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Synthesis and Spectroscopic and X-ray Structural Characterization of R_2Sn^{IV}–Oxydiacetate and –Iminodiacetate Complexes

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Seven novel R_2Sn^{IV}–oxydiacetate (oda) and –iminodiacetate (ida) compounds of the form $[R_2Sn(oda)(H_2O)]_2$ (R = Me, ^{n}Bu, and Ph) (**1**–**3**), $[(R_2SnCl)_2(oda)(H_2O)_2]_n$ (R = Et, ^{i}Bu, and ^{t}Bu) (**4**–**6**), and $[Me_2Sn(ida)(MeOH)]_2$ (**7**) have been synthesized and characterized by IR, ^{1}H, ^{13}C, and ^{119}Sn NMR (solution), solid-state ^{119}Sn CPMAS NMR, and ^{119m}Sn Mössbauer spectroscopy. The crystal structure of $[Me_2Sn(oda)(H_2O)]_2$, **1**, shows it to be dinuclear (centrosymmetric), with two seven-coordinated tin atoms, bridged by one arm of the carboxylate group from each oda. By contrast, the crystal structure of $[(Et_2SnCl)_2(oda)(H_2O)_2]_n$, **4**, comprises a zigzag polymeric assembly containing a pair of different alternating subunits, $\{Et_2SnCl(H_2O)\}$ and $\{Et_2SnCl(H_2O)(oda)\}$, which are connected by way of bridging oda carboxylates, thus giving seven-coordinate tin centers in both components. Finally, the structure of $[Me_2Sn(ida)(MeOH)]_2$, **7**, also centrosymmetric dinuclear, is comprised of a pair of mononuclear units with seven-coordinate tin. The ^{119}Sn solid-state CPMAS NMR and ^{119m}Sn Mössbauer suggest the presence of seven-coordinate Sn metal atoms in some derivatives and the existence of two different tin sites in the $[(R_2SnCl)_2(oda)(H_2O)_2]_n$ compounds.

Introduction

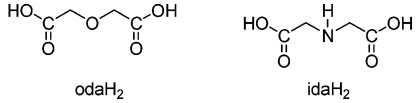

Figure 1. Acids $odaH_2$ and $idaH_2$.

The oxydiacetate anion [oda = $O(CH_2COO)_2^{2-}$] is a versatile ligand having five potential oxygen-donor atoms from two carboxylate groups and from an ethereal function (Figure 1).[1] It has been widely explored as a multidentate bridging and chelating unit toward several metal acceptors,[2−5] mainly d-[6−15] and f-[16−22] block metals. Spectral and structural studies on a number of metal complexes have shown that the oda ligand may bind in mono-, bi-, tri-, and multidentate fashion but can also exist as an anionic noncoordinated species.[23] The more usual chelating mode is tridentate,

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whereby two isomers may be possible, where oda is planar[9,10,24−28] or puckered.[6,27,29] Moreover, in several cases oda can act further as a connecting donor in various homo- and heterometallic extended solids, generally structured as two-dimensional sheets with oda ligands connecting the metal centers through the carboxylate groups.[30,31] Despite the possibility of different coordination modes, only a few organometallic compounds, limited to some cyclopentadienyltitanium and -zirconium derivatives,[25] have been isolated hitherto.

There has been some interest in incorporating tin(IV) carboxylate groups into polymers because of their potential as slow-release antifouling coatings on ships.[32] Dialkyltin dicarboxylates, mainly dibutyltin laurate, are used as catalysts in silicone vulcanization processes that involve the cross-linking of silicone chains with a tetraalkoxysilane.[33] As an extension of our previous work on R_2Sn^{IV} with several types of O-donors, such as β-diketonate,[34] acylpyrazolonate,[35] and pyrazolonecarboxylate donors,[36] we have initiated a study of the interaction of $odaH_2$ with R_2Sn^{IV} moieties in the presence of strong bases. There appear to be only two relevant reports in the literature, on thermodynamic and NMR studies of a dimethyltin(IV) oda complex in aqueous solution;[37,38] to our knowledge, X-ray structural characterizations of oxydiacetate p-block complexes have only been reported for lead.[4,5] We now report the synthesis and spectroscopic characterization of six new compounds and the crystal structures of two of them, the dinuclear $[Me_2Sn(oda)(H_2O)]_2$, **1**, and the polynuclear $[(Et_2SnCl)_2(oda)(H_2O)_2]_n$, **4**. We also report a dialkyltin derivative, **7**, with the "isoelectronic" iminodiacetate anion [ida $= HN(CH_2COO)_2{}^{2-}$] (Figure 1), a donor similar to oda, which was prepared and characterized for comparative purposes.

Experimental Section

Materials and Measurements. All reagents and solvents were obtained from commercial sources and were used without further purification. Samples for microanalysis were dried in a vacuum to constant weight (20 °C, about 0.1 Torr). Elemental analyses (C, H, N) were performed with a Fisons Instruments 1108 CHNS-O elemental analyzer. IR spectra were recorded from 4000 to 200 cm^{-1} with a Perkin-Elmer System 2000 FT-IR instrument. ^1H, ^{13}C, and ^{119}Sn NMR spectra were recorded on a VXR-300 Varian spectrometer operating at room temperature (300 MHz for ^1H, 75 MHz for ^{13}C, and 117.9 MHz for ^{119}Sn). Proton and carbon chemical shifts are reported in parts per million vs Me_4Si, while tin chemical shifts are reported in parts per million vs neat Me_4Sn. Melting points were determined using an IA 8100 electrothermal instrument. The electrical conductances of the CH_3OH and DMSO solutions were measured with a Crison CDTM 522 conductimeter at room temperature.

^{119m}Sn Mössbauer Measurements. ^{119m}Sn Mössbauer spectra were recorded on solid samples at liquid-nitrogen temperature using a conventional constant-acceleration spectrometer, coupled with a multichannel analyzer (Aen, Ponteranica (BG), Italy) equipped with a cryostat Cryo (Rial, Parma, Italy). The solid sample placed into the cryostat was dried with a flow of helium and then dried under vacuum. A $Ca^{119}SnO_3$ Mössbauer source, 10 mCi (Ritverc, St. Petersburg, Russia), moving at room temperature with constant acceleration in a triangular waveform was used. The velocity calibration was made using a ^{57}Co Mössbauer source, 10 mCi, and an iron foil as absorber (from Ritverc, St Petersburg, Russia).

^{119}Sn Solid-State NMR. High-resolution solid-state ^{119}Sn magic-angle-spinning (MAS) NMR spectra were acquired at ambient temperatures using a Bruker MSL-400 NMR spectrometer (B_o = 9.4 T) operating at the ^{119}Sn frequency of 149.20 MHz. These experiments were conducted using a Bruker 4 mm double-air-bearing MAS probe from which rotational frequencies of ∼3−12 kHz were implemented. All experimental data were acquired under $^1H-^{119}Sn$ cross-polarization conditions which used recycle delays of 5−20 s, Hartmann−Hahn contact periods of 2 ms, and an initial ^1H $\pi/2$ pulse width of 3.5 μs. A nominal ^1H decoupling field strength of ∼80 kHz was employed during acquisition. Each spectrum was externally referenced to Me_4Sn via a secondary external reference of Cy_4Sn that is located upfield from Me_4Sn at −97.35 ppm;[39] this sample of Cy_4Sn was also used to establish the Hartmann−Hahn contact condition required for cross-polarization

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spectral acquisition. The ^{119}Sn CPMAS spectrum of each complex was acquired at three different MAS frequencies to allow an unambiguous assignment of the isotropic chemical shift (δ_{iso}), and to clearly identify the chemical shift tensor elements δ_{11}, δ_{22}, and δ_{33}, particularly where multiple Sn sites were present. The MAS NMR spectra acquired at ∼3 kHz were more selectively utilized to identify δ_{11}, δ_{22}, and δ_{33} since increased MAS rates invoked the appearance of biasing the downfield tensorial positions to lower ppm values and the upfield tensorial positions to higher ppm values. Parameters defining the chemical shift interaction were calculated from these measured chemical shift tensorial elements δ_{11}, δ_{22}, and δ_{33} according to IUPAC-recommended conventions as discussed by Mason[40] and Mackenzie et al.;[41] here $\delta_{11} > \delta_{22} > \delta_{33}$ with the isotropic chemical shift $\delta_{iso} = (\delta_{11} + \delta_{22} + \delta_{33})/3$, span $\Omega = \delta_{11} - \delta_{33}$, and skew $\kappa = 3(\delta_{22} - \delta_{iso})/(\delta_{11} - \delta_{33})$, where $1 \geq \kappa \geq -1$. Additional representations of chemical shift interaction parameters such as the anisotropy ($\Delta\delta$) and asymmetry (η) can be calculated if an alternate frequency convention $|\delta_{33} - \delta_{iso}| \geq |\delta_{11} - \delta_{iso}| \geq |\delta_{22} - \delta_{iso}|$ is invoked; in this case the anisotropy $\Delta\delta = \delta_{33} - (\delta_{11} + \delta_{22})/2 = 3(\delta_{33} - \delta_{iso})/2$ and asymmetry $\eta = (\delta_{22} - \delta_{11})/(\delta_{33} - \delta_{iso})$, where η is restricted within the range $1 \geq \eta \geq 0$.

X-ray Structure Determinations. Full spheres of "low-temperature" CCD area-detector data were measured (Bruker AXS instrument, ω-scans, monochromatic Mo Kα radiation, $\lambda = 0.710\ 7_3$ Å; T ca. 153 K) yielding $N_{t(otal)}$ reflections. These were merged to N unique after "empirical"/multiscan absorption correction (proprietary software), N_o with $F > 4\sigma(F)$ being considered "observed" and used in the full-matrix least-squares refinements, refining anisotropic displacement parameter forms for the non-hydrogen atoms and with $(x, y, z, U_{iso})_H$ constrained at estimated values (exception: the water molecule hydrogen atoms in **2** which could not be confidently located in difference maps). Conventional residuals R and R_w (weights: $(\sigma^2(F) + 0.000n_wF^2)^{-1}$) are quoted on $|F|$ at convergence. Neutral atom complex scattering factors were employed within the context of the Xtal 3.7 program system.[42] Pertinent results are given below and in the tables and figures, the latter showing non-hydrogen atoms with 50% probability amplitude displacement ellipsoids, hydrogen atoms having arbitrary radii of 0.1 Å.

Syntheses of Complexes. [Me$_2$Sn(oda)(H$_2$O)]$_2$ (1). Oxydiacetic acid (odaH$_2$) (0.134 g, 1.0 mmol) and KOH (0.112 g, 2.0 mmol) were added to a MeOH solution (50 mL) containing Me$_2$SnCl$_2$ (0.219 g, 1.0 mmol). The reaction mixture was stirred at 60 °C for 48 h and then filtered off. Colorless crystals of **1** were obtained upon slow evaporation of the methanol filtrate. Yield: 52%. Mp: >350 °C (dec). Anal. Calcd for $C_6H_{12}O_6Sn$: C, 24.11; H, 4.05. Found: C, 24.08; H, 4.26. IR (Nujol, cm^{-1}): 3461 br ν(H$_2$O), 1675 m δ(H$_2$O), 1646 s, 1598 s ν_{sym}(C=O), 1428 m ν_{asym}(C=O), 1147 s ν_{sym}(OCO), 562 s ν(Sn−C), 440 m, 372 s, 356 sh ν(Sn−O). ^{1}H NMR (D$_2$O, 20 °C): δ 0.88 (s, 12H, $^2J(^{119}$Sn−^{1}H) - 110.6 Hz, $^2J(^{117}$Sn−^{1}H) = 105.5 Hz, SnC*H$_3$*), 4.23 (s, 4H, *H$_2$*O), 4.77 (s, 8H, C*H$_2$* of oda). ^{13}C NMR (D$_2$O, 20 °C): δ 12.9 (s, Sn*C*H$_3$), 67.5 (s, *C*H$_2$), 175.2 (s, *C*OO). ^{119}Sn NMR (D$_2$O, 22 °C): δ −365.

[^{n}Bu$_2$Sn(oda)(H$_2$O)]$_2$ (2). Compound **2** has been obtained using a procedure similar to that reported for **1**, in 64% yield. Mp: 202−205 °C. Anal. Calcd for $C_{12}H_{24}O_6Sn$: C, 37.63; H, 6.32. Found: C, 37.63; H, 6.98. IR (Nujol, cm^{-1}): 3276 br ν(H$_2$O), 1633 s, 1579 s ν_{asym}(C=O), 1434 m ν_{sym}(C=O), 1124 s ν_{sym}(OCO), 592 m ν(Sn−C), 460 s, 349 s ν(Sn−O). ^{1}H NMR (CD$_3$OD, 20 °C): δ 1.02 (t), 1.40−1.65 (m) (18H, Sn^{n}Bu), 4.35 (s, 2H, *H$_2$*O), 4.99 (s, 4H, C*H$_2$* of oda).

[Ph$_2$Sn(oda)(H$_2$O)]$_2$ (3). Compound **3** has been synthesized using a procedure similar to that reported for **1**. Yield: 51%. Mp: 327−330 °C. Anal. Calcd for $C_{16}H_{16}O_6Sn$: C, 45.43; H, 3.81. Found: C, 45.51; H, 4.26. IR (Nujol, cm^{-1}): 3366 br ν(H$_2$O), 3052 m ν(C−H$_{arom}$), 1653 s, 1635 s, 1582 s ν_{sym}(C=O), 1427 m ν_{asym}(C=O), 261 m, 226 m ν(Sn−C), 461 vs, 301 s ν(Sn−O). ^{1}H NMR (DMSO-d_6, 20 °C): δ 3.32 (s, 2H, *H$_2$*O), 3.75 (s, 4H, C*H$_2$* of oda), 7.20−7.40 (m) 7.67 (d br) (10H, Sn−Ph).

[(Et$_2$SnCl)$_2$(oda)(H$_2$O)$_2$]$_n$ (4). Compound **4** has been obtained using a procedure similar to that reported for **1**. Yield: 41%. Mp: 156−159 °C. Anal. Calcd for $C_{12}H_{26}O_6Cl_2Sn_2$: C, 25.08; H, 4.56. Found: C, 25.85; H, 4.66. IR (Nujol, cm^{-1}): 3250 br ν(H$_2$O), 1651 m δ(H$_2$O), 1592 s, 1574 s ν_{sym}(C=O), 1440 m ν_{asym}(C=O), 1125 s ν_{sym}(OCO), 548 m ν(Sn−C), 448 w, 375 m ν(Sn−O), 295 s, 287 s, 280 s ν(Sn−Cl). ^{1}H NMR (CD$_3$OD, 20 °C): δ 1.17 (t, 12H, $^3J(^{119}$Sn−^{1}H) = 179.5 Hz, $^3J(^{117}$Sn−^{1}H) = 171.4 Hz, SnCH$_2$C*H$_3$*), 1.58 (q, 8H, $^2J(^{119}$Sn−^{1}H) = 105.5 Hz, $^2J(^{117}$Sn−^{1}H) = 100.7 Hz, SnC*H$_2$*CH$_3$), 4.24 (s, 2H, *H$_2$*O), 4.98 (s, 8H, C*H$_2$* of oda). ^{13}C NMR (CD$_3$OD, 20 °C): δ 10.2 (s, $^2J(^{119/117}$Sn−^{13}C) = 52 Hz, SnCH$_2$*C*H$_3$), 25.4 (s, $^1J(^{119}$Sn−^{13}C) = 796 Hz, $^1J(^{117}$Sn−^{13}C) = 744 Hz, Sn*C*H$_2$CH$_3$), 68.8 (s, *C*H$_2$COO of oda), 175.0 (s, CH$_2$*C*OO of oda).

[(^{i}Bu$_2$SnCl)$_2$(oda)(H$_2$O)$_2$]$_n$ (5). Compound **5** has been prepared using a procedure similar to that reported for **1**. Yield: 62%. Mp: 146−149 °C. Anal. Calcd for $C_{20}H_{44}O_7Cl_2Sn_2$: C, 32.98; H, 6.92. Found: C, 33.16; H, 6.73. IR (Nujol, cm^{-1}): 3234 br ν(H$_2$O), 1648 m δ(H$_2$O), 1632 s, 1596 s br ν_{sym}(C=O), 1442 m ν_{asym}(C=O), 1115 s ν_{sym}(OCO), 596 m ν(Sn−C), 454 w, 394 m ν(Sn−O), 301 s, 290 s, 283 s ν(Sn−Cl). ^{1}H NMR (CD$_3$OD, 20 °C): δ 0.91 (t), 1.28−1.60 (m) (18H, Sn^{i}Bu), 4.23 (s, 4H, *H$_2$*O), 4.86 (s, 4H, C*H$_2$* of oda).

[(^{t}Bu$_2$SnCl)$_2$(oda)(H$_2$O)$_2$]$_n$ (6). Compound **6** has been prepared using a procedure similar to that reported for **1**. Yield: 68%. Mp: 141−148 °C. Anal. Calcd for $C_{20}H_{44}O_7Cl_2Sn_2$: C, 32.98; H, 6.92. Found: C, 32.95; H, 6.58. IR (Nujol, cm^{-1}): 3443 br ν(H$_2$O), 1644 m δ(H$_2$O), 1620 m, 1596 s ν_{sym}(C=O), 1443m ν_{asym}(C=O), 1142 s ν_{sym}(OCO), 592 m ν(Sn−C), 440 w, 348 m ν(Sn−O), 283 s, 230 s br ν(Sn−Cl). ^{1}H NMR (CD$_3$OD, 20 °C): δ 1.54 (s, 18H, $^2J(^{119}$Sn−^{1}H) = 112.6 Hz, $^2J(^{117}$Sn−^{1}H) = 107.4 Hz, Sn^{t}Bu), 4.55 (s, 8H, *H$_2$*O), 4.98 (s, 4H, C*H$_2$* of oda).

[Me$_2$Sn(ida)(MeOH)]$_2$ (7). Compound **7** has been obtained by using a procedure similar to that reported for **1** but using idaH$_2$ instead of odaH$_2$. Yield: 57%. Mp: 293−296 °C. Anal. Calcd for $C_7H_{15}O_5NSn$: C, 26.96; H, 4.85; N, 4.49. Found: C, 27.15; H, 4.96; N, 4.26. IR (Nujol, cm^{-1}): 3366 br ν(O−H), 3169 m ν(N−H), 1680 s, 1654 s, 1631 sh ν_{sym}(C=O), 1441 sh ν_{asym}(C=O), 572 m ν(Sn−C), 399 s, 344 s ν(Sn−O), 263 s ν(Sn−N). ^{1}H NMR (CD$_3$OD, 20 °C): δ 1.54 (s, 6H, $^2J(^{119}$Sn−^{1}H) = 68.7 Hz, $^2J(^{117}$Sn−^{1}H) = 65.7 Hz, SnMe), 4.55 (s, 3H, C*H$_3$*OH), 4.87 (s, 4H, C*H$_2$* of ida). ^{13}C NMR (DMSO-d_6, 20 °C): δ 6.5 (s br, Sn*C*H$_3$), 50.7 (s, *C*H$_2$), 170.6 (s, *C*OO). ^{119}Sn NMR (DMSO-d_6, 22 °C): δ −222.

[Me$_2$Sn(ida)]$_2$ (8). Compound **8** has been obtained by maintaining compound **7** at 70 °C under vacuum for 6 h. Mp: 293−296 °C. Anal. Calcd for $C_6H_{11}O_4NSn$: C, 25.75; H, 3.96; N, 5.00. Found: C, 25.56; H, 4.03; N, 5.08. IR (Nujol, cm^{-1}): 3096 br ν(N−H), 1643 s, 1590 s, 1558, 1494 sh ν_{sym}(C=O), 1407 s ν_{asym}(C=O), 589 m, 551 m, 523 w ν(Sn−C), 491 s, 415 w, 398 m, 350 m, ν(Sn−O), 279 ν(Sn−N). ^{1}H NMR (DMSO-d_6, 20 °C): δ 0.66 (s, 6H, $^2J(^{119}$Sn−^{1}H) = 93.4, Hz, $^2J(^{117}$Sn−^{1}H) = 90.1 Hz,

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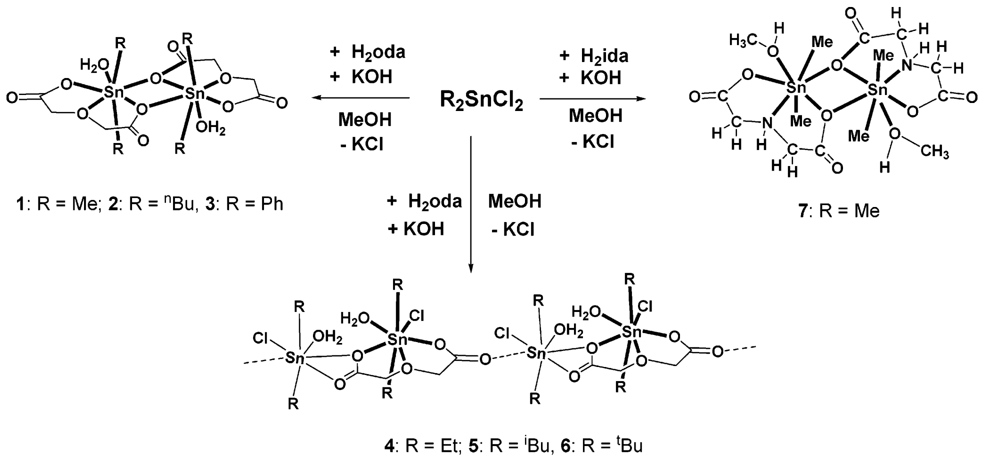
Scheme 1



SnMe), 3.34 (dq, 4H, CH_2 of ida), 6.6 (m, 1H, NH). ^{13}C NMR (DMSO-d_6, 20 °C): δ 6.5 (s br, SnCH_3), 50.7 (s, CH_2), 170.6 (s, COO). ^{119}Sn NMR (DMSO-d_6, 22 °C): δ −222.

Results and Discussion

The interaction of oxydiacetic acid (odaH$_2$) with an equimolar amount of R_2SnCl_2 (R = Me, ^{n}Bu, Ph) in the presence of 2 equiv of KOH in methanol afforded the dinuclear derivatives **1**−**3**, [$R_2Sn(oda)(H_2O)]_2$ (R = Me, ^{n}Bu, Ph), in high yield (Scheme 1).

By contrast under the same conditions, the reaction of odaH$_2$ with R_2SnCl_2 (R = Et, ^{i}Bu, ^{t}Bu) yielded the polynuclear derivatives $[(R_2SnCl)_2(oda)(H_2O)_2]_n$, **4**−**6** (Scheme 1), in which a different ligand-to-metal ratio has been found, only one chloride group being substituted in the tin coordination sphere by a carboxylate group. Compounds **4**−**6** were also formed when an excess of KOH and odaH$_2$ ligand was employed or when the reaction was carried out under forcing conditions as, for example, refluxing solvents and long reaction times. This could be ascribed to a progressive increase in steric hindrance about the tin center on going from Et_2Sn to $^iBu_2Sn$ and $^tBu_2Sn$ moieties, which, presumably, inhibits complete substitution of the chlorides by oda.

Finally, the interaction of iminodiacetic acid (idaH$_2$) with an equimolar amount of Me_2SnCl_2 in the presence of KOH in methanol afforded the dinuclear complex [Me_2Sn(oda)(MeOH)]$_2$, **7**, in high yield. When compound **7** was stored under vacuum at 60 °C for 6 h, the anhydrous amorphous form [Me_2Sn(oda)] was obtained.

Greater yields have been obtained when the reactions described above were carried out in methanol rather than water or DMSO as solvent, crystalline deposits generally forming on slow evaporation (many days) of the cooled solutions.

All derivatives **1**−**6** show limited solubility in DMSO but are insoluble in chlorinated solvents, diethyl ether, aromatics, and aliphatic hydrocarbons. Compound **1** is also soluble in D_2O, whereas derivatives **2**−**6** are quite soluble in MeOH. Derivatives **7** and **8** are only slightly soluble in MeOH. All are nonelectrolytes in DMSO solution, the Λ_m values being always less than 4.5 Ω^{-1} cm^2 mol^{-1}.

Single-Crystal X-ray Studies. The results of the "low-temperature" single-crystal X-ray structure determinations for **1**, **4**, and **7** are consistent with the above formulations, all solvent residues being coordinated. For **1** and **4**, oda ligands may be viewed as oda^{2-}, all being quasi-planar in respect of their non-hydrogen components and behaving as tridentates toward closely associated tin atoms; the peripheral oxygen atoms of both types, coordinated and not to the central tin, interact diversely with other tin atoms, leading in the case of **1** to a binuclear complex and in the case of **4** to a quasi-one-dimensional polymer. Interactions of the latter type and the stacking of planar ligand motifs may be viewed as determinants of the interesting lattice array; hydrogen-bonding interactions may also be postulated from the limited proportion of water molecules in the array, approximately half of these seemingly internal to the molecular units. About all tin(IV) atoms, the pairs of alkyl groups are trans, quasi-linear, the axial component of a stereochemistry which, in all cases, may be viewed as seven-coordinate pentagonal bipyramidal, although the equatorial interactions are diverse in their strengths.

Compound **1** is binuclear (Figure 2), the two halves of the dimer being related by a crystallographic center of symmetry, with half comprising the asymmetric unit; the complement of coordinating atoms in the equatorial plane about each tin atom comprises the tridentate oda, the water molecule oxygen atom, and O(11) bridging from the oda ligand of the other tin. The carboxylate oxygen O(21) is more strongly bound to tin than the ethereal O(1) atom, the latter

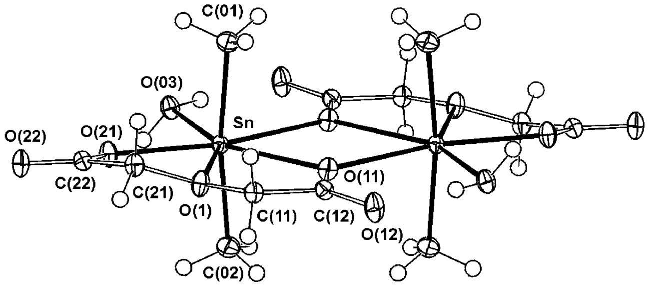


Figure 2. Single centrosymmetric dimer of **1**: Sn−C(01,02),O(03,1,11,21,11′), 2.103(2), 2.104(2), 2.218(1), 2.357(2), 2.498(2), 2.200(2), 2.505(2) Å; O(11)···O(11′), 2.771(2); Sn···Sn′, 4.1653(4) Å; C(01)−Sn−C(02), 171.59(7)°.

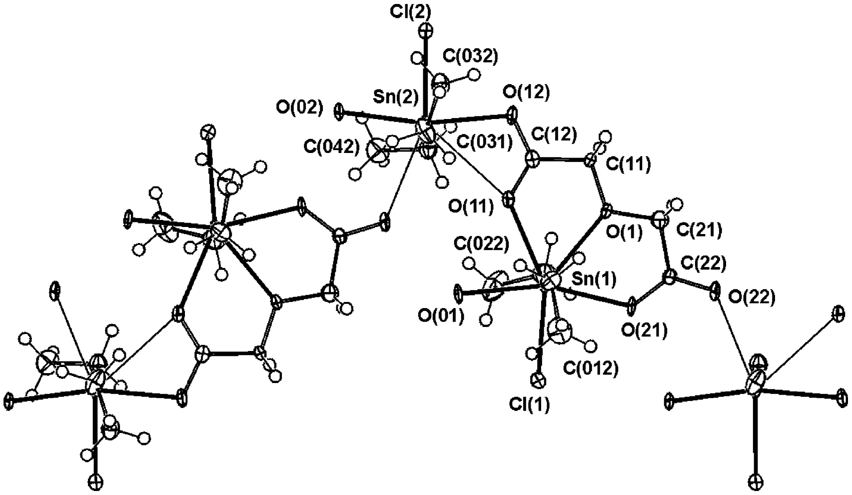


Figure 3. Single strand of the "polymer" of **4** (*c* lies horizontal in the page): Sn(1)−C(011,021),Cl(1),O(01, 1, 11, 21), 2.114(7), 2.103(9), 2.505(2), 2.281(6), 2.525(5), 2.450(5), 2.333(5) Å; C(011)−Sn(1)−C(021), 167.9(3)°; Sn(2)−C(031,041),Cl(2),O(02,11,22′,12), 2.132(7), 2.103(7), 2.446(2), 2.272(5), 2.953(5), 2.797(5), 2.278(5) Å; C(031)−Sn−C(041), 155.9(3)°; Sn(1)···Sn(2),Sn(2)($x - 1/2$, $1/2 - y$, $z + 1/2$), 5.2707(8), 6.1402(8) Å.

in turn being more strongly bound than the bridging O(11) atom, with the two Sn−O(11) distances, tridentate and bridging, identical.

The different natures of the two carboxylate groups are reflected in the variations in their associated geometrical parameters C(*n*2)−O(*n*1,2) and, more sensitively, in the associated angular parameters which differ appreciably on either side of the ligand, even about the central O(1). This type of coordination mode is not common, and it has been defined only in the cadmium−oda derivative [Cd(oda)(H$_2$O)$_3$]$_2$.[43] Although quasi-planar (Figure 2), the chelate rings of the tridentate are somewhat puckered. One of the water molecules hydrogen bonds to the other half of the dimer (O(3),H(03b)···O(12)($1/2 - x$, $1/2 - y$, $1 - z$) = 2.592(3), 1.8$_0$ Å (estimate)), and the other to an adjacent dimer (O((3),H(03a)···O(21)($1 - x$, y, $3/2 - z$) = 2.744(2), 1.8$_6$ Å (estimate)).

In **4**, although the asymmetric unit of the structure contains a pair of tin atoms, their roles are quite different; the complex may be considered as an aggregate: [Et$_2$SnCl(H$_2$O)]$^+$[Et$_2$SnCl(H$_2$O)(oda)]$^-$ with bridging peripheral carboxylate oxygens from a pair of anions making up the (otherwise rather sparse) coordination sphere of each of the cation metal atoms (Figure 3). Interestingly, whereas the bridging interaction in **1** arose from one of the "endo" peripheral oxygen atoms, i.e., an O(1) of the tridentate, here that interaction is weak, perhaps only consequent on the now strong interaction of O(12), one of a pair arising from both O(*n*2)'s (that involving O(22) much weaker) which link anions and cations alternately into a one-dimensional polymeric string. Although in consequence of the use of less congenial material the precision of this determination is inferior to that of **1**, it suffices to define similarly diverse differences in geometries between the two halves of the tridentate, both within **4** and relative to **1**. Whereas the distances within the equatorial plane about (anionic) Sn(1) in **4** are similar (Sn−O, Sn−Cl ranging between 2.281(6) and 2.525(5) Å), those about (cationic) Sn(2) are much more diverse (2.272(5)−2.953(3) Å); Sn(2)−O(11),O(22)($x - 1/2$, $1/2 - y$, $1/2 + z$) are long (2.953(5), 2.797(5) Å) with Sn(2)−Cl(2) now shortened to 2.446(2) Å and Sn(2)−O(02,12) < 2.28 Å. The coordination sphere is now quite unsymmetrical, with the "axial" C−Sn−C angle closing away from Cl(2) to 155.9(3)°. Although water molecule hydrogen atoms were not located, they may be tentatively inferred as reinforcing the polymeric linkage: O(01)···O(22)($x - {}^1/_2$, $1/2 - y$, $1/2 + z$), O(02)···O(21) ($x - 1/2$, $1/2 - y$, $1/2 + z$) = 2.685(7), 2.679(7) Å. The bridging coordination mode of the oda ligand in **4** is uncommon and has only been defined in a cadmium complex Cd(oda):H$_2$O (2:7).[44]

The structure of **7** is closely related to the known binuclear [Me$_2$Sn(ida)(H$_2$O)]$_2$ complex[45] but with water replacing the methanol ligand. Compound **7** is also analogous to **1** (compare the unit cells, Table 1), the asymmetric unit again containing one tin atom with associated ligands; the equatorial aqua ligand of **1** is replaced by a methanol molecule, somewhat disordered and, interestingly, pivoting about the hydroxyl hydrogen, which is hydrogen-bonded to O(11) of the inversion-related ligand (Figure 4). The O(11)−Sn−O(21) angle is much smaller in **7** than in **1** (144.85(8)°; cf. 158.40(5)°), presumably a consequence of replacing the quasi-planar O(1) by a quasi-tetrahedral N(1). The distance to the latter is the shorter (Sn−N(1) = 2.282(2); cf. Sn−O(1) =2.357(2) Å), with the range of angles between axial and equatorial donors in **1** (86.15(5)−94.89(7)°) less diverse than that in **7** (80.7(1)−97.2(3)° or 72.4(3)−100.4(1)° if the minor component O(03′) is considered). The overall outcome of the aggregate of the above effects is a more compact tridentate, with more closely bound central atom (and, presumably, concomitant trans effect) and weaker methanol compared to H$_2$O donor. Additionally, the dimer formation, with the centrosymmetrically related second monomer, is

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Table 1. Crystal/Refinement Details

param	1	4[a]	7[b]
formula	$C_{12}H_{24}O_{12}Sn_2$	$C_{12}H_{28}Cl_2O_7Sn_2$	$C_7H_{15}NO_5Sn$
M_r/Da	597.7	592.7	311.9
cryst system	monoclinic	monoclinic	monoclinic
space group	$C2/c$ (No. 15)	$P2_1/n$ (No. 14)	$P2_1/c$ (No. 14)
a/Å	22.608(2)	8.137(1)	10.6103(7)
b/Å	6.6669(7)	17.648(3)	6.7816(5)
c/Å	15.527(7)	14.085(2)	15.501(1)
β/deg	125.015(2)	98.296(4)	107.231(1)
V/Å^3	1917	2002	1085
D_c/g cm^{-3}	2.071	1.967	1.944
Z/f.u.	4	4	4
μ_{Mo}/mm^{-1}	2.7	2.8	2.4
specimen/mm	0.40 × 0.35 × 0.32	0.32 × 0.18 × 0.10	cuboid, 0.10
$T_{min/max}$	0.77	0.62	0.89
$2\theta_{max}$/deg	75	55	70
N_t	19 338	40 395	21 952
$N(R_{int})$	5001 (0.028)	4613 (0.068)	4562 (0.032)
N_o	4646	3905	3887
R[c]	0.024	0.058	0.034
R_w (n_w)[c]	0.043(1)	0.090(5)	0.047(0.7)

[a] Sample quality presented difficulty, being badly twinned. [b] The methanol ligand was modeled in terms of a pair of H_3CO components disposed over a pair of sites, occupancies 0.81(1) and complement, pivoted about a common hydroxyl hydrogen. [c] $R = \Sigma\Delta/\Sigma|F_o|$; $R_w = (\Sigma w\Delta^2/wF_o{}^2)^{1/2}$.

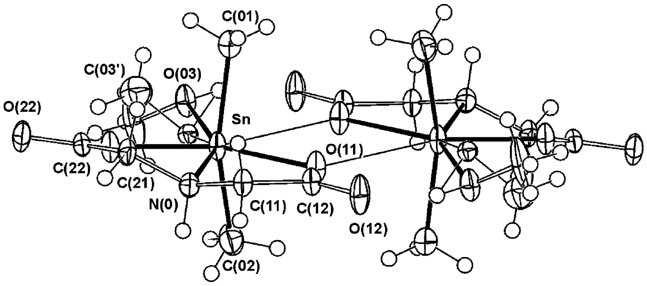

Figure 4. Centrosymmetric mutual approach of the pair of molecules of **7**. Note the disordered minor component of the methanol molecule. Sn−C(01,2),O(3,03′,11,21),N(1): 2.107(4), 2.109(4), 2.391(4), 2.35(1), 2.346(2), 2.156(2), 2.282(2) Å. C(01)−Sn−C(02): 159.5(1)°.

much more tenuous with the Sn···O(11)(2 − x, 1 − y, 1 − z) approach now very long (2.953(2) Å).

Spectroscopy. IR Spectroscopy. It has been previously reported[46] that bands due to carboxylate groups can be used to distinguish between the various $-COO^-$ group coordination modes. Upon coordination to tin centers, the strong IR absorptions due to ν_{as}(COO) in the free odaH$_2$ (ν_{as}(COO): 1734 cm^{-1}) and idaH$_2$ (ν_{as}(COO): 1733 cm^{-1}) are generally displaced to lower frequencies (from 1680 to 1570 cm^{-1}), whereas a negligible shift to higher frequencies (ranging from 1450 to 1430 cm^{-1}) has been detected for the ν_s(COO) which appear in the free ligands at ca. 1420 cm^{-1}. Here the highest values of ν_{as} have been found for species **1** and **7** for which dimeric structures containing uncoordinated C═O groups have been established on the basis of X-ray studies. By contrast, lower values have been found in the derivative **4** for which a polynuclear structure containing chelating and bridging carboxylate groups has been found. The Δ values (=[$\nu_{asym}(CO_2^-) - \nu_{sym}(CO_2^-)$]) for compounds **1** and **7** are 218 and 239 cm^{-1}, respectively which support unidentate carboxylate coordination. In the case of **4**−**6**, the Δ range from 152 (**4**) to 180 (**6**) cm^{-1} in accordance with chelating and bridging coordination of oda.[46] However, in some cases some additional bands are present in the 1700−1600 cm^{-1} region which could be indicative of a different coordination mode for the ligands in the same complexes. Thus, e.g., the spectrum of **6** exhibits, for ν_{as}, two different absorptions, the first similar to that reported for compound **4** and the second similar to that reported for derivative **1** and indicative of a free C═O group. Also, in accordance with the ^{119}Sn CPMAS and ^{119}Sn Mössbauer data, some structural differences between compounds **4** and **6** are likely.

It has been recently proposed,[28] and theoretically supported,[15] that the IR band corresponding to the antisymmetric COC stretching at the ethereal oxygen can be discriminative of the coordination mode adopted by the oxydiacetate ligand. Thus, a planar oxydiacetate is characterized by a sharp and strong band in the region 1120−1150 cm^{-1}, while this IR band falls in the region around 1100 cm^{-1} when the arrangement is puckered. For all oda complexes, **1**−**6**, this absorption appears within the range 1115−1147 cm^{-1}, i.e., at higher values than a limit of 1100 cm^{-1}, so that the planar disposition of oda may be invariably presumed, consistent with the X-ray structural determinations of **1** and **4**.

Only one ν(Sn−C) stretching vibration is found, at ca. 560 cm^{-1} in the spectra of derivatives **1** and **4**, as expected for an axial *trans*-R$_2$Sn configuration, also supported by the X-ray data (see below). Analogous absorptions have been found in the spectra of derivatives **2**, **3**, **5**, and **6** at ca. 590, 260, 596, and 490 cm^{-1}, respectively. Strong absorptions in the region 450−350 cm^{-1} may be ascribed, on the basis of literature data, to ν(Sn−O) stretching vibrations.[47] Finally, Sn−Cl vibration modes are assigned below 300 cm^{-1} in the spectra of **4**−**6**.[48]

NMR Solution Studies. The ^{1}H NMR spectrum of **1** was recorded in D$_2$O whereas the spectra of **2**−**7** were recorded in DMSO-d_6 or CD$_3$OD, the choice depending on the solubility of the species. The $^2J(^{119/117}Sn-^1H)$ values of **1** and **4** are typical of trans six-coordinated tin centers. The same trans disposition is likely for **4** and **6**, their $^3J(^{119/117}Sn-^1H)$ values being harmonious with those reported in the literature for analogous compounds.[49] The CH$_2$ chemical shifts of (oda)$^{2-}$ and (ida)$^{2-}$ in the spectra of **1**−**7** are always to lower field with respect to the corresponding resonances in the spectra of free odaH$_2$ and idaH$_2$, and water (in **1**−**6**) or methanol (in **7**) have been detected as narrow signals, thus indicating that they are coordinated to tin also in solution. The poor solubility in almost all solvents has precluded the measurement of ^{13}C and ^{119}Sn NMR of almost all the derivatives **2**−**7**, apart from **4**. The $^1J(^{119}Sn-^{13}C)$ in **4** is 796 Hz. This application of the linear relationship previously proposed for R$_2$Sn^{IV} [49,50] derivatives indicates a θ(C−Sn−C) angle of 157.4°; cf. the value of 155.9(3)° found

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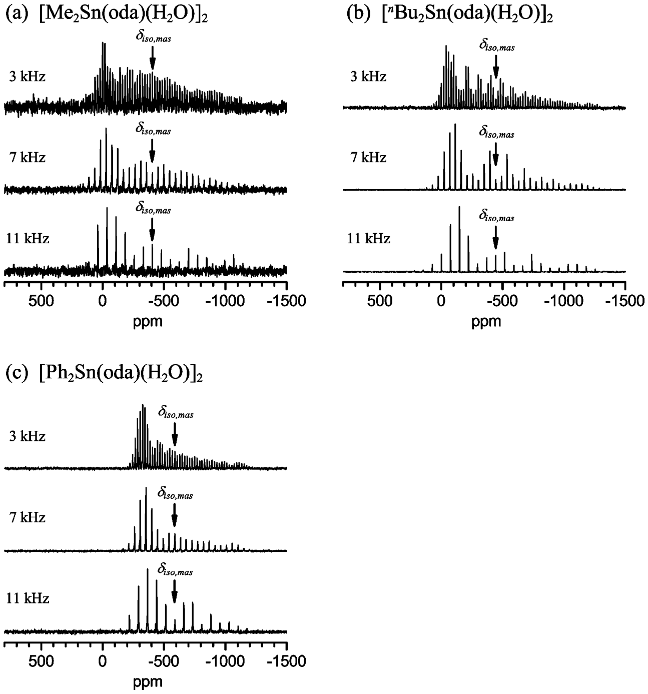

Figure 5. The ^{119}Sn CPMAS NMR spectra of (a) $[Me_2Sn(oda)(H_2O)]_2$ (**1**), (b) $[^nBu_2Sn(oda)(H_2O)]_2$ (**2**), and (c) $[Ph_2Sn(oda)(H_2O)]_2$ (**3**) acquired at MAS frequencies of 3, 7, and 11 kHz.

for the $\{Et_2SnCl(H_2O)(oda)\}$ subunit in the crystal structure of **4** (see below) and 167.0(2)° observed in the other $\{Et_2SnCl(H_2O)\}$ subunit. The ^{119}Sn chemical shift of **1** in D_2O is −365 ppm consistent with a six-coordinate tin coordination environment which suggests dissociation of the dimeric species in solution.[51]

^{119}Sn Solid-State CPMAS NMR Discussion. The ^{119}Sn CPMAS NMR spectra of complexes **1**−**3** are shown in Figure 5; each spectrum has been acquired at MAS frequencies of 3, 7, and 11 kHz, allowing accurate identification of $\delta_{iso,mas}$, δ_{11}, δ_{22}, and δ_{33}. The isotropic chemical shifts ($\delta_{iso,mas}$ and $\delta_{iso,calc}$), the chemical shift tensorial values (δ_{11}, δ_{22}, and δ_{33}) and the calculated parameters defining the chemical shift interaction (span Ω, skew κ, anisotropy $\Delta\delta$, asymmetry η) are summarized in Table 2. From Table 2 it can be observed that excellent agreement exists between the measured isotropic shift ($\delta_{iso,mas}$) and the calculated isotropic shift ($\delta_{iso,calc}$) (calculated from the tensorial values δ_{11}, δ_{22}, and δ_{33}), suggesting that nominated positions of δ_{11}, δ_{22}, and δ_{33} from each ^{119}Sn CPMAS spectrum have been determined accurately. The ^{119}Sn chemical shift tensor of each dimeric complex **1**−**3** appears to exhibit strict axial symmetry, possessing spans which range from ~828 ppm (3, phenyl) to ~1230 ppm (2, *n*-butyl) (Table 2). These Sn(IV) complexes represent a deviation from the conventional notion of tensor axial symmetry of metals in coordination environments. Usually, axial symmetry in a chemical shift tensor is identified with coordination environments possessing strict tetrahedral or octahedral symmetry (i.e. where proper *n*-fold ($n \geq 3$) axes of symmetry exist). The X-ray crystal structure analysis of **1** defines overall pentagonal bipyramidal coordination about each Sn(IV) site, comprised of a quasi-planar, equatorial five-coordinate oxo environment coupled with trans, quasi-linear (or axial) coordination of the aliphatic or aromatic substituents. Although no formal axis of rotation perpendicular to this planar oxo environment exists, there must be sufficient uniformity in the deshielding characteristics of this present arrangement to invoke axial character in the ^{119}Sn chemical shift tensor. Given the diversity of the Sn(IV)−O interactions within this oxo environment, with each Sn site within the asymmetric unit being more dominantly influenced by tridendate coordination from bridging O(11) atoms and the O(21) carboxylate oxygen and with weaker contributions exerted by the ethereal O(1) and the water molecule oxygen O(03), some degree of fortuitous symmetry in bond strengths and bond angles is manifested. For complexes **1**−**3** the skew $\kappa = 1$ with δ_{11} and δ_{22} represents the most deshielded components, which thus corresponds to a prolate representation of the ^{119}Sn shift tensor.[40,41,52] Although the crystal structures of complexes **2** and **3** have not been obtained, from these ^{119}Sn CPMAS NMR observations it can be inferred that they are isostructural with complex **1**.

The measured isotropic chemical shifts $\delta_{iso,mas}$ of complexes **1**−**3** increase monotonically from −403.8 ppm (methyl) to −442.0 ppm (*n*-butyl) and −587.9 ppm (phenyl), reflecting the increasing electron withdrawal (or deshielding) capability of the trans-organic substituents. Similar isotropic chemical shifts and behavioral trends with changing substituents have been observed with seven-coordinate tris(tropolonato) systems which feature nonplanar six-coordinate oxo coordination, with $\delta_{iso,mas}$ values of −532 and −585 ppm being reported for $BuSn(trop)_3$ and $PhSn(trop)_3$, respectively.[53] The spans reported for complexes **1**−**3** of up to ~1230 ppm (see Table 2) represent the largest Ω values for Sn(IV) systems with direct oxo coordination,[52−55] but these Ω magnitudes are still much smaller than those reported for monomeric, two-coordinate Sn(II) systems such as $[Sn(X)\text{-}C_6H_3\text{-}2,6\text{-}Trip_2]$,[56] where Ω values can exceed 4000 ppm.

The X-ray crystal structure determination of complex **4** defines a very different binuclear Sn(IV) system with a quasi-one-dimensional polymeric linkage being created essentially by an adjacent $[Et_2SnCl(H_2O)]^+[Et_2SnCl(H_2O)(oda)]^-$ ion pair connected by bridging peripheral carboxylate oxygens. This gives rise to two very distinct Sn(IV) sites, both of which are seven-coordinate and very different from the pentagonal bipyramidal environments described in **1**−**3**. Although X-ray data for compounds **5** and **6** are unavailable, it is concluded from the IR analyses given above that they

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Table 2. ^{119}Sn Isotropic Chemical Shifts and Chemical Shift Tensorial Parameters Measured from the ^{119}Sn CPMAS NMR Spectra of Figures 5 and 6[a]

complex	$\delta_{iso,mas}$ (±2 ppm)	δ_{11}	δ_{22} (±30 ppm)	δ_{33}	$\delta_{iso,calc}$ (±30 ppm)	Ω (ppm)	κ	$\Delta\delta$ (ppm)	η
$[Me_2Sn(oda)(H_2O)]_2$ (**1**)	−403.8	1.2	1.2	−1146. 0	−381. 2	1133. 2	1	−1133 .2	0
$[^{n}Bu_2Sn(oda)(H_2O)]_2$ (**2**)	−442.0	−39.8	−39.8	−1269. 7	−449. 8	1229. 9	1	−1229 .9	0
$[Ph_2Sn(oda)(H_2O)]_2$ (**3**)	−587.9	−324.7	−324.7	−1152. 5	−600. 6	827.8	1	−827. 8	0
$[(^{t}Bu_2SnCl)_2(oda)(H_2O)_2]_n$ (**5**)									
site 1	−229.3	134.8	−68.4	−731.1	−221. 6	865.9	0.53	−764. 2	0.40
site 2	N/D	~125	~125	N/D	N/D	N/D	~1	N/D	~0
$[(^{i}Bu_2SnCl)_2(oda)(H_2O)_2]_n$ (**6**)									
site 1	−391.6	−4.3	−4.3	−1147.1	−385. 1	1142. 8	1	−1142 .8	0
site 2	~−445	~246	~−115	N/D	N/D	N/D	N/D	N/D	N/D

[a] Parameters defining the chemical shift interaction are calculated from the measured chemical shift tensorial elements δ_{11}, δ_{22}, and δ_{33} according to the (IUPAC recommended) conventions: $\delta_{11} > \delta_{22} > \delta_{33}$, isotropic chemical shift $\delta_{iso} = (\delta_{11} + \delta_{22} + \delta_{33})/3$, span $\Omega = (\delta_{11} - \delta_{33})$, skew $\kappa = 3(\delta_{22} - \delta_{iso})/(\delta_{11} - \delta_{33})$, where $1 \geq \kappa \geq -1$. Additional representations: $|\delta_{33} - \delta_{iso}| \geq |\delta_{11} - \delta_{iso}| \geq |\delta_{22} - \delta_{iso}|$, isotropic chemical shift $\delta_{iso} = (\delta_{11} + \delta_{22} + \delta_{33})/3$, anisotropy $\Delta\delta = \delta_{33} - (\delta_{11} + \delta_{22})/2 = 3(\delta_{33} - \delta_{iso})/2$, asymmetry $\eta = (\delta_{22} - \delta_{11})/(\delta_{33} - \delta_{iso})$, where $1 \geq \eta \geq 0$. N/D ≡ not determined.

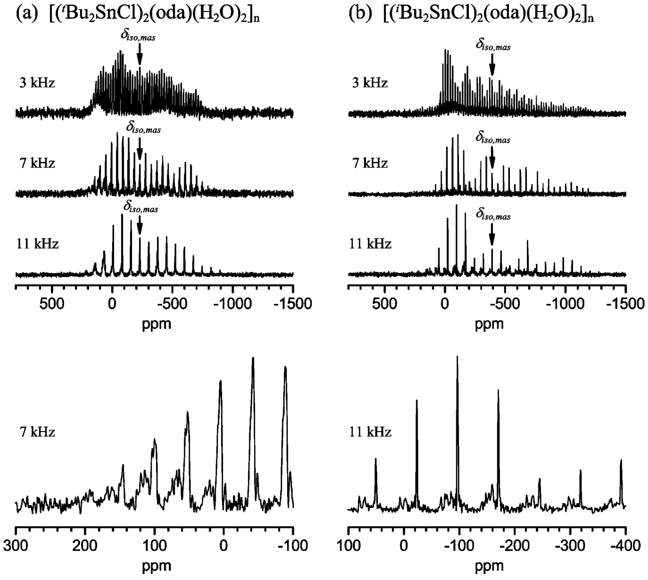

Figure 6. ^{119}Sn CPMAS NMR spectra of (a) $[(^{t}Bu_2SnCl)_2(oda)(H_2O)_2]_n$ (**5**) and (b) $[(^{i}Bu_2SnCl)_2(oda)(H_2O)_2]_n$ (**6**) acquired at MAS frequencies of 3, 7, and 11 kHz. The expansions of the MAS spectra acquired at 7 kHz (for **5**) and 11 kHz (for **6**) show the existence of a second Sn(IV) site which is influenced by $^{1}J(^{119}Sn,^{35/37}Cl)$ coupling.

should have a form similar to **4** even though some different coordination modes may prevail. This conclusion is further corroborated by the ^{119}Sn CPMAS spectra of Figure 6a,b from which it is observed that one Sn site appears more dominant in intensity; an expansion of Figure 6a,b for complexes **5** and **6** shows that $^{1}J(^{119}Sn,^{35/37}Cl)$ fine structure is observed to influence the spinning sideband manifold defining the spans of only one of the two observed ^{119}Sn tensors. For the less intense site $^{1}J(^{119}Sn,^{35/37}Cl)$ coupling observed between these $I = 1/2$ ^{119}Sn nuclei and the $I = 3/2$ $^{35/37}$Cl nuclei constitutes an example of quadrupolar perturbed combined dipolar (direct)/scalar (indirect) coupling. This phenomenon has been treated by many authors[57−62] with particular emphasis being directed toward the Sn−Cl case.[57−60] The residual $^{1}J(^{119}Sn,^{35/37}Cl)$ coupling scheme obtained after MAS is B_o-field dependent and is complicated by the influence of many parameters.[59,61,62] Previous ^{119}Sn CPMAS studies of organotin halides of the form R_3SnX (R = alkyl, aryl; X = Cl, Br) have demonstrated that residual $^{1}J(^{119}Sn,^{35/37}Cl)$ couplings are not always observable, and this has been attributed to fast relaxation of the halogen which thus introduces efficient self-decoupling.[52,60] It is assumed that this halogen relaxation phenomenon is influencing the more intense Sn sites in the polymeric structures of **5** and **6**, facilitating a partial or total collapse of $^{1}J(^{119}Sn,^{35/37}Cl)$ coupling fine structure. Furthermore, differing $^{1}H-^{119}Sn$ cross-polarization efficiencies and ^{1}H T_1's may also hinder the achievement of true quantitation for the site 1 and site 2 sites in each complex.

From Table 2, the more easily observed (self-decoupled) Sn sites of complexes **5** and **6** are denoted as "site 1" in each case, and they afford reliable measurement of all the chemical shift parameters (the labels "site 1" and "site 2" in Table 2 are not to be confused with labels "Sn(1)" and "Sn(2)" generated by the X-ray crystal structure determination, and no direct correlation with them is inferred as there is no basis on which to attempt a formal assignment of these sites). This is verified by the excellent agreement observed between $\delta_{iso,mas}$ and $\delta_{iso,calc}$ for these Sn sites in each polymeric complex. It is of interest to note that the span and the skew for these sites are markedly different; for **6**, Ω is considerably larger (~1143 ppm as compared to ~866 ppm) and κ is 1, suggesting far greater axial symmetry. These differences inply that **5** and **6** may not be strictly isostructural, as suggested by the IR analysis that alludes to possible coordination differences among complexes **4**−**6**. However, this analysis is not conclusive since only incomplete data describing the chemical shift interactions of the $^{1}J(^{119}Sn,^{35/37}Cl)$ coupled sites in **5** and **6** are accessible. A poor signal/noise ratio obtained for the spans of these sites makes the low-field (δ_{11}) and high-field (δ_{33}) edges of the chemical shift tensor difficult to locate with accuracy, and $\delta_{iso,mas}$ is not discernible due to the severe spectral overlap with the more intense span of the self-decoupled site.

^{119m}Sn Mössbauer Study. Compounds **1**−**4** and **7** were examined by ^{119m}Sn Mössbauer spectroscopy, and the results are reported in Table 3. Complex **1** shows a well-resolved

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Table 3. ^{119m}Sn Mössbauer Data

complex	$\delta^{a,b}$ (mm s^{-1})	Δ^{b} (mm s^{-1})	$\Gamma\pm^{b,c}$ (mm s^{-1})	A (%)^{d}
[Me$_2$Sn(oda)(H$_2$O)]$_2$ (**1**)	1.43	4.56	0.95	100
[^{n}Bu$_2$Sn(oda)(H$_2$O)]$_2$ (**2**)				
first doublet	1.49	4.63	0.83	50
second doublet	1.30	3.52	0.95	50
[Ph$_2$Sn(oda)(H$_2$O)]$_2$ (**3**)				
first doublet	1.04	4.18	0.80	50
second doublet	1.43	4.22	0.80	50
[(Et$_2$SnCl)$_2$(oda)(H$_2$O)$_2$]$_n$ (**4**)				
first doublet	1.57	4.68	0.90	50
second doublet	1.61	4.50	0.90	50
[Me$_2$Sn(ida)(MeOH)]$_2$ (**7**)	0.93	2.46	0.81	100

[a] With respect to room temperature spectrum of CaSnO$_3$. [b] ±0.01 mm s^{-1}. [c] Full width at half-maximum. [d] Percentage area.

doublet with a Γ± value of 0.95 mm/s that indicates a similar environment in the two tin sites of the dinuclear complex. The quadrupole splitting Δ, 4.56 mm/s, confirms the *trans*-Me$_2$ arrangement; the large value is consistent with a seven-coordination of the Sn(IV) atoms, and it is comparable to that of heptacoordinated [^{n}Bu$_2$Sn{O$_2$CC$_6$H$_3$-2,6(OH)$_2$}$_2$].[63]

Compound **4** shows a slightly asymmetrical doublet with different Γ values; Γ$_1$, 1.03 mm/s, and Γ$_2$, 0.91 mm/s. The spectrum was deconvoluted with two doublets with similar δ, Δ, and Γ parameter values (see Table 3), the Δ values being consistent with seven-coordinate tin atoms. The larger Δ value, 4.68 mm/s, can be assigned to the cationic subunit that shows a distorted pentagonal bipyramidal geometry with Sn−O and Sn−Cl bond distances varying in a wide range; cf. the anionic subunit.

The spectrum of **7** shows a single doublet, and the Γ± value of 0.81 mm/s is characteristic of a single Sn(IV) site. The Δ parameter value is lower than those generally found in *trans*-Me$_2$ six- and seven-coordinated complexes. The discrepancy between Mössbauer and X-ray results can arise from loss of methanol-coordinated molecule which yields compound **8** and also from the possible dissociation of the dimeric complex followed by a subsequent rearrangement around the tin atom. The Δ value, in fact, agrees with TBP or with octahedral distorted geometries.[64]

The spectra of the dinuclear complexes **2** and **3** have been recorded to obtain further information on the structure in the solid state in the absence of X-ray data. These spectra are similar, but the contribution of two doublets is more evident in **2** (Figure 7), indicating the presence of two different tin sites. One doublet (δ$_1$ and Δ$_1$ values 1.49 and 4.63 mm/s, respectively) can be associated with a hepta-coordinated tin atom, as in **1**; the parameters of the second doublet (δ$_2$ and Δ$_2$ values 1.30 and 3.52 mm/s, respectively) address a six-coordinated, *trans*-^{n}Bu$_2$Sn moiety. In **3** the two doublets have similar parameters, and they can be assigned to two slightly different seven-coordinated *trans*-Ph$_2$Sn^{IV} sites although a six-coordinated arrangement cannot be excluded.[64]

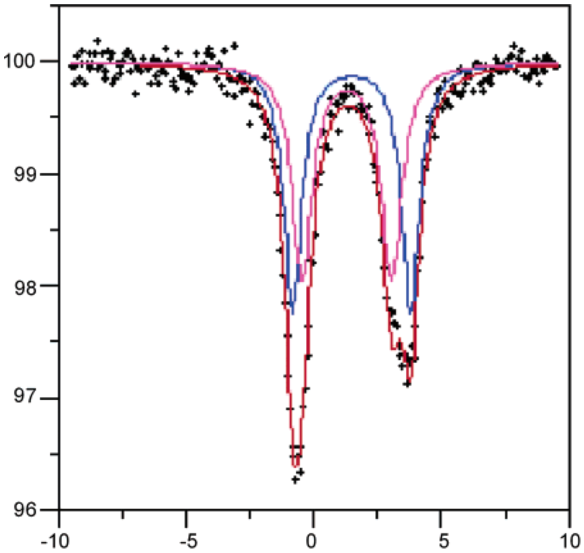

Figure 7. Mössbauer spectrum of [^{n}Bu$_2$Sn(oda)(H$_2$O)]$_2$ (**2**).

Conclusions

In this work we have prepared and characterized, through a variety of techniques, an array of new oxydiacetate derivatives of tin(IV) and, for comparison, an iminodiacetate compound of the same metal. The results reported expand our knowledge of oxydiacetate compounds of p-block metals, a field hitherto poorly developed, particularly from a structural perspective, in contrast to the abundant structural information available for transition metal oxydiacetate complexes. It is of interest that different kinds of compounds may be obtained depending on the nature of the R group bonded to tin(IV), no [(R$_2$SnCl)$_2$(oda)(H$_2$O)$_2$]$_n$ resulting when R = Me, Ph, or ^{n}Bu (**1**−**3**) or [R$_2$Sn(oda)(H$_2$O)]$_2$ when R = Et, ^{i}Bu, or ^{t}Bu (**4**−**6**) respectively, presumably due to a combination of different factors such as the electronic and steric properties of R and crystal packing forces.

Detailed study by way of a number of spectroscopic techniques such as ^{119m}Sn Mossbauer, ^{119}Sn CPMAS NMR, and ^{119}Sn NMR (solution) are useful in the assignment of structures to tin(IV) species when single-crystal X-ray studies are not accessible: ^{119m}Sn Mössbauer data confirm seven-coordinated tin sites in the complexes **1**, **3**, and **4**, while in complex **2** two different *trans*-R$_2$Sn^{IV} geometries are suggested, one with a seven-coordinated tin atom, as in **1**, and the other with an octahedral *trans*-^{n}Bu$_2$Sn moiety. The Mössbauer results of compound **7** are indicative of a six- or five-coordinated distorted geometry arising by the loss of the methanol-coordinated molecule, the Δ parameters value suggesting a remarkable deviation of the C−Sn−C bond from the linearity.

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Supporting Information Available: An X-ray crystallographic file in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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