

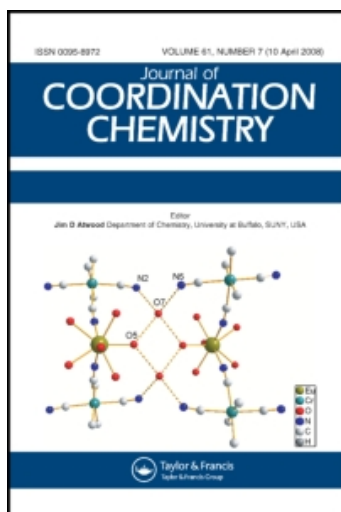
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### MÖSSBAUER STUDIES OF TIN(IV) COMPLEXES WITH ANIONIC CHELATING LIGANDS HAVING OXYGEN DONORS

Datta V. Naik<sup>a</sup>; Joan C. May<sup>a</sup>; Columba Curran<sup>a</sup>

<sup>a</sup> Department of Chemistry and the Radiation Laboratory, University of Notre Dame, Notre Dame, Indiana

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# MÖSSBAUER STUDIES OF TIN(IV) COMPLEXES WITH ANIONIC CHELATING LIGANDS HAVING OXYGEN DONORS

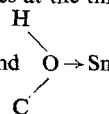
DATTA V. NAIK, JOAN C. MAY and COLUMBA CURRAN

Contribution from the Department of Chemistry and the Radiation Laboratory,<sup>1</sup> University of Notre Dame, Notre Dame, Indiana 46556.

(Received August 20, 1971; in final form May 22, 1972)

Mössbauer spectra have been obtained for thirty-two complexes of tin(IV), including those with kojic acid, tropolone, chloranilic acid, benzoic and ortho- and para-chlorobenzoic acids and salicylic acid, as well as *o*-phenanthroline complexes with the tin(IV) carboxylates. Quadrupole splittings reveal *trans* C—Sn—C bonds in all the octahedral diorganocompounds except diphenylbis(kojato)tin(IV) and diphenylbis(tropolonato)tin(IV). Oxygen-tin and pyridine-type nitrogen-tin dative bonds are observed to effect similar electron densities at the tin

nucleus. *o*-Phenanthroline interacts with the carboxylate compounds to replace chelate C=O → Sn and C—O → Sn dative bonds by N → Sn bonds.

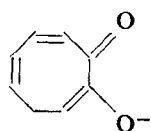


Mössbauer studies of tin(IV) complexes having ligands of the type  $\begin{pmatrix} \text{O} \\ \text{O}^- \end{pmatrix}$  have included complexes

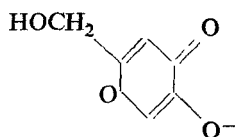
with anions of acetylacetone,<sup>2,3,4</sup> salicylaldehyde<sup>5</sup> and carboxylic acids.<sup>6,7</sup> The first two form six-membered chelate rings. Carboxylate complexes are usually bridged polymers, but there is some

evidence for monomers containing  $\begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{C} \quad \text{Sn} \\ \diagdown \quad \diagup \\ \text{O} \end{array}$  chelate rings in  $\text{R}_2\text{Sn}(\text{OCOCH}_3)_2$ .<sup>8</sup>

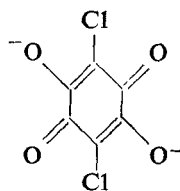
The present investigation is concerned with anions of tropolone (I), kojic acid (II), chloranilic acid (III), benzoic and substituted benzoic acids, and salicylic acid (IV).



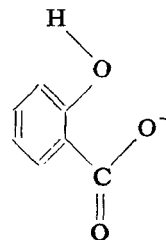
I



II



III



IV

Fitzsimmons and coworkers<sup>3</sup> have shown that quadrupole splittings for *trans* octahedral  $\text{R}_2\text{SnL}_2$  compounds are about twice the values for similar

*cis* compounds. The concluded that dimethyl-bis-(acetylacetonato)tin(IV) has a *trans* configuration and that the corresponding diphenyl compound has a *cis* arrangement of C—Sn—C bonds. It is of interest to ascertain from Mössbauer spectra the configuration of other octahedral complexes having two Sn—C and four Sn—O bonds. It is also of interest to compare the electron density at the tin nucleus in these compounds with that in compounds having Sn—N and Sn—S bonds.

## EXPERIMENTAL SECTION

### Preparation and Purification of Compounds

Kojic acid and tropolone were obtained from Aldrich Chemical Co. and chloranilic acid and *o*-phenanthroline from Eastman Kodak. Tin

tetrachloride was a Baker Analyzed reagent. The other tin tetrahalides and the organotin halides were obtained from Alfa Inorganics, Inc.

Dimethylbis(kojato)tin(IV) was supplied by Dr. Toshio Tanaka.<sup>9</sup>

*Di-n-butyl* and *diphenylbis(kojato)tin(IV)* were prepared by refluxing a solution of diorganotin dichloride and kojic acid in a 1:2 ratio in absolute ethanol for one hr, adding an equivalent amount of NaOH to precipitate NaCl, filtering, and flash evaporating the filtrate to an oil, extracting with benzene and evaporating the benzene solution. The dibutyl compound was recrystallized from methanol and the diphenyl from benzene. All compounds were dried in a vacuum over  $P_4O_{10}$ .

*Dihalobis(kojato)tin(IV)* compounds were prepared by mixing methanol solutions of tin(IV) halides and kojic acid in a 1:2 ratio and stirring overnight. The buff colored precipitates were separated by filtration, washed with methanol and dried at 110°. *Bromo-* and *iodotris(kojato)tin(IV)* were prepared in the same manner as the corresponding picolates.<sup>10</sup>

*Chlorotris(kojato)tin(IV)* was prepared by mixing methanol solutions of dichlorobis(kojato)tin(IV) and sodium kojate, 1:1, and stirring for two days at room temperature. The buff precipitate obtained on concentrating the solution was separated by filtration and washed with methanol.

Sodium tropolonate was prepared by the method of Cooke et al.<sup>11</sup> and also by neutralizing tropolone with an equivalent amount of sodium methylate in methanol. The salt is soluble in hot methanol.

*Diorganobis(tropolonato)tin(IV)* compounds were prepared by adding methanol solutions of the diorganotin dichlorides to a boiling methanol solution of sodium tropolonate in a 1:2 ratio with stirring. Crystals obtained on concentrating and cooling were recrystallized from hot methanol.

*n-Butyltris(tropolonato)tin(IV)* and *methyltris(tropolonato)tin(IV)·CH<sub>3</sub>OH* were prepared similarly, using a 1:3 ratio. The i.r. spectrum of the latter compound showed sharp O—H and O—C absorptions at 3480 and 1035  $cm^{-1}$ , respectively. The diiodo compound was also prepared in the same manner, starting with tin(IV) iodide. Dibromobis(tropolonato)tin(IV) was supplied by Dr. R. Okawara.<sup>12</sup> The remaining tropolonato compounds listed in Table I were prepared by the method of Muetterties and Wright.<sup>13</sup> The *diorganobis(benzoato)tin(IV)*

compounds listed in Table I were prepared by the method of Reichle,<sup>14</sup> starting with the benzoic acids and triethylamine in benzene solution.

*Di-n-butylbis(salicylato)tin(IV)* was prepared by mixing methanol solutions of dibutyltin dichloride and sodium salicylate, the latter in slight excess. The sodium chloride formed was separated by filtration and the filtrate evaporated to a dense oil which yielded crystals on standing. The compound was recrystallized from anhydrous ether. The *o*-phenanthroline complex of this compound was formed by mixing methanol solutions of the components, the *o*-phenanthroline being in slight excess. The benzoate complexes with *o*-phenanthroline were obtained by mixing benzene solutions, the latter in slight excess. The products were washed with or recrystallized from anhydrous ether.

*Di-n-butyl-* and *diphenylchloranilatotin(IV)* were prepared by adding, 1:1, a methanol solution of the diorganotin dichloride to a suspension of the sodium salt of chloranilic acid in methanol and stirring for two hours. The dark blue dibutyl and the green diphenyl precipitates were separated and washed with methanol.

#### Mossbauer Spectra

These were obtained, and the data processed, as indicated previously.<sup>10</sup> Isomer shifts relative to barium stannate,  $\delta$ , and quadrupole splittings,  $\Delta E_Q$ , listed in Table I are considered to be accurate to  $\pm 0.05$  mm/sec with a relative precision of  $\pm 0.03$ .  $\Gamma_1$  and  $\Gamma_2$  are the absorption half widths. The spectrum of *di-n-butylbis(kojato)tin(IV)* is illustrated in Figure 1.

#### Infrared Spectra

These were obtained with a Perkin-Elmer 457 spectrometer. The frequencies reported for absorption maxima are considered to be accurate to  $\pm 3$   $cm^{-1}$ . Values listed are for spectra in KBr disks unless otherwise indicated. The spectra of *di-n-butylbis(benzoato)tin(IV)* and its complex with *o*-phenanthroline are illustrated in Figure 2. Dielectric constants of benzene solutions of  $Bu_2Sn(benzoate)_2$  were obtained as before,<sup>15</sup> and a dipole moment of  $1.76 \pm 0.03$  Debyes was calculated for this compound by the method of Higashi.<sup>16</sup>

## DISCUSSION OF RESULTS

*Mössbauer Spectra*

**Diorganotin Complexes** The magnitudes of the quadrupole splittings, Table I, reveal *trans* alkyl groups and *cis* phenyl groups in the kojic acid and tropolone complexes. The  $\Delta E_Q$  values for the chloranilic acid complexes reveal *trans* butyl and phenyl groups, indicating thread-like polymers with coplanar rings. Some complexes having  $-\text{Sn}-X-\text{Sn}-$  bridging, where  $X = \text{halogen}$ , pseudo-halogen or oxygen, show resonance absorption at room temperature; the chloranilic acid complexes showed no such absorption. The  $\Delta E_Q$  values for

all carboxylates listed in Table I indicate *trans* C—Sn—C bonds. The large line widths obtained for a number of the compounds cannot be accounted for at this time.

The value of the  $J^{119}\text{Sn}-\text{CH}$  coupling constant for dimethyl-bis(kojato)tin(IV), 83.3 cps,<sup>9</sup> compared to the value of 99.3 cps for dimethylbis(acetylacetonato)tin(IV),<sup>17</sup> led Tanaka and coworkers to suggest a significant deviation from 180° of the C—Sn—C bond angle in the kojic acid complex. Sage and Tobias<sup>18</sup> have proposed a *cis* arrangement of methyl groups in dimethylbis(tropolonato)tin(IV) from the values of the coupling constants, 75.8 cps in  $\text{DCCl}_3$  and 71.8 cps in benzene.

TABLE I

Characterization, infrared frequencies ( $\text{cm}^{-1}$ ) and Mössbauer parameters (mm/sec) at 80°K

	M.P.	%C		%H		$\nu_{\text{Sn}-\text{O}}$	$\delta^a$	$\Delta E_Q$	$\Gamma_1$	$\Gamma_2$
	°C	Calcd	Found	Calcd	Found					
1. $(\text{CH}_3)_2\text{Sn}(\text{koj})_2$						552	1.22	3.60	1.41	1.42
2. $(n\text{-C}_4\text{H}_9)_2\text{Sn}(\text{koj})_2$	157–159	61.5	61.2	5.85	6.00	550	1.35	3.70	1.22	1.21
3. $(\text{C}_6\text{H}_5)_2\text{Sn}(\text{koj})_2$	140–142	51.9	52.8	3.60	3.87	557	0.80	1.98	1.09	1.10
4. $\text{F}_2\text{Sn}(\text{koj})_2$	>280*	32.8	32.6	2.28	2.28	585	–0.01	—	1.75	
5. $\text{Cl}_2\text{Sn}(\text{koj})_2$	241–243d	30.6	30.8	2.14	2.29	578	0.30	—	1.60	
6. $\text{Br}_2\text{Sn}(\text{koj})_2$	266–268d	25.7	25.9	1.80	2.05	573	0.45	—	1.66	
7. $\text{I}_2\text{Sn}(\text{koj})_2$	234–236d	22.0	22.2	1.53	1.50	565 570	0.65	—	1.51	
8. $\text{ClSn}(\text{koj})_3$	>280*	37.4	37.4	2.60	2.83	555 565	0.18	—	1.94	
9. $\text{BrSn}(\text{koj})_3$	>280*	34.7	34.9	2.42	2.56	551 563	0.26	—	1.74	
10. $\text{ISn}(\text{koj})_3$	>280*	32.3	32.6	2.24	2.53	550 562	0.34	—	2.00	
11. $(n\text{-C}_4\text{H}_9)_2\text{Sn}(\text{trop})_2$	110–111	55.6	55.8	5.90	6.03	510	1.30	3.68	1.29	1.30
12. $(\text{C}_6\text{H}_5)_2\text{Sn}(\text{trop})_2$	218–220d	60.6	60.8	3.88	3.99	540 550	0.75	1.88	1.30	1.30
13. $\text{Cl}_2\text{Sn}(\text{trop})_2$	>300	38.9	38.8	2.31	2.42	583 588	0.28	—	1.36	
14. $\text{Br}_2\text{Sn}(\text{trop})_2$						580 583	0.40	—	1.39	
15. $\text{I}_2\text{Sn}(\text{trop})_2$	>300	27.3	27.7	1.63	1.82	575 582	0.59	—	1.42	
16. $\text{ClSn}(\text{trop})_3$	>300	48.7	48.3	2.90	3.51	562 590	0.12	—	1.82	
17. $\text{CH}_3\text{SnCl}(\text{trop})_2$	289–291d	43.7	44.6	3.16	3.45	535 560	0.53	1.70	1.48	1.57
18. $\text{CH}_3\text{Sn}(\text{trop})_3 \cdot \text{CH}_3\text{OH}$	288–291d	52.2	52.1	4.16	4.09	535 561	0.57	2.00	1.20	1.14
19. $n\text{-C}_4\text{H}_9\text{Sn}(\text{trop})_3$	241–243d	55.7	55.5	4.45	4.56		0.66	2.11	1.23	1.21
20. $\text{C}_6\text{H}_5\text{Sn}(\text{trop})_3$	300–302d	58.0	57.7	3.58	3.86	538 560	0.49	1.91	1.21	1.21
21. $(n\text{-C}_4\text{H}_9)_2\text{Sn}(\text{chloran})$	>300*	38.2	38.0	4.08	4.35	445 to 488	1.49	3.88	1.51	1.48
22. $(\text{C}_6\text{H}_5)_2\text{Sn}(\text{chloran})$	>300*	45.0	44.4	2.10	2.55	440 450	1.29	3.84	1.10	1.14
23. $(n\text{-C}_4\text{H}_9)_2\text{Sn}(\text{bz})_2$	66–68	55.6	56.2	5.90	5.81		1.46	3.67	1.32	1.35
24. $(n\text{-C}_4\text{H}_9)_2\text{Sn}(\text{bz})_2 \cdot \text{phen}$	121–123	62.4	62.4	5.50	5.65		1.41	3.98	1.14	1.16
25. $(\text{C}_6\text{H}_5)_2\text{Sn}(\text{bz})_2 \cdot \text{phen}$	202–204	65.6	65.5	4.03	4.33		1.16	3.59	1.25	1.30
26. $(n\text{-C}_4\text{H}_9)_2\text{Sn}(p\text{-Clbz})_2$	125–127	48.5	48.5	4.78	4.84		1.34	3.26	0.96	1.05
27. $(\text{C}_6\text{H}_5)_2\text{Sn}(p\text{-Clbz})_2 \cdot \text{phen}$	202–204	59.7	59.4	3.40	3.68		1.21	3.81	1.00	1.05
28. $(n\text{-C}_4\text{H}_9)_2\text{Sn}(o\text{-Clbz})_2$	78–80.5	48.5	48.3	4.78	4.92		1.44	3.56	1.10	1.18
29. $(n\text{-C}_4\text{H}_9)_2\text{Sn}(o\text{-Clbz})_2 \cdot \text{phen}$	132–134	56.4	55.5	4.70	5.11		1.41	4.05	1.00	1.13
30. $(\text{C}_6\text{H}_5)_2\text{Sn}(o\text{-Clbz})_2 \cdot \text{phen}$	207–209	59.7	60.4	3.40	3.96		1.22	3.71	1.02	1.09
31. $(n\text{-C}_4\text{H}_9)_2\text{Sn}(\text{sal})_2$	76–78	52.1	52.1	5.52	5.55		1.47	3.60	1.25	1.29
32. $(n\text{-C}_4\text{H}_9)_2\text{Sn}(\text{sal})_2 \cdot \text{phen}$	160–162	59.4	59.1	5.24	5.37		1.48	4.28	1.21	1.19

Hkoj = kojic acid, Htrop = tropolone,  $\text{H}_2\text{chloran}$  = chloranilic acid, Hbz = benzoic acid, Hsal = salicylic acid, phen = *o*-phenanthroline.

\* Starts decomposing above 200°. <sup>a</sup> Relative to Barium Stannate.

However, the large quadrupole splitting reported for dimethylbis(picolinato)tin(IV), 4.43 mm/sec,<sup>19</sup> compared to the  $J^{119}\text{Sn}-\text{CH}$  coupling constant in  $\text{DCCl}_3$ , 77.6 cps,<sup>17</sup> indicates a poor correlation of C—Sn—C bond angles with coupling constants.

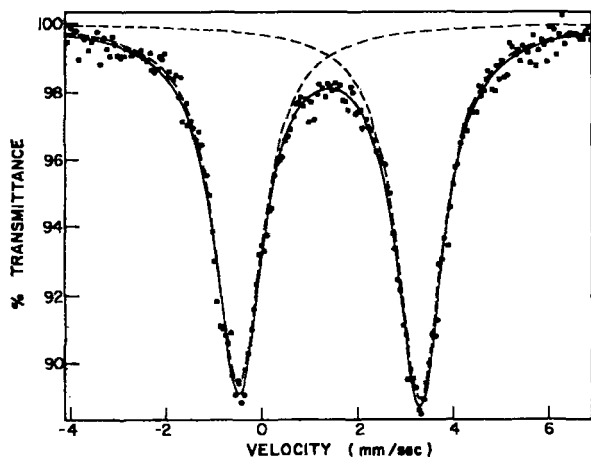


FIGURE 1 Mössbauer spectrum of di-*n*-butylbis(kojato)tin(IV).

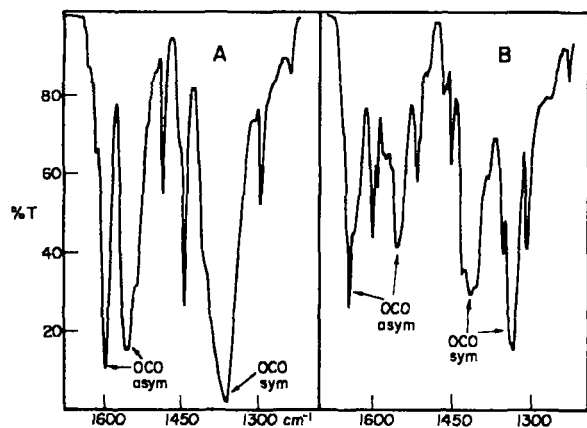


FIGURE 2 Infrared spectra in KBr disks.

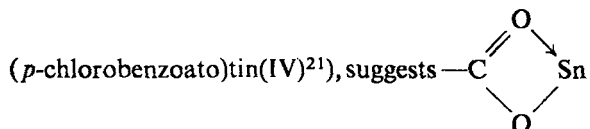
A, di-*n*-butylbis(benzoato)tin(IV).

B, di-*n*-butylbis(benzoato)tin(IV)·*o*-phenanthroline.

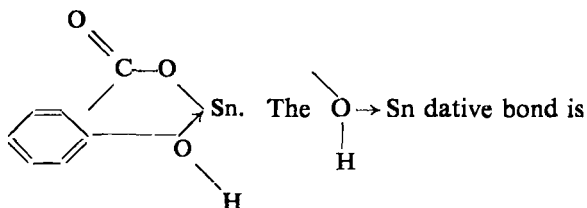
In the light of the quadrupole splitting for the dibutyl compound, a *cis* configuration for dimethylbis(tropolonato)tin(IV) appears very unlikely. The quadrupole splittings obtained for the dialkyltin tropolonates and kojates, 3.6–3.7 mm/sec, are somewhat smaller than the value for  $\text{Me}_2\text{Sn}(\text{acac})_2$ ,

3.93 mm/sec,<sup>2</sup> suggesting a deviation from 180° of the C—Sn—C bond angles in these compounds. The larger  $\Delta E_Q$  values for the chloranilic acid complexes indicates more nearly linear C—Sn—C bonds in these polymers. Despite the high electronegativity of the chloranilate group, the isomer shift for  $\text{Bu}_2\text{Sn}(\text{chloranilate})$  is larger than the values for the corresponding kojate and tropolonate, another indication of a C—Sn—C bond angle close to 180°.<sup>10,20</sup>

Infrared data, coupled with the lack of Mössbauer absorption at room temperature (resonance absorption at room temperature has been noted for —Sn—O—C=O→Sn— bridged dimethylbis-



chelation for the  $\text{R}_2\text{Sn}(\text{benzoate})_2$  complexes listed in Table I. The dipole moment of di-*n*-butylbis(benzoato)tin(IV), 1.76 Debyes, suggests a mixture of *cis* and *trans* O→Sn dative bonds in this compound. (A precise value for the moment of a complex having *cis* carbonyl groups is not known, but it is expected to be significantly larger than 1.8 Debyes.) The decrease in  $\delta$  from the benzoate to the *p*-chlorobenzoate complex, 1.46 to 1.34 mm/sec, is the reverse of that obtained on halogen substitution (in the  $\text{OCOCH}_3$  group) in bridged trialkyltin acetates.<sup>7</sup> Unlike the dithiocarbamate complexes of tin(IV), the benzoates react with *o*-phenanthroline, with the replacement of  $\text{CO} \rightarrow \text{Sn}$  dative bonds by  $\text{N} \rightarrow \text{Sn}$  bonds. Infrared spectra reveal that in the salicylate complexes the bonding is



also readily broken by *o*-phenanthroline. The similar isomer shifts, 1.46 and 1.47 mm/sec obtained for  $\text{Bu}_2\text{Sn}(\text{benzoate})_2$  and  $\text{Bu}_2\text{Sn}(\text{salicylate})_2$  indicate a similar electron release by the hydroxyl and carbonyl groups in forming dative bonds with tin. The  $\Delta E_Q$  values are also similar for these compounds. The benzoates and salicylates undergo significant increases in quadrupole splitting on

complex formation with *o*-phenanthroline, despite unchanged isomer shifts. The picolates, with two OCO-Sn and two N→Sn bonds, also have significantly larger  $\Delta E_Q$  values<sup>10</sup> than do the benzoates, kojates and tropolonates.

The increase in isomer shift,  $\Delta\delta$ , from the *cis* diphenyl to the *trans* dibutyl complexes is the same, 0.55 mm/sec, for both the kojic acid and tropolone complexes. This contrasts with the smaller values of  $\Delta\delta$ , 0.20 mm/sec for the chloranilic acid complexes and 0.25 mm/sec for the benzoic acid-phenanthroline complexes, with *trans* phenyl groups. This variation in  $\Delta\delta$  had been noted<sup>22</sup> and interpreted<sup>10</sup> previously.

### Halotin Complexes

Both the kojic acid and tropolone series of complexes show the expected change in  $\delta$  with change in halogen electronegativity, and the expected decrease from  $X_2\text{SnL}_2$  to  $X\text{SnL}_3$  (as noted previously for the oxinates<sup>5</sup> and dithiocarbamates<sup>23</sup>), in which the coordination number of tin increases from six to seven. The  $X_2\text{Sn}(\text{koj})_2$  and  $X_2\text{Sn}(\text{trop})_2$  complexes, along with the acetylacetone and salicylaldehyde complexes, show no quadrupole splitting, although the large line widths suggest an unresolved splitting. This is in contrast to the complexes of 8-hydroxyquinoline-*N*-oxide, which also have four Sn—O bonds, for which  $\Delta E_Q$  values of about 0.6 mm/sec have been obtained.<sup>24</sup>

The isomer shifts for the dihalo complexes are equal, within experimental error, to those obtained for the corresponding oxinates,<sup>5</sup> and picolates,<sup>10</sup> suggesting that the electron release by a pyridine-type nitrogen is similar to that of oxygen in forming a dative bond with tin. As noted above, this is in line with the similar values of  $\delta$  for the benzoates and their *o*-phenanthroline complexes. The isomer shifts for the kojic acid complexes (with nonequivalent oxygen donors) are consistently slightly larger than those for the corresponding tropolone compounds, and are significantly larger than those for the corresponding salicylaldehyde complexes, with six-membered chelate rings.<sup>5</sup>

### Tristropolonato Compounds

Methyltris(tropolonato)tin(IV), # 18, crystallized with a molecule of methanol. This is common for tristropolonato compounds. The crystal structures of solvated  $\text{ClSn}(\text{trop})_3$  and  $\text{HOSn}(\text{trop})_3$  reveal that the solvent molecules are not bonded to tin.<sup>25</sup>

It is very probable that the methanol of crystallization does not affect the isomer shift of #18; the differences between  $\delta$  for this compound and the values for the corresponding butyl and phenyl compounds, # 19 and # 20, are as expected.

$J^{119}\text{Sn-CH}$  coupling constants reveal that the carbon-tin bond(axial) in seven-coordinate  $\text{CH}_3\text{Sn}(\text{S}_2\text{CNR}_2)_3$  has a greater tin *s* character than in octahedral  $\text{CH}_3\text{SnCl}(\text{S}_2\text{CNR}_2)_2$ .<sup>23</sup> The isomer shift is also larger, by 0.1 mm/sec, for the former compound. Solubility limitations prevented similar nmr measurements on the tropolone compounds, but there is an indication from Mössbauer data that greater tin *s* character in axial C—Sn bonds in seven-coordinate(pentagonal bipyramidal) than in octahedral tin compounds is a general phenomenon.<sup>26</sup> Other things being equal, an increase in coordination number results in a decrease in isomer shift; this is related to the decreased tin share of bonding electrons with increasing number of bonds.

Whereas dithiocarbamate complexes (above) show an increase in  $\delta$  from six- to seven-coordination, compounds #17 and 18 have  $\delta$  values differing by only 0.04 mm/sec and the value for  $\text{BuSn}(\text{ox})_3$  is 0.15 mm/sec less than that for  $\text{BuSnCl}(\text{ox})_2$ .<sup>27</sup> This appears significant. A number of investigators have attributed the general decrease in  $\delta$  with increasing coordination number to a shielding effect, and the isomer shifts for five-coordinate  $\text{CH}_3\text{Sn}(\text{OOCH}_n\text{F}_{3-n})$  support this interpretation.<sup>7</sup> However, it appears that shielding does not account for the change in  $\delta$  from six- to seven-coordinate tin complexes. It is generally agreed that tin has a greater share of bonding electrons in Sn—S than in Sn—O bonds. If shielding effects were dominant, one would expect a larger decrease in  $\delta$  for dithiocarbamates than for complexes with oxygen-donor ligands on increasing the coordination number from six to seven. The reverse experimental result indicates that the tin *s* character of the Sn—S and Sn—O bonds is the dominant factor. The weaker tin share of the electrons of the additional Sn—O bonds (compared to additional Sn—S bonds) neutralizes or overrides the increased tin *s* character of the Sn—C bond from six- to seven-coordinate complexes, and the isomer shift is practically unchanged or decreased. In the dithiocarbamate complexes, with less positive residual charge on tin, the increased tin *s* character of the Sn—C bonds in the seven-coordinate compound is the determining factor in bringing about a greater *s*-electron density.

### Infrared Spectra

Sn—O stretching frequencies have been assigned for complexes of tropolone,<sup>12</sup> kojic acid,<sup>8</sup> acetylacetone<sup>28</sup> and picolinic acid.<sup>10</sup> The frequencies listed in Table I check rather well with those reported previously. The relatively low values of  $\nu_{\text{Sn-O}}$  for the chloranilic acid complexes are expected; the high electronegativity of this ligand results in a relatively weak electron release of oxygen to tin. Okawara and coworkers<sup>12</sup> have pointed out that there is a linear relation between  $\nu_{\text{Sn-O}}$  for tropolone complexes and the sum of the Taft $\sigma^*$  values of the substituents except for the dialkyl compounds. It is now evident that the low Sn—O values for the latter result from the decreased tin s character of the Sn—O bonds in these compounds.<sup>10</sup> Precise values for the tin-oxygen stretching frequencies in the spectra of the carboxylate complexes could not be assigned. The spectrum of  $\text{Bu}_2\text{Sn}(\text{benzoate})_2$  shows a broad peak centering at  $450\text{ cm}^{-1}$  which probably includes the absorption associated with this vibration; no other significant absorption occurs between 450 and  $300\text{ cm}^{-1}$ .

The spectra of all the solid *o*-phenanthroline complexes of the diorganotin benzoates reveal absorptions corresponding to coordinated *o*-phenanthroline. This coordination is indicated by the shifts to high frequency of the absorptions at 1085, 1132, 1210, 1413 and  $1496\text{ cm}^{-1}$  on complex formation. The complexity of the spectra of solid  $\text{R}_2\text{Sn}(\text{acetate})_2$  compounds in the  $1500\text{--}1600$  and  $1400\text{--}1300\text{ cm}^{-1}$  region led Maeda and Okawara<sup>8</sup> to postulate mixtures of chelated and bridged complexes. However, the complexity of the spectrum of  $\text{Bu}_2\text{Sn}(\text{benzoate})_2 \cdot \text{phen}$ , Figure 2B, in which the benzoate ligand is monodentate, suggests a coupling effect similar to that observed in *trans*  $\text{R}_2\text{Sn}(\text{picolinate})_2$  complexes,<sup>10</sup> resulting in two absorptions for each of the antisymmetric and symmetric OCO stretching modes. The broad absorption at  $1362\text{ cm}^{-1}$  in the spectrum of dibutyltin-(benzoate)<sub>2</sub>, Figure 2A, suggests an unresolved splitting of the symmetric mode.

Alkyltin benzoates<sup>21</sup> and acetates<sup>8,29</sup> have been shown to be monomeric in dilute solution. Solid, bridged,  $\text{Bu}_3\text{Sn}(\text{acetate})$  absorbs at 1572 and  $1410\text{ cm}^{-1}$  and the monomers in dilute solution absorb at 1647 and  $1300\text{ cm}^{-1}$ .<sup>30</sup> In contrast, the  $\text{Bu}_2\text{Sn}(\text{benzoate})_2$  OCO absorptions, Table II, are the same in a nujol mull as in chloroform solution, indicating chelation rather than bridging in the solid. The changes in these absorptions on com-

plexing with *o*-phenanthroline reflect the change from a chelated to a monodentate benzoate group—a spreading apart of the antisymmetric peaks and a splitting of the broad absorption associated with

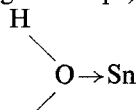
TABLE II  
OCO Stretching frequencies ( $\text{cm}^{-1}$ )<sup>a</sup>

	asym	sym
$n\text{-Bu}_2\text{Sn}(\text{bz})_2$	1600 1558	1362
solid film	1598 1560	1365
nujol mull	1603 1567	1363
in $\text{CHCl}_3$	1603 1567	1360
$n\text{-Bu}_2\text{Sn}(\text{bz})_2 \cdot \text{phen}$	1638 1545	1408 1325
$n\text{-Bu}_2\text{Sn}(p\text{-Clbz})_2$	1590 1560	1342 (broad)
$n\text{-Bu}_2\text{Sn}(o\text{-Clbz})_2$	1590 1555	1385 1350
$n\text{-Bu}_2\text{Sn}(o\text{-Clbz})_2 \cdot \text{phen}$	1640 1578	1400 1335
$n\text{-Bu}_2\text{Sn}(\text{sal})_2$	1620	not assigned
$n\text{-Bu}_2\text{Sn}(\text{sal})_2 \cdot \text{phen}$	1620	

<sup>a</sup> in KBr disks unless otherwise indicated

the symmetric vibration, with shifts to high and low frequencies. The high frequency OCO peaks are at 1640, 1640 and  $1620\text{ cm}^{-1}$  in the spectra of compounds 25, 27 and 30, the three diphenyltin complexes. The complexity of these spectra precluded the assignment of the other OCO absorptions.

The spectrum of  $\text{Bu}_2\text{Sn}(\text{salicylate})_2$  reveals a strong symmetrical absorption (slightly larger in area than the butyl C—H stretching envelope)

centering at  $3114\text{ cm}^{-1}$ , indicating 

bonding, and a high frequency OCO absorption at  $1620\text{ cm}^{-1}$ , indicating a monodentate carboxylate group. Complex formation with *o*-phenanthroline leaves the 1620 peak unchanged and results in a replacement of the  $3114\text{ cm}^{-1}$  peak by a weaker broad absorption in the  $2800\text{ cm}^{-1}$  region, characteristic of the intramolecular O—H— — —OC bridge.

The spectrum of  $\text{Bu}_2\text{Sn}(\text{benzoate})_2 \cdot \text{phen}$  in chloroform corresponds to that of the chelated benzoate and uncoordinated *o*-phenanthroline. In the light of this dissociation it is interesting that the spectrum of  $\text{Bu}_2\text{Sn}(\text{salicylate})_2 \cdot \text{phen}$  is unchanged in chloroform solution. This indicates that the intramolecular hydrogen bridge stabilizes the complex sufficiently to maintain the  $\text{N} \rightarrow \text{Sn}$  bonds in solution.

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