plotted in Figure 1 vs. pK_{a_2} (F) and $pK_{a_1} + pK_{a_2}$ (F'). As in the isophthalate case, no correlation with the other data is found. The enhanced stability for log β_{101} over that expected from the pK_{a_2} value ($\Delta \log \beta_{101} \approx 0.6$) was attributed to an increased negative charge of the binding carboxylate as a result of transmission of electron density through the ligand π system from the unbonded carboxylate group. Similar charge transmission in the isophthalate ligand would account for its enhanced bonding ($\Delta \log \beta_{101} \approx 0.5$).

It is noteworthy that SmF^+ and $Sn(iP)^+$ have the same value of log β_{101}. Moreover, this value corresponds to a pK_a of ca. 5.5 for the correlation fit. This value also corresponds to the upper limit observed for pK_a values of monocarboxylic acids, both aliphatic and aromatic.[11,12] A simple explanation is that the saturation negative charge density for carboxylate groups correlates with a value of pK_a slightly greater than 5. Therefore, the amount of charge transmitted to the binding carboxylate in the fumarate and the isophthalate complexes is limited by this saturation value, leading to similar stability constants in both cases.

If the increased binding of lanthanides to isophthalate (relative to benzoate) is due to polarization of electronic charge density to the binding carboxylate, the hydration of the unbonded carboxylate should decrease. This would result in an increased positive entropy, in accord with the experimental values (e.g., ΔS_{101} = 68 J/(mol K) for SmB^{2+} and 90 J/(mol K) for $Sm(iP)^+$). It would also cause the enthalpy change for the isophthalate to be more endothermic, which is also observed.

In summary, the thermodynamic parameters for lanthanide benzoate complexation are similar to those measured for analogous alkyl monocarboxylates. The stability constants fit the correlation with pK_a of the alkyl ligand, indicating no effect due to the phenyl ring. However, the isophthalate complexes are stronger than expected, which can be explained by an increase in the electronic charge density at the binding carboxylate. This increased charge transmitted via the π system from the nonbonding carboxylate results in a decrease of hydration, which increases (positively) both the entropy and enthalpy of complexation when compared to the case for the benzoate complexation.

Acknowledgment. This research was supported by the U.S. DOE. P.A.B. acknowledges an NSF Predoctoral Fellowship.

(10) G. R. Choppin, A. Dadgar, and R. Stampfli, *J. Inorg. Nucl. Chem.*, **35**, 875 (1973).
(11) H. C. Brown, D. H. McDaniel, and O. Haflinger, "Determination of Organic Structures by Physical Methods", E. A. Brande and F. C. Nachod, Eds., Academic Press, New York, 1955, Chapter 14.
(12) "CRC Handbook of Chemistry and Physics", Chemical Rubber Publishing Co., Cleveland, OH, 1976.

Contribution from the Department of Chemistry and Institute for Materials Research, McMaster University, Hamilton, Ontario, Canada L8S 4M1

Preparation and Characterization of Mixed-Oxidation-State Tin Carboxylates and Related Tin(IV) Carboxylates

THOMAS BIRCHALL* and JAMES P. JOHNSON

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The solvolysis of hexaphenylditin by carboxylic acids leads to the formation of compounds with empirical formula $Sn(O_2CR)_3$. ^{119}Sn Mössbauer spectroscopy shows that these compounds contain tin in both the II and IV oxidation states. The Mössbauer data taken together with the vibrational data, IR and Raman, lead to the conclusion that these compounds are best formulated as $[Sn^{II}Sn^{IV}O(O_2CR)_4O(OCR)_2]_2$. The four tin atom cluster is held together by two μ_3-oxo bridges and bridging acetato ligands, which result in the Sn(IV) atoms being in octahedral environments, while the Sn(II) atoms have pentagonal-bipyramidal geometry in which the μ_3-oxo bridge occupies one axial position and the Sn(II) nonbonding electron pair the other axial position. The equatorial positions accommodate four acetato oxygens and an anhydride oxygen atom. ^{119}Sn Mössbauer data for $Sn(O_2CR)_4$ are also presented for the first time.

Introduction

It is well-known that the solvolysis of tetraalkyltin(IV) compounds in acidic solvents leads to the successive loss of alkyl groups to produce first trialkyltin(IV) and finally dialkyltin(IV) species. These have been characterized by a variety of techniques.[1-4] Similar products can be obtained from the solvolysis of hexamethylditin through cleavage of the tin–tin bond. However, by careful control of the reaction conditions the tin–tin bond can be retained and tetramethylditin(IV) compounds can be isolated.[4] Solvolysis of hexaphenylditin might have been expected to lead to analogous products since tetraphenylditin dicarboxylates are known.[5] Reaction of hexaphenylditin with acetic acid results in the cleavage of all of the tin–carbon bonds to give a compound formulated as $Sn_2(O_2CCH_3)_6$.[6] It was suggested that this compound was a ditin species in which the tin–tin bond was stabilized by bridging acetato ligands. However, little spectroscopic evidence was presented to support this contention, which was based upon the consumption of 1 mol of bromine to give $BrSn(O_2CCH_3)_3$. This latter reaction is normally taken as evidence for the presence of a tin–tin bond.

We have repeated this solvolysis of hexaphenylditin using seven different carboxylic acids, and in all cases we have been able to isolate compounds with the empirical formula $Sn(O_2CR)_3$. The acetato compound (R = CH_3) appears to be identical with that of $Sn_2(O_2CCH_3)_6$ reported earlier by Wiberg and Behringer.[6] However, ^{119}Sn Mössbauer spectroscopic results presented in this paper clearly establish that these compounds contain tin atoms in both the II and the IV oxidation states and should be formulated as mixed-oxidation-state compounds of tin rather than as ditin species. Raman and infrared spectroscopic data are also presented, which, taken with the Mössbauer evidence, establish that these compounds have structures very similar to two previously reported mixed-oxidation-state tin carboxylates.[7,8] We also

(1) Yeats, P. A.; Ford, B. F. E.; Sams, J. R.; Aubke, F. *J. Chem. Soc., Chem. Commun.* **1969**, 791.
(2) Levchuk, L. E.; Sams, J. R.; Aubke, F. *Inorg. Chem.* **1972**, *11*, 2634.
(3) Birchall, T.; Chan, P. K. H.; Pereira, A. *J. Chem. Soc., Dalton Trans.* **1974**, 2157.
(4) Birchall, T.; Johnson, J. P. *Can. J. Chem.* **1979**, *57*, 160.
(5) Plazzogna, G.; Peruzzo, V.; Tagliavini, G.; *J. Organomet. Chem.* **1970**, *24*, 667.
(6) Wiberg, E.; Behringer, H. *Z. Anorg. Allg. Chem.* **1964**, *329*, 290.
(7) Ewings, P. F. R.; Harrison, P. G.; Morris, A.; King, T. J. *J. Chem. Soc., Dalton Trans.* **1976**, 1602.

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report ^{119}Sn Mössbauer data for some new tin(IV) carboxylates.

Experimental Section

1. Chemicals. Hexaphenylditin was obtained from Ventron Corp. and was used after recrystallization from benzene. The carboxylic acids and anhydrides were commerical products of reagent or analytical grade and were used without further purification. Preparations were carried out in an all-glass apparatus after the design of Dean et al.[9] All preparations were carried out under anhydrous conditions with the necessary transfer of materials being carrier out in a dry nitrogen atmosphere glovebox.

2. Preparations. Mixed-Oxidation-State Tin Carboxylates $Sn(O_2CR)_3$. (i) R = CF_3. To one side of a two-bulb reaction vessel was added 6.785 g (9.692 mmol) of hexaphenylditin and the system evacuated on a vacuum line. A mixture of 30 mL (46 mmol) of trifluoroacetic acid and 5 mL of trifluoroacetic anhydride, which had been vacuum condensed into a storage vessel and stirred at ambient temperature for 1 day, was condensed into the other side of the vessel; the reactants were then mixed, and the white suspension was stirred at ambient temperature for 2 days, during which time the solvent turned pale yellow. A white, talc-like powder was removed from the yellow solvent by filtration. The solvent was recondensed onto the solid, and the process was repeated until no yellow impurities remained. The solvent side of the vessel was sealed, and the white solid was pumped dry overnight. A total of 8.079 g (8.825 mmol) of product was obtained.

(ii) R = CCl_3. Hexaphenylditin, 4.342 g (6.203 mmol), was added to one side of a two-bulb reaction vessel. Trichloroacetic acid, 19.48 g (119.2 mmol), which had been dried over P_4O_{10} for 6 h, was added to the opposite side of the vessel, and the vessel was evacuated. Dry benzene (9.5 mL) was condensed onto the acid. The acid–benzene mixture was poured onto the hexaphenylitin, and the suspension was stirred for 3 days. The solvent was removed by filtration and condensed back onto the white solid, and some dry liquid SO_2, 1–2 mL, was then added to aid filtration. After repeated filtrations, the solvent side of the vessel was sealed and the white solid was pumped dry on a vacuum line. A total of 7.183 g (5.923 mmol) of product was obtained.

(iii) R = $CHCl_2$. Hexaphenylditin, 1.745 g (2.493 mmol), was added to a reaction bulb attached to a U-trap. Excess $CHCl_2COOH$ (10 mL, 120 mmol) was added to the trap, degassed on a vacuum line, and decanted onto the solid. The mixture was stirred for 5 days, during which time all of the solid dissolved. The benzene produced was removed under vacuum, and the excess acid was condensed into the U-trap, which was cooled in liquid nitrogen. The connection between the bulb and the U-trap was sealed, and the white solid was further dried on a vacuum line. The yield was 1.50 g (1.49 mmol).

(iv) R = CH_2Cl. Hexaphenylditin, 2.465 g, (3.521 mmol), was reacted with an excess of $CH_2ClCOOH$, 8.97 g (94.9 mmol) at 80 °C in a sealed two-bulb reaction vessel as in the previous cases. Dissolution was complete after 1 h, and the mixture was maintained at 80 °C for 48 h, after which the benzene produced was condensed into the other bulb, cooled in liquid nitrogen, and the connection between the two bulbs sealed. The excess acid was removed from the white solid by repeated high-vacuum sublimation at 40 °C using a dry ice–acetone cold finger. The yield was not recorded but was sufficient to completely characterize the compound.

(v) R = CH_3. This compound was prepared by the reaction of hexaphenylditin, 6.754 g (9.648 mmol), with acetic acid (25 mL, 360 mmol) in the presence of acetic anhydride (5 mL, 53 mmol), as for the CF_3 derivative. Since no reaction occurred at room temperature, the mixture was heated to 100 °C for 40 h, during which time all of the solid dissolved. When the solution cooled to room temperature, a wet, spongelike material was produced. The solvent was removed under vacuum to give 5.71 g (9.65 mmol) of a white fibrous solid.

(vi) R = $CF_2CF_2CF_3$. Hexaphenylditin, 2.560 g (3.658 mmol), was added to one side of a two-bulb vessel that did not contain a glass frit. Excess $CF_3(CF_2)_2COOH$ (20 mL, 140 mmol) was added to the other bulb, degassed on a vacuum line, and then poured onto the solid. All of the solid dissolved to give a clear liquid after 48 h of stirring the mixture. The excess acid solvent was then condensed under vacuum to the opposite bulb, which was cooled in a liquid-nitrogen bath. The glass connection between the two bulbs was sealed, and the white fibrous solid was pumped dry overnight. The yield was 3.88 g (2.56 mmol).

(vii) R = $C(CH_3)_3$. Hexaphenylditin, 3.387 g (4.838 mmol), and excess $(CH_3)_3CCOOH$ (20 mL, 180 mmol) were added to opposite sides of a two-bulb reaction vessel that did not contain a glass frit. The system was evacuated, sealed, and heated to 100 °C, and the reagents were mixed. All of the solid has dissolved after 8 h, and the mixture was maintained at this temperature overnight, after which the bulk of the solvent was condensed into the opposite bulb, which was then sealed. The residual acid was then removed under high vacuum, to produce a white flaky solid. The yield was 3.20 g (3.79 mmol).

Tin(IV) Carboxylates. Tetrakis(trifluoroacetato)tin(IV) was prepared as follows. To one side of a Dean-type reaction vessel was added 1.775 g (4.153 mmol) of tetraphenyltin. To other other side of this vessel were added 20 g (175 mmol) of CF_3COOH and 1 cm^3 of $(CF_3CO)_2O$, which were then degassed. The liquid mixture was poured onto the tetraphenyltin and stirred for 10 h, during which time almost all of the solid had dissolved and the solution was a straw-yellow color. The excess acid was removed under vacuum, leaving a white solid contaminated by a yellow impurity. Dry SO_2 was condensed onto the solid and the mixture stirred, concentrated to 5 cm^3, and filtered. This procedure was repeated three times to yield pure $Sn(O_2CCF_3)_4$ in 76.3% yield based on tetraphenyltin; mp 115–116 °C. (Anal. Calcd: Sn, 20.80; acid ligand, 79.20. Found: Sn, 20.50; acid ligand, 79.33.)

A similar procedure was adopted for the other $Sn(O_2CR)_4$ compounds, but only for R = CF_3 was it possible to remove completely all of the excess acid. These products ranged in appearance from a red oil (R = CCl_3) through a tan-colored viscous liquid (R = $CHCl_2$) and a tan-colored solid (R = CH_2Cl) to a white solid for R = CF_3.

Analytical data and melting points for the tin compounds are presented in Table I. C, H, and halogen analyses were performed by Swarzkopf Microanalytical Laboratory Inc., Woodside, NY 11377; tin analyses and analyses for total acid ligand were carried out by standard procedures.[10]

3. Instrumentation. Spectroscopic measurements were carried out on equipment that has already been described.[4] The ^{119}Sn Mössbauer isomer shifts were measured against a $CaSnO_3$ absorber maintained at room temperature. The source, $Ca^{119m}SnO_3$, was obtained from New England Nuclear and was maintained at room temperature throughout. Mössbauer spectra were computer fitted with use of the program written by Stone[11] and subsequently modified by Dr. D. H. Grundy of the Department of Geology, McMaster University.

Results

1. Physical Characteristics. Carboxylic acids react quantitatively with hexaphenylditin to cleave all of the carbon–tin bonds according to

$$x(C_6H_5)_6Sn_2 + 6xRCO_2H \rightarrow [Sn_2(O_2CR)_6]_x + 6xC_6H_6$$

no other products being detected. When R = CH_3, the product appears to be identical with that reported earlier by Wiberg and Behringer,[6] namely, $Sn_2(O_2CCH_3)_6$. Their compound reacted stoichiometrically with an equivalent amount of bromine according to

$$Sn_2(O_2CCH_3)_6 + Br_2 \rightarrow 2BrSn(O_2CCH_3)_3$$

On this basis they proposed that the original compound contained a tin–tin bond.

All of these compounds are colorless, fibrous solids with high melting or decomposition temperatures (Table I). These temperatures are much higher than those of either of the corresponding tin(II) or tin(IV) carboxylates. Except when R = CF_3 or CCl_3 the compounds are soluble in the parent acid without change. The trifluoro- and trichloroacetates are only slightly soluble in benzene. In contrast $Sn(O_2CCF_3)_4$ and

(8) Birchall, T.; Johnson, J. P. *J. Chem. Soc., Dalton Trans.* **1981**, 69.
(9) Dean, P. A. W.; Gillespie, R. J.; Ummat, P. K. *Inorg. Synth.* **1974**, *15*, 213.
(10) Vogel, A. I. "A Text-Book of Quantitative Inorganic Analysis", 3rd ed.; Longmans, Green and Co.: London, 1961.
(11) Bancroft, G. M.; Ong. W. K.; Maddock, A. F.; Prince, R. K.; Stone, A. J. *J. Chem. Soc. A* **1967**, 1966.

Table I. Analytical Data for Mixed-Oxidation-State Tin Carboxylates $[Sn^{II}Sn^{IV}O(O_2CR)_4O(OCR)_2]_2$

R		% Sn	% C	% H	% halogen	% acid ligand (O_2CR)	mp, °C	% yield[a]
CF_3	calcd	25.93	15.74	0.0	37.34	74.07		100
	found	26.54	15.75	0.09	36.49	73.84	184–186.5	
		26.35	15.80	0.06	36.44			
C_3F_7	calcd	15.66	19.02	0.0	52.66	84.34		70.0
	found	15.50	18.97	0.15	49.12	83.78	118 dec	
						83.41		
CCl_3	calcd	19.59	11.89	0.0	52.66	80.41		95.6
	found	19.13	11.90	0.19	48.37	79.78	155–156	
		19.09				80.71		
$CHCl_2$	calcd	23.62	14.34	0.60		76.38		59.6
	found	25.10	13.64	0.69		76.51	117 dec	
CH_2Cl	calcd	29.74	18.05	1.52		70.27		
	found	30.11	17.52	1.64		74.56	135 dec	
CH_3	calcd	40.12	24.36	3.06		59.88		100
	found	39.52	24.43	3.30		58.61	310 dec	
			24.39	3.13				
C_4H_9	calcd	28.12	42.60	6.45		71.88		81.3
	found	28.80	43.03	6.51		72.89	184 dec	

[a] Percent yield is based on the $(C_6H_5)_6Sn_2$ used in the preparation.

Table II. Mössbauer Data for Some Mixed-Oxidation-State Tin Carboxylates and Related Tin(II) and Tin(IV) Carboxylates

compd	temp, K	parameters, mm s^{-1} δ	Δ	Γ	rel area Sn(IV)/Sn(II)	χ^2/deg of freedom
$[Sn_2(O_2CCF_3)_6]_2$[a]	77	−0.03	0.52	0.81	1.16	1.01
		3.94	1.11	0.85		
	4	−0.02	0.52		0.91	1.15
		3.93	1.20			
$Sn(O_2CCF_3)_4$	77	−0.04	1.56	0.95		0.91
$Sn(O_2CCF_3)_2$[12]	77	3.16	1.76			
$[Sn_2(O_2CC_3F_7)_6]_2$[a]	77	−0.03	...	0.96	1.13	1.08
		3.88	1.14	0.84		
$Sn(O_2CC_3F_7)_4$	77	0.03	1.27	0.97		1.00
$[Sn_2(O_2CCCl_3)_6]$[a]	77	−0.01	...	0.97	1.22	1.24
		3.98	1.05	0.95		
$Sn(O_2CCCl_3)_4$	77	0.15	0.91	0.96		1.04
$Sn(O_2CCCl_3)_2$[12]	77	3.29	1.78			
$[Sn_2(O_2CCHCl_2)_6]_2$[a]	77	0.07	0.54	0.95	1.31	1.23
		3.80	1.81	1.09		
$Sn(O_2CCHCl_2)_4$	77	−0.01	0.79	1.04		0.96
$Sn(O_2CCHCl_2)_2$[12]	77	3.48	1.64			
$[Sn_2(O_2CCH_2Cl)_6]_2$[a]	77	0.13	0.79	0.98	1.25	1.17
		3.56	1.71	1.11		
$Sn(O_2CCH_2Cl)_4$	77	0.29	0.55	1.13		1.17
$Sn(O_2CCH_2Cl)_2$[12]	77	3.10	1.66			
$[Sn_2(O_2CCH_3)_6]_2$[a]	77	0.14	0.47	0.90	0.68	1.06
		3.48	1.83	0.85		
	4	0.20	0.45	0.89	0.75	0.97
		3.49	1.83	0.91		
$Sn(O_2CCH_3)_4$[13]	77	0.08	...	1.45		
$Sn(O_2CCH_3)_2$[12]	77	3.31	1.77			
$[Sn_2(O_2CC(CH_3)_3)_6]_2$[a]	77	0.18	0.50	0.83	0.74	1.12
		3.32	2.20	0.83		
$Sn_2(O_2CC(CH_3)_3)_2$[12]	77	3.25	1.88			

[a] $[Sn_2(O_2CR)_6]_2$ is a simplification of the formula $[Sn^{II}Sn^{IV}O(O_2CR)_4O(OCR)_2]_2$.

$Sn(O_2CCCl_3)_4$ are very soluble in benzene and all of the pure $Sn(O_2CR)_2$ and $Sn(O_2CR)_4$ compounds are very soluble in their parent acids. These few physical properties suggest that the $[Sn_2(O_2CR)_6]_x$ compounds are not simple mixtures of the tin(II) and tin(IV) carboxylates, and the spectroscopic evidence presented below confirms this suggestion.

2. ^{119}Sn Mössbauer Data. All of the ^{119}Sn Mössbauer data are summarized in Table II: the data for the $Sn(O_2CR)_2$ series are from the literature,[12] as are those for $Sn(O_2CCH_3)_4$,[13] but the other $Sn(O_2CR)_4$ data are reported here for the first time. None of the compounds examined showed any significant resonance absorption at room temperature, but good spectra were obtained at 77 K. A spectrum of $[Sn_2(O_2CCH_3)_6]_x$, recorded at liquid-nitrogen temperature, is shown in Figure

(12) Donaldson, J. D.; Jelen, A. *J. Chem. Soc. A* **1968**, 1448.
(13) Batchelor, R. J.; Ruddick, J. N. R.; Sams, J. R.; Aubke, F. *Inorg. Chem.* **1977**, *16*, 1414.

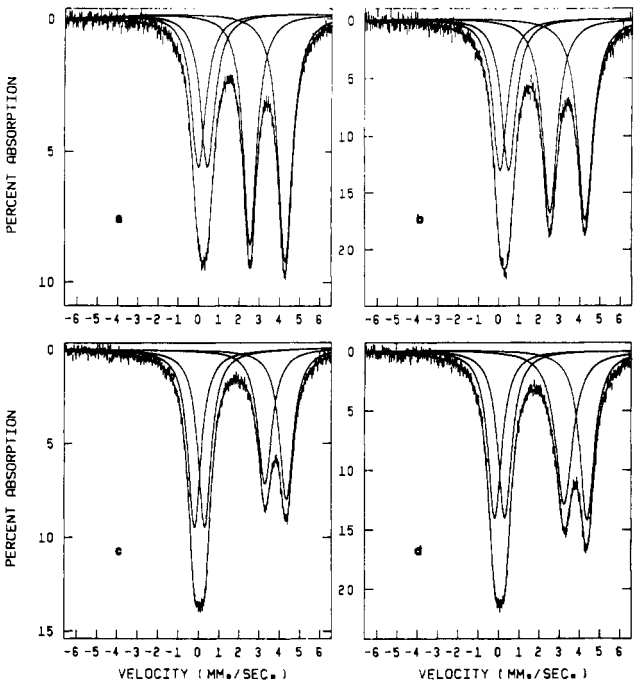

Figure 1. ^{119}Sn Mössbauer spectra of $[Sn^{II}Sn^{IV}O(O_2CCH_3)_4O(OCCH_3)_2]_2$ at (a) 77 K and (b) 4 K and of $[Sn^{II}Sn^{IV}O(O_2CCF_3)_4O(OCCF_3)_2]_2$ at (c) 77 K and (d) 4 K.

1a. This spectrum clearly establishes that there is more than one kind of tin environment in the compound. The only significant change that occurs on cooling the sample to 4 K is that the absorption at ~0 mm s^{-1} increases in intensity relative to the two absorptions at higher velocity (Figure 1b). All of the other compounds in this $[Sn_2(O_2CR)_6]_x$ series give similar spectra with three absorption peaks, the positions and relative intensities of which vary as the substituent R or the temperature is changed.

It is extremely unlikely, on the basis of what is known for other tin carboxylate systems, that these spectra could arise from compounds containing three different tin nuclei all in near-cubic environments. While $Sn(O_2CR)_2$ compounds do have isomer shift values of ~3 mm s^{-1}, they also have quadrupole splittings of ~1.7 mm s^{-1}.[12] The only Sn(II) compounds known to have isomer shifts of ~4.5 mm s^{-1} and zero quadrupole splittings are $Sn(SbF_6)_2$,[14] the Sn(II) in $Sn_2(O_3SCF_3)_6$,[13] and Sn(II) when complexed with the crown ether 15-crown-5.[15] The relative areas of the individual absorptions and their temperature dependencies rule out the possibility that these spectra are composed of two doublets with their low-velocity components nearly coincident. The only realistic assignment is that the absorption at ~0 mm s^{-1} is due to a Sn(IV) species in a near-cubic environment, with the other two absorptions being a quadrupole doublet from a Sn(II) species in a distorted environment.

It is clear (Table II) that the compounds containing both Sn(II) and Sn(IV) can not be simple mixtures of the corresponding $Sn(O_2CR)_2$ and $Sn(O_2CR)_4$ compounds. This confirms the conclusion reached earlier from the physical properties of the compounds.

The Mössbauer isomer shifts for the Sn(II) sites in these mixed-oxidation-state compounds range from 3.98 to 3.32 mm s^{-1} with quadrupole splittings of 1.02–2.20 mm s^{-1}. A plot of isomer shift against quadrupole splitting in this series results in a good correlation (Figure 2) with only the $-CHCl_2$ compound deviating significantly from the least-squares line. This deviation could be because the $-CHCl_2$ compound contained a small amount of a Sn(II) impurity, which resulted in the Sn(II) region of the spectrum being less well resolved than in the other cases. In this regard it should also be noted that the analytical data for this compound deviate somewhat from the theoretical values. These systematic changes (Table II and Figure 2) correlate with the electronegatitivities of the substituent R. As R becomes more electronegative, then the isomer shift associated with the Sn(II) becomes more positive; i.e., the s-electron density on the tin increases. At the same time the tin(II) environment becomes more symmetric since the quadrupole splitting decreases. There are other series of tin(II) compounds for which correlations of this kind exist such as $[SnX_3]^-$, where X can be a halide or another anion[12] and where the compounds in the series have the same structure. This is no reason to expect such a correlation if the compounds are not structurally related. On the basis of the systematic changes that are observed in the Mössbauer parameters, we conclude that the geometry about the tinII) in these compounds is basically the same.

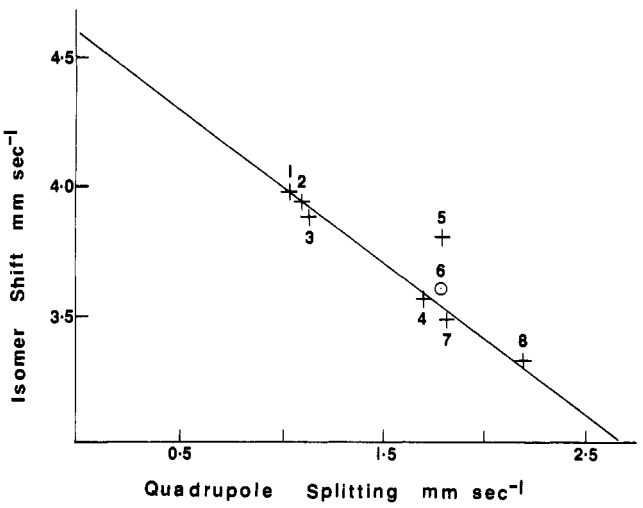

Figure 2. Plot of the isomer shift of the Sn(II) site vs. the quadrupole splitting of this site for the series $[Sn^{II}Sn^{IV}O(O_2CR)_4O(OCR)_2]_2$: 1, R = CCl_3; 2, R = CF_3; 3, R= C_3F_7; 4, R = CH_2Cl; 5, R = $CHCl_2$; 6, R = (*o*-NO_2)C_6H_4; 7, R = CH_3; 8, R = $C(CH_3)_3$.

The Mössbauer parameters for the simple $Sn(O_2CR)_2$ compounds vary over a much smaller range (δ, 3.48–3.10 mm s^{-1}; Δ, 1.88–1.64 mm s^{-1}) and are not correlated in any obvious way. It has been supposed that these compounds all have the Sn(II) in a trigonal-pyramidal arrangement,[16] but a recent X-ray structure of $Sn(O_2CH)_2$ indicates that the tin(II) in this compound is in a rather distorted trigonal-bipyramidal environment. Perhaps, when other structures have been determined, it will be shown that there are a variety of different coordination environments for the tin atom in these bis(carboxylates). In any case since the Mössbauer parameters for any particular $Sn(O_2CR)_2$ are quite different from those of the Sn(II) site in the corresponding mixed-oxidation-state compound, it is reasonable to infer that the coordination about the Sn(II) in the latter series will also be different.

Harrison and co-workers[7] have reported the structure of a mixed-oxidation-state compound of tin in which the acid ligand is *o*-nitrobenzoate. The geometry about the Sn(II) in their compound is that of a pentagonal bipyramid with the nonbonding electron pair occupying one of the axial positions, the other axial site being occupied by an oxygen atom that forms a μ_3 bridge between the Sn(II) and two Sn(IV) atoms. In the equatorial plane there are four oxygens from the benzoate

(14) Birchall, T.; Dean, P. A. W.; Gillespie, R. J. *J. Chem. Soc. A* **1971**, 1777.

(15) Herber, R. H.; Carrosquillo, G. *Inorg. Chem.* **1981**, *20*, 3693.

(16) Alcock, N. W.; Tracy, V. L. *Acta Crystallogr., Sect. B* **1979**, *B35*, 80.

Table III. Infrared and Raman Data for $Sn(O_2CCF_3)_4$ and the Mixed-Oxidation-State Carboxylates of Tin ($[Sn^{II}Sn^{IV}O(O_2CR)_4O(OCR)_2]_2$)[a]

$Sn(O_2CCF_3)_4$		R										
		CF_3		C_3F	CCl_3		$CHCl_2$	CH_2Cl	CH_3		C_4H_9	
IR	Raman	IR	Raman	IR	IR	Raman	IR	IR	IR	Raman	IR	assignt
							3020 (w)		3000 (w)	3015 (24)	2970 (m)	
							2990 (w)			3001 (27)		
										2952 (100)	2930 (w)	
									2920 (w)	2936 (92)	2880 (w)	ν(C–H)
										2731 (1)	2720 (w)	
							2220 (w, b)	2200 (m, b)			2200 (w)	
							2100 (w, b)	2060 (m, b)			2100 (w)	
1760 (s)	1763 (37)	1765 (s)	1764 (25)	1755 (s)	1740 (s)	1733 (32)	1745 (m)	1720 (w, sh)			1705 (w)	
1670 (s, sh)		1720 (m, sh)	1720 (22)	1690 (s)	1712 (w)	1709 (17)						
		1680 (s)		1660 (s)	1675 (m, sh)	1622 (32)	1640 (s)	1625 (s)		1638 (1)		
					1655 (s, sh)							
		1650 (s)	1629 (42)	1610 (s, b)	1650 (s)	1607 (19)			1590 (m, sh)	1594 (4)	1610 (vs)	$\nu_{as}(CO_2)$, (C=O)
					1605 (s)							
1600 (s)		1615 (s)	1616 (33)									
	1580 (17)	1575 (s)	1575 (4)				1560 (m, sh)			1536 (14)	1565 (s)	
								1520 (s)	1520 (s)	1517 (12)	1500 (sh)	
1490 (m)	1503 (43)	1480 (m)	1482 (52)							1475 (14)	1485 (vs)	
		1463 (s)	1466 (15)								1460 (m)	
		1450 (s)	1449 (11)						1435 (sh)	1433 (10)		
		1433 (s)	1433 (8)	1415 (s)		1395 (11)	1400 (sh)	1420 (m, sh)	1400 (s)	1401 (16)	1405 (s)	$\nu_s(CO_2)$, ν(C–O–C)
1365 (s)	1370 (20)	1370 (s)	1368 (10)		1365 (s)		1360 (s)	1380 (s)				
				1340 (s)	1350 (s)			1315 (m, sh)	1350 (m, sh)	1358 (6)	1360 (vs)	
									1334 (m, sh)	1335 (7)		
					1255 (m)		1225 (m)	1240 (s)	1047 (w)		1215 (vs)	
					1245 (w, sh)		1210 (m)		1012 (m)		1030 (w)	δ(C–H), $\nu_s(CO_2)$, ν(C–O–C)
							1195 (m)					
				1270 (s, sh)								
1240 (s, sh)		1220 (s)	1227 (5)	1215 (s)								
1180 (vs)		1190 (s)	1180 (6)	1180 (s)	850 (s)	855 (21)	825 (m)					$\nu_{as}(CX_3,CX_2)$, $\nu_s(CX_3,CX_2)$
		1150 (s)	1153 (2)	1150 (s)	830 (s)	830 (25)	815 (m)				795 (m)	
		1130 (s)		1120 (s)	825 (w, sh)		795 (w)				780 (m)	
				1080 (s)			780 (w)	790 (s)				ν(C–Cl)
985 (m)				965 (s)	970 (w, sh)				965 (w)	975 (91)		
830 (m)					965 (w)	968 (13)						
				925 (s)	952 (w)	951 (8)	950 (m)	925 (s)	930 (w)	937 (67)	925 (s)	
870 (w)	876 (29)	869 (w)	865 (100)								895 (w)	$\delta(CO_2)$, ν(C–C)
850 (m)	846 (23)	855 (m)										
830 (w, sh)		850 (m)	848 (35)	810 (s)								
		840 (m)										
780 (m)		789 (m)						790 (s)			820 (m)	
		785 (m)	782 (2)								780 (m)	
		778 (m)		755 (m)	749 (s)	761 (53)					745 (m)	
					740 (m, sh)	743 (74)						
				735 (s)			730 (w)			726 (7)		
							715 (m)					
				710 (s)			705 (m)	700 (s)	705 (m)			$\nu(CO_2)$, ν(Sn–O–Sn)
					680 (s)	680 (15)	680 (s)	680 (s)		670 (w)		
									657 (m)			
									625 (w)	627 (3)		
										620 (8)		
									610 (w)	610 (2)	610 (vs)	

730 (s)	730 (9)	729 (s)	726 (8)											
655 (w, sh)	643 (100)							620 (w)	620 (w)					
635 (m, sh)	540 (43)	701 (s)	715 (3)					600 (w)						
620 (m)	500 (17)							550 (m)						
550 (w)	435 (29)	629 (m)	635 (36)	645 (m)										
520 (w)		619 (m)		600 (m)					565 (vs)					
		585 (m)			565 (w)	567 (15)						570 (vs)		
				550 (m)	550 (w)							550 (vs)		ν(Sn–O)
		525 (m)	531 (15)									535 (vs)		CX_3 bend
			514 (22)	520 (m)										
		500 (w)	492 (9)					495 (vs)		430 (m)	485 (22)			CO_2 bend
		452 (w)	453 (12)	475 (w)										
		432 (w)	438 (6)										430 (w)	
			424 (8)											
	313 (51)		331 (39)			384 (32)					333 (15)			
	270 (9)		289 (6)			296 (64)					300 (54)			
	190 (26)		263 (13)			278 (100)					271 (29)			
	148 (37)		237 (13)											
	135 (20)		219 (27)											
	105 (9)		189 (23)											

[a] Abbreviations: vs = very strong, s = strong, m = medium, w = weak, sh = shoulder, b = broad. Intensities are given in parentheses for Raman bands.

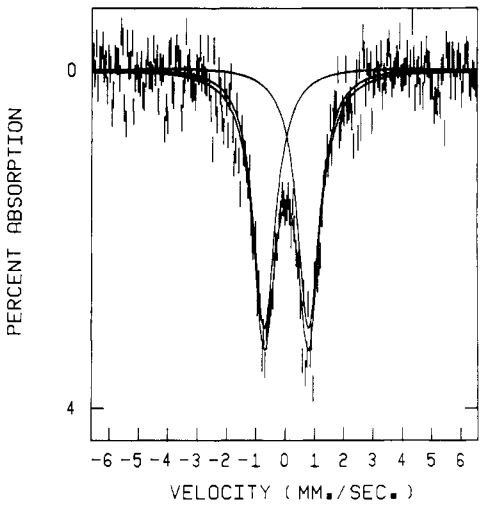

Figure 3. ^{119}Sn Mössbauer spectrum of $Sn(O_2CCF_3)_4$ at 77 K.

ligands and a fifth from a molecule of tetrahydrofuran. The Mössbauer parameters reported for this compound correlate reasonably well with our results shown in Figure 2, suggesting a similarity in the environments of the tin(II) atoms. We have recently reported the structure of a compound of composition $[Sn^{II}Sn^{IV}O(O_2CCF_3)_4]_2 \cdot C_6H_6$.[8] This compound has a structure that is very similar to that of Harrison's, being a tetramer of tin atoms, two Sn(II) and two Sn(IV), held together by two μ_3-oxo bridges and bridging trifluoroacetato groups. The tin(II) environment is that of a pentagonal bipyramid with the nonbonded electron pair in an axial position but with one of the equatorial positions vacant. One molecule of benzene is also incorporated into the structure which appears to form a link between the clusters. The Mössbauer parameters for this compound are indistinguishable from those of the mixed-oxidation-state compound $[Sn^{II}Sn^{IV}(O_2CCF_3)_6]_x$ reported here, indicating that their structures are closely related.

The isomer shifts of the Sn(IV) in these $[Sn^{II}Sn^{IV}(O_2CR)_6]_x$ compounds behave in the manner expected; i.e., as the electronegativity of the carboxylate ligand increases so the isomer shift becomes more negative. None of the Sn(IV) absorptions show a clearly resolved quadrupole splitting (Figure 1). The splitting values given in Table II are the result of fitting the Sn(IV) absorptions to two lines of equal width and intensity: fitting only one line to this absorption resulted in rather large line widths. This indicates a near-regular environment about the Sn(IV) like those found in the two related structures reported earlier.[7,8]

By contrast the Mössbauer data for the $Sn(O_2CR)_4$ series are quite different from those of the Sn(IV) site in $[Sn^{II}Sn^{IV}(O_2CR)_6]_x$. The isomer shifts do not correlate well with ligand electronegativity, and the quadrupole splittings are in some cases quite large ($Sn(O_2CCF_3)_4$, Δ = 1.56 mm s^{-1}, Figure 3), while in $Sn(O_2CCH_3)_4$ no quadrupole splitting is obvious, though the computed line width in this case is large, suggesting an unresolved splitting. A zero, or small, unresolved quadrupole splitting would be consistent with the known structure of $Sn(O_2CCH_3)_4$, which has been shown to have the tin atom surrounded by four bidentate acetato groups, thus giving it eight-coordination.[17] It is clear that the tin environment in $Sn(O_2CCF_3)_4$ is much more irregular. If only some of the trifluoroacetate groups are bidentate, then the Sn(IV) could be seven- or six-coordinated or possibly even lower. An octahedral structure arising from two monodentate and two bidentate ligands attached to the tin such as has been found for SnF_4[18] and postulated for $Sn(SO_3F)_4$[19] is likely. Seven-

(17) Donaldson, J. D. *Prog. Inorg. Chem.*, **1967**, *8*, 287.

coordination such as has been found for $[Sn^{IV}(O_2CCH_3)_5]^-$, which has a pentagonal–bipyramidal arrangement of oxygens about the tin(IV),[20] is another possibility. Unfortunately, the ^{119}Sn Mössbauer spectrum of this latter compound has not yet been reported, though one might anticipate a resolvable quadrupole splitting for this species. Because of their physical properties and the lack of a significant Mössbauer absorption at room temperature it is unlikely that these $Sn(O_2CR)_4$ compounds will have polymeric structures.

From an examination of the results in Table II it is clear that, in the mixed-oxidation-state compounds, the Sn(IV) gives a stronger resonance at 77 K than the Sn(II) for all of the compounds except when R = CH_3 or $C(CH_3)_3$. In these latter cases the tin(II) appears to be more rigidly bound in the lattice than the Sn(IV). This is borne out by the two measurements that have been made at 4 K when the relative areas of the peaks change in the manner expected. However, it is clear that a more extensive temperature-dependence study will be needed before one can make any definitive statements about the lattice dynamics. Another point that needs further investigation is the slight asymmetry of the Sn(II) doublet, which is apparent in all of the spectra and is illustrated in Figure 1. This asymmetry appears to decrease at 4 K, suggesting that the cause is due to an anisotropy in the recoil-free fraction.[21] We have eliminated crystalline orientation as the cause of this asymmetry by grinding with a powdered diluent.

3. Vibrational Spectroscopy. Infrared spectra were recorded for all of the compounds, but only some of the compounds gave satisfactory Raman spectra due to fluorescence problems. The data that were obtained are summarized in Table III. Because of the complexity of the spectra it is not possible to make unambiguous assignments, particularly in the IR spectra, where overtones and combination bands are likely. However, certain features can be identified that allow us to draw some conclusions about the structures of the molecules. Assignments are based on vibrational data for organotin carboxylates where the mode of coordination of the carboxylate ligand has been confirmed crystallographically. Spectroscopic data for all of the $Sn(O_2CR)_4$ series were not included in Table III because we were unable to obtain all of these completely free of the parent acid. The latter materials all gave a strong OH band in the IR spectra, and these spectra could therefore not be used to make assignments for the other molecules. None of the mixed-oxidation-state molecules showed any bands in the OH region of the spectrum, indicating that there is no free or coordinated acid present in these compounds.

Each carboxylate group has bands in its spectrum characteristic of the R substituent. These generally give rise to quite complex patterns, and while they are diagnositic of the particular acid, they are of little use in assigning the mode of coordination of the carboxylate ligand. We have indicated some of these bands in Table III. The vibrational frequency of the C–C bond is a much more useful indicator of the coordinating role of the ligand. The presence of more than one C–C vibration in the region 850–950 cm^{-1} indicates that there is more than one type of carboxylate ligand present. However, reliable assignment is only possible in the Raman spectrum, where the ν (C—C) stretch occurs as an intense band. The spectral bands arising from the O_2C moiety of the carboxylate ligand are the most sensitive to the bonding situation. From ~1220 to 1770 cm^{-1} one finds strong bands which are associated with the symmetric and antisymmetric stretches of the O_2C group. The number of such bands indicates that there are several different types of O_2C linkages present in the molecule.

The region from ~1500 to 1770 cm^{-1} spans the entire range for $\nu_{as}(O_2C)$ for all types of carboxylate bonded to tin, and there are several prominent bands in this range for our compounds. In the middle to lower end of this range ~1500–1650 cm^{-1} there are several absorptions which can be attributed either to bidentate carboxylate[22,23] or to carboxylate groups bridging two different tin atoms.[24] There are also bands in the asymmetric stretching region 1700–1765 cm^{-1} which are usually associated with unidentate carboxylates. Such assignments have been confirmed for several organotin(IV) carboxylates.[25] However, such an assignment here is unlikely since the presence of both unidentate and bidentate carboxylates at Sn(IV) would lead to a large quadrupole splitting as is observed in $Sn(O_2CCF_3)_4$ (Table II). It is also unlikely that these bands at ~1700 cm^{-1} are associated with unidentate carboxylates linked to Sn(II) since these bands usually occur below 1650 cm^{-1}. For example $K[Sn(O_2CR)_3]$, which contains only unidentate carboxylates, has $\nu_{as} < 1650$ cm^{-1}.[26] Unfortunately none of the $Sn(O_2CR)_2$ compounds in Table II seem to have been examined by single-crystal X-ray diffraction so that it is not known if these compounds contain unidentate carboxylate groups or not. In the mixed-oxidation-state compounds the bands at ~1700 cm^{-1} are, however, in the right range to arise from an anhydride molecule coordinated to a tin(II). Free anhydride has $\nu_{as} \approx 1800$ cm^{-1}, and one might reasonably expect this to shift to lower values (1700–1750 cm^{-1}) on coordination to a Sn(II). This behavior has been reported for the $Sn^{IV}X_4(O(OCR)_2)_2$ (X = Cl, Br) complexes, when the ν(C=O) shifts from 1775, 1820 cm^{-1} for free anhydride to 1688, 1742 cm^{-1} upon complex formation.[27] Anhydrides also have characteristic bands at 900–1250 cm^{-1} due to ν(C=O), and all of the mixed-oxidation-state compounds examined here have bands in this region. Unfortunately, carboxylates containing C–H or C–F bonds also have prominent bands in this region of the spectrum so that only in the case when R = CCl_3 can the presence of anhydride be confirmed by the band at 1255 cm^{-1}. It is unlikely that this band arises from $\nu_s(O_2C)$, because of the low frequency. Some further evidence to support the idea that coordinated anhydride molecules are present comes from a comparison of the relative areas of $\nu_{as}(O_2C)$ and $\nu_s(O_2C)$ bands in the Raman spectra of the CF_3 and CCl_3 derivatives. If the bands at 1700–1765 cm^{-1} are not due to anhydride coordinated to Sn(II), then the $\nu_{as}(O_2C)$ modes would have a greater total intensity than the $\nu_s(O_2C)$ modes. In $Sn(O_2CCF_3)_4$, which must contain unidentate and bidentate carboxylates, ν_{as} is less intense than ν_s and the mixed-oxidation-state compounds only fall in line with these area ratios if those bands at ~1700 cm^{-1} are attributable to anhydride.

The region 400–700 cm^{-1} also contains many bands, some of which undoubtedly arise from vibrations associated with the R group. However, vibrations associated with oxygen atoms bridging two or more tin atoms also have bands in the region 400–700 cm^{-1}.[28] In addition, the IR spectra of organotin(IV) carboxylates which are known to have a μ_3-oxo bridge to tin atoms[23] are similar to those spectra reported here. We believe that the spectra that we have obtained are con-

(18) Hoppe, R.; Dähne, W. *Naturwissenschaften* **1962**, *49*, 254.
(19) Yeats, P. A.; Poh, B. L.; Ford, B. F. E.; Sams, J. R.; Aubke, F. *J. Chem. Soc. A* **1970**, 2188.
(20) Alcock, N. W.; Tracy, V. L. *J. Chem. Soc., Dalton Trans.* **1976**, 2246.
(21) Goldanskii, V. I.; Gorodinskii, G. M.; Kargagin, S. V.; Korytho, L. A. *Dokl. Akad. Nauk SSSR* **1961**, *147*, 127.
(22) Garner, C. D.; Hughes, B.; King, T. J. *Inorg. Nucl. Chem. Lett.* **1976**, *12*, 859.
(23) Faggiani, R.; Johnson, J. P.; Brown, I. D.; Birchall, T. *Acta Crystallogr., Sect. B* **1978**, *B34*, 3743.
(24) Ford, B. F. E.; Liengme, B. V.; Sams, J. R. *J. Organomet. Chem.* **1969**, *19*, 53. Simons, P.; Graham, W. A. G. *Ibid.* **1967**, *10*, 457.
(25) Alcock, N. W.; Tracy, V. M.; Waddington, T. C. *J. Chem. Soc., Dalton Trans.* **1976**, 2243.
(26) Donaldson, J. D.; Jelen, A. *J. Chem. Soc. A* **1968**, 2244.
(27) Malhotra, K. C.; Katoch, D. S. *Aust. J. Chem.* **1974**, *27*, 1413.
(28) Ogden, J. S.; Ricks, M. J. *J. Chem. Phys.* **1970**, *53*, 896.

sistent with the presence of μ-oxo bridges in these compounds.

4. Conclusions. The solvolysis of hexaphenylditin by carboxylic acids produces compounds with the empirical formula $Sn(O_2CR)_3$. Spectroscopic evidence discussed above establishes that there are two distinct types of tin, one Sn(II) and the other Sn(IV). The Sn(II) is in a very distorted environment which is rather sensitive to the nature of the carboxylate ligand coordinated to it, while the Sn(IV) is in a nearly regular environment and is much less influenced by the nature of ligand. Comparison with the analogous $Sn(O_2CR)_2$ and $Sn(O_2CR)_4$ compounds clearly shows that these new compounds are not mixtures of the corresponding Sn(II) and Sn(IV) species. Vibrational spectroscopy suggests that the carboxylate ligands bridge the Sn(II) and Sn(IV) atoms. If all of the carboxylate groups were involved in bridging the tin atoms, then a polymeric structure would be most likely. However, there is strong evidence that some of the carboxylates are present in the form of coordinated anhydride, and furthermore the lack of any significant Mössbauer absorption at room temperature, while not conclusive, argues against a polymeric structure.

We have noted above the good correlation between our Mössbauer data and those obtained by Harrison and coworkers for $[Sn^{II}Sn^{IV}O(O_2CC_6H_4\text{-}o\text{-}NO_2)_4THF]_2$. The structure of $[Sn^{II}Sn^{IV}O(O_2CCF_3)_4]_2\cdot C_6H_6$ recently reported by us[8] is also very similar in structure to Harrison's compound. It was obtained by a modification of the preparation reported here and contains a molecule of benzene, but no trifluoroacetic anhydride, and one coordination site in the equatorial plane about the tin(II) site is vacant. All of the spectroscopic evidence presented on the compounds reported here indicates that they have the same basic structure as these two compounds.[7,8] The central cluster of two Sn(II) and two Sn(IV) atoms would then be held together by two μ_3-oxo bridges and eight carboxylate ligands, each of which would bridge a Sn(IV) and a Sn(II). In this way the Sn(IV) atoms could achieve six-coordination from two μ_3-bridging oxygens, which are cis to one another, and from four carboxylate oxygens to give an almost regular octahedral arrangement. Around the Sn(II) atoms a pentagonal-bipyramidal arrangement is proposed with a bridging oxygen in one apical position and the nonbonding electron pair in the other apical site. In the equatorial plane, four positions are envisaged as being occupied by four carboxylate oxygens, and the fifth position, which is vacant in $[Sn^{II}Sn^{IV}O(O_2CCF_3)_4]_2\cdot C_6H_6$ and occupied by THF in $[Sn^{II}Sn^{IV}O(O_2CC_6H_4\text{-}o\text{-}NO_2)_4THF]_2$, is assumed to be occupied by an oxygen from a coordinated anhydride molecule.

The molecules are then best formulated as $[Sn^{II}Sn^{IV}O(O_2CR)_4O(OCR)_2]_2$. We are presently attempting to obtain single crystals of one of these compounds containing anhydride that would be suitable for X-ray crystallographic analysis.

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Registry No. $Sn(O_2CCF_3)_3$, 82661-20-9; $Sn(O_2CCCl_3)_3$, 82661-21-0; $Sn(O_2CCHCl_2)_3$, 82661-22-1; $Sn(O_2CCH_2Cl)_3$, 82661-23-2; $Sn(O_2CCH_3)_3$, 82665-07-4; $Sn(O_2CCF_2CF_2CF_3)_3$, 82661-24-3; $Sn(O_2CC(CH_3)_3)_3$, 82661-25-4; $Sn(O_2CCF_3)_4$, 16424-89-8; $Sn(O_2CCCl_3)_4$, 82661-27-6; $Sn(O_2CCHCl_2)_4$, 66096-29-5; $Sn(O_2CCH_2Cl)_4$, 62487-22-3; $(C_6H_5)_6Sn_2$, 1064-10-4; $(C_6H_5)_4Sn$, 595-90-4; $Sn(O_2CC_3F_7)_4$, 82661-26-5.

Contribution from the Department of Chemistry, University of Regina, Regina, Saskatchewan S4S 0A2, Canada

Preparation and Crystal and Molecular Structure of a Novel Cleavage Product from the Reaction of a Bis(tertiary arsine) with $Re_2(CO)_{10}$

RICHARD J. BARTON, SHENGZHI HU,[1] LYNN M. MIHICHUK,* and BEVERLY E. ROBERTSON

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The bis(tertiary arsine) *cis*-$(CH_3)_2AsC(CF_3)=C(CF_3)As(CH_3)_2$ reacts with $Re_2(CO)_{10}$ to give a compound of formula $C_{11}H_6AsF_6O_5Re$, the structure of which was determined by X-ray crystallography. The compound crystallizes in the space group $P\bar{1}$ with a = 8.189 (3) Å, b = 8.950 (2) Å, c = 25.471 (3) Å, α = 101.49 (1)°, β = 90.28 (2)°, γ = 116.78 (2)°, and Z = 4. The structure was refined by blocked full-matrix least squares, with 5690 unique reflections, to R = 0.046 and R_w = 0.056. The coordination around Re is close to octahedral. An $-As(CH_3)_2$ group has been cleaved from the ligand. The $Re(CO)_4$ unit is coordinated to the remaining arsenic atoms and to a CO group, which has inserted between the rhenium atom and the olefinic carbon atom to form a five-membered ring.

Introduction

Many of the reactions of bis(tertiary phosphines and arsines) with metal carbonyls afford simple carbonyl-substituted complexes.[2] However there are also many reports of reactions resulting in novel products as a result of ligand rearrangement or cleavage of ligand moieties.[3] In particular, the reactions of $M_2(CO)_{10}$ (M = Mn, Re) with cis-$(CH_3)_2AsC(CF_3)=C(CF_3)As(CH_3)_2$ afforded two different types of complexes.[3a] The Mn reaction resulted in a novel complex containing a fluorinated π-allyl group.[4] We had previously reported[3a] that the rhenium system gave a complex containing a CH_2O fragment σ bonded to rhenium through either the carbon or oxygen atom on the basis of spectroscopic evidence.

In order to verify the above findings, we determined the molecular structure of the complex that is described below.

Experimental Section

The fluorinated arsine ligand (L–L) was prepared as described in the literature.[5] Infrared spectra were recorded on a Perkin-Elmer 457 instrument. ^{19}F and ^1H NMR spectra were recorded by using Varian T-60 and XL-100 spectrometers with chemical shifts given

(1) Visiting Scholar, Department of Chemistry, University of Amoy, Amoy, People's Republic of China.
(2) McAuliffe, C. A.; Levason, W. "Phosphine, Arsine, and Stibine Complexes of the Transition Elements"; Elsevier: New York, 1979.
(3) See, for example: (a) Cullen, W. R.; Mihichuk, L.; Einstein, F. W. B.; Field, J. S. *J. Organomet. Chem.* **1974**, *73*, C53. (b) Cobbledick, R. E.; Cullen, W. R.; Einstein, F. W. B.; Mangayarkarasy, W. *Inorg. Chem.* **1981**, *20*, 186. (c) Chia, L. S.; Cullen, W. R.; Harborne, D. A. *Can. J. Chem.* **1972**, *50*, 2182. (d) Einstein, F. W. B.; Jones, R. D. G. *J. Chem. Soc., Dalton Trans.* **1972**, 2563. (e) Barrow, M. J.; Davidson, J. L.; Harrison, W.; Sharp, D. W. A.; Sim, G. A.; Wilson, F. B. *J. Chem. Soc., Chem. Commun.* **1973**, 583. (f) Patel, H. A.; Fischer, R. G.; Carty, A. J.; Naik, D. V.; Palenik, G. J. *J. Organomet. Chem.* **1973**, *60*, C49.
(4) Einstein, F. W. B.; Field, J. S. *J. Chem. Soc., Dalton Trans.* **1975**, 172.
(5) Crow, J. P.; Cullen, W. R.; Herring, F. G.; Sams, J. R.; Tapping, R. L. *Inorg. Chem.* **1971**, *10*, 1616.

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