$^{117/119}$Sn) (420−440 Hz) coupling probably through μ_2-OR groups. Similar values were indeed reported in the case of [Sn(O^{i}Pr)$_4$·HO^{i}Pr]$_2$[16] and Sn(O^{i}Pr)$_4$Sn(O^{i}Pr)$_2$,[14] which exist as dimers in solution. The ^{19}F NMR spectrum exhibits a singlet at −120 ppm, with doublet satellites such as ^1J(^{119}Sn−F) = 2800 Hz, confirming the chemical equivalence of the two fluorine atoms. The ^{1}H NMR spectrum at room temperature of **1b** shows two systems of peaks in a 3:1 ratio for the expected resonances of the O^{t}Am groups (methylene and methyl regions), suggesting the presence of two kinds of alkoxides in **1b**. In addition,

---

(12) Ewings, P. F. R.; Harrison, P. G.; Morris, A.; King, T. J. *J. Chem. Soc., Dalton Trans.* **1976**, 1602.

(13) (a) Birchall, T.; Manivannan, V. *J. Chem. Soc., Chem. Commun.* **1986**, 1441. (b) Birchall, T.; Fagiani, R.; Lock, C. J. L.; Manivannan, V. *J. Chem. Soc., Dalton Trans.* **1987**, 1675.

(14) Teff, D. J.; Minear, C. D.; Baxter, D. V.; Caulton, K. G. *Inorg. Chem.* **1998**, *37*, 2547.

(15) (a) Hani, R.; Geanangel, R. A. *Coord. Chem. Rev.* **1982**, *44*, 229. (b) Hampden-Smith, M. J.; Wark, T. A.; Brinker, C. J. *Coord. Chem. Rev.* **1992**, *112*, 81. (c) Teff, D. J.; Huffman, J. C.; Caulton, K. G. *Inorg. Chem.* **1996**, *35*, 2981.

(16) Hampden-Smith, M. J.; Wark, T. A.; Rheingold, A.; Huffman, J. C. *Can. J. Chem.* **1991**, *69*, 121.

(17) Birchall, T.; Dénès, G. *Can. J. Chem.* **1984**, *62*, 591.

(18) (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.

Table 1. Mössbauer Parameters Deduced from Spectra Recorded at *T* of **1a**, Hydrolyzed **1a** (**1a/THF/4**), and Hydrolyzed and Then Calcined **1a** (**1a/THF/4/550 °C**)[a]

		Sn(IV)			Sn(II)		
sample	*T* (K)	δ (mm/s)	Δ (mm/s)	*A* (%)	δ (mm/s)	Δ (mm/s)	*A* (%)
1a	77	−0.008(6)	0.606(6)	54	3.253(9)	2.106(9)	46
1a/THF/4	293	−0.084(8)	0.565(8)	74.5	3.252(20)	1.883(20)	25.5
	77	−0.049(9)	0.621(9)	54.3	3.326(9)	1.929(9)	45.7
1a/THF/4/550 °C	293	0.042(5)	0.835(5)	>99			<1
α-SnF_2[20]					3.472(4)	1.520(4)	
SnO[20]					2.708(4)	1.308(4)	
Sn_2F_2O[20]: site 1					3.071(4)	2.420(4)	
site 2					3.115(4)	2.057(4)	

[a] δ = isomeric shift with $CaSnO_3$ as a reference; Δ = nuclear quadrupole splitting; *A* = area of each signal.

Table 2. Evolution of the Resistivity ρ and the Composition of Calcined **1a/THF/4** as a Function of the Temperature *T* of the Thermal Treatment[a]

T (°C)	ρ ($\Omega\cdot$cm)	F/Sn	C/Sn
50	∞	0.97	0.18
400	10000	0.41	0.04
550	0.7	0.14	<0.025
700	4	0.03	<0.025

[a] F/Sn and C/Sn = atomic ratios between fluorine and tin, and carbon and tin.

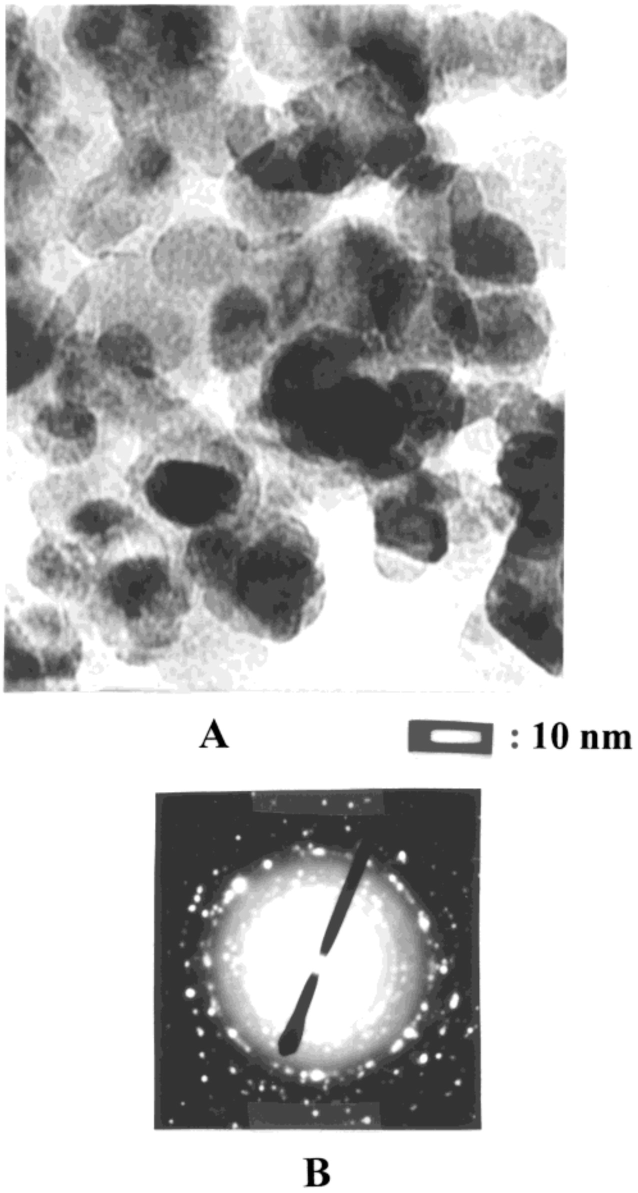


Figure 3. **A**: TEM image of F-doped tin dioxide particles derived from the hydrolysis product of **1b** treated at 550 °C. **B**: FFT of the particles.

correlation peaks were observed by ^{2}D-NOESY spectroscopy between the resonances of the two alkoxides, showing that through-space coupling occurs. This was confirmed by variable-temperature $^{13}C\{^1H\}$ NMR measurements. The alkoxide quaternary carbon region exhibits two peaks at 25 °C in a 3:1 ratio: a broadened band at 80.6 ppm, and a sharp line at 75.6 ppm, near that of the starting alkoxide. Upon cooling to −40 °C, the downfield peak split into two new resonances in a 2:1 ratio at 80.5 and 80.7 ppm, both peaks exhibiting doublet satellites ($^2J(^{13}C-^{119/117}Sn) = 25$ Hz) characteristic of bridging alkoxides.[16] The upfield resonance (75.6 ppm) was unchanged with doublet satellites ($^2J(^{13}C-^{119/117}Sn) = 50$ Hz) corresponding to a terminal alkoxide.[16] Consequently, adduct **1b** includes three bridging and one terminal alkoxide groups, the bridging alkoxide becoming unequivalent at low temperature.[19]

The oxidation state of each tin site in **1a** was determined by Mössbauer spectroscopy. A strong energy dissipation occurred at room temperature, leading to no signal (Figure 2a), which accounts for the presence of organic ligands. Conversely, the 77 K spectrum exhibits two groups of well-defined resonances in a 1:1 ratio (Figure 2b), assigned to resonances of a tin(IV) atom and a tin(II) atom, respectively (Table 1). For the latter, the isomeric shift comprised between that of SnO and the one of α-SnF_2,[20] and the quadrupole splitting, near that described for Sn_2OF_2,[20] are in favor of a tin(II) site linked to both oxygen and fluorine atoms. In addition, the splitting of the tin(IV) signal indicates a distorted tin(IV) site. These spectroscopic data are therefore consistent with the dimeric structure proposed above.

Adducts **1** were then hydrolyzed in THF with hydrolysis ratio $[H_2O]/[Sn] = 4$. The atomic ratios F/Sn (0.97) and C/Sn (0.4) determined by elemental analysis in the resulting powder show that the fluorine was retained and most of the alkoxide groups were removed upon hydrolysis. According to Mössbauer data, the oxidation state and the chemical neighborhood of each tin site remained unaffected upon hydrolysis (Table 1).[21] The two kinds of tin sites were observed at room temperature, confirming the loss of most of the organic ligands. However, X-ray diffraction experiments and conductivity measurements performed on powders dried at 50 °C account for a poorly insulating crystallized material (Table 2). In this type of material,

---

(19) **1a** behaves similarly. Two peaks in a 3:1 ratio are indeed observed by ^{1}H NMR spectroscopy in the methyl region corresponding to the resonances of the *tert*-butyl groups.

(20) Fournès, L.; Grannec, J.; Mirambet, C.; Hagenmuller, P. *Z. Anorg. Allg. Chem.* **1991**, *601*, 93.

(21) See the Supporting Information.

deep subband gap energy states exist, as a result of structural defects, acting as electron traps. These inhibit the electronic mobility and thereby cause a decrease in conductivity. To improve their physical properties, the powders were thermolyzed at various temperatures. The materials progressively crystallized, the fluorine content decreased as the temperature was increased, and the resistivity reached a minimum after treatment in air at 550 °C for 15 min (Table 2). In this case, the resulting material was completely oxidized, as indicated by Mössbauer data (Table 1),[21] and showed the lowest resistivity (0.7 $\Omega \cdot$cm). It also exhibited an X-ray diffraction pattern characteristic of crystallites having the SnO_2 cassiterite structure[22] and an average size estimated to be 7 nm.[23] The particle size observed by transmission electron microscopy (TEM) appeared in general agreement with the XRD determinations, though there was some distribution in size (Figure 3). According to elemental analysis, this slightly gray material contains fluorine ($F/Sn = 0.14$) and a few contaminating carbon atoms ($C/Sn < 0.025$). Although the fluorine content is slightly higher than the best doping amount in SnO_2 thin films, which leads to the highest conductivity and IR reflectivity,[6] the resistivity of this F-doped SnO_2 nanocrystalline powders is 3 times lower than that reported for Sb-doped SnO_2 powders.[4] Thermal treatment at higher temperature induced fluorine content in the materials too small to obtain low resistivity, even if the crystallite size was larger (Table 2).

As was recently shown in the case of sol−gel materials prepared from alkoxyfluorodi(β-diketonate)tin(IV) complexes,[24] the fluorine loss likely occurs from 250 °C as fluorhydric acid resulting from the Sn−F bond cleavage in the presence of water traces. This shows that a precursor containing a large excess in fluorine is necessary to reach the suitable fluorine amount, leading to SnO_2 materials of low resistivity.

Conclusion

The structure in solution of the new hydrolyzable mixed-valence $Sn^{II}Sn^{IV}F_2(OR)_4$ adducts is reported. They include a four-coordinated Sn(IV) site and a five-coordinated Sn(II) bearing two equivalent terminal fluorines, the two tin atoms being bridged via three μ_2-OR groups. After hydrolysis and thermal treatment in air at 550 °C, these compounds yield nanocrystalline F-doped SnO_2 materials with high electronic conductivity. This work constitutes the faster route toward such materials, which are good candidates for the preparation of tin oxide thin films.[5] The preparation of F-doped SnO_2 thin films by spray pyrolysis and spin-coating is presently being developed with these mixed-valence compounds as precursors.[25]

Acknowledgment. Dr. A. Gamard and Dr. H. Cachet are acknowledged for the thin film preparation by spray pyrolysis. Mrs. Sellier, Mr. Barbe, and Mr. Petraud are thanked for their precious assistance.

Supporting Information Available: Mössbauer spectra for **1a/THF/4** and **1a/THF/4/550 °C** and X-ray diffraction data for Xerosol **1a/THF/4**. This material is available free of charge via the Internet at http://pubs.acs.org.

IC000111Z

---

(22) See the Supporting Information. Also see: *Powder Diffraction File*; JCPDS International Center for Diffraction Data: Swarthmore, PA, 1997; No. 41-1445.

(23) The mean particle size was calculated applying the Laue−Scherrer formula to the 110 reflection. See the Supporting Information. Also see: Eberhardt, J. P. *Structural and Chemical Analysis of Materials*; John-Wiley & Sons: New York, 1991; p 203.

(24) (a) Gamard, A. Ph.D. Thesis, University Bordeaux I, 1999. (b) Gamard, A.; Babot, O.; Jousseaume, B.; Rascle, M.-C.; Toupance, T.; Campet, G. *Chem. Mater.*, submitted for publication.

(25) Preliminary results show that transparent conductive F-doped SnO_2 thin films were obtained at 500 °C by spray pyrolysis of a solution 0.1 M **1b** in *tert*-amyl alcohol (film thickness 90 nm; $\rho = 0.03$ $\Omega \cdot$cm; optical transmission >80%; $F/Sn = 0.12$).