A Bridge-type Sn···O Coordination of Bis(trialkyltin) Carbonates[1]

Hiroyasu SATO[2]

Department of Applied Chemistry, Faculty of Engineering, Osaka University, Higashinoda, Miyakojima, Osaka

(Received May 14, 1966)

After ionic structures for methyltin and methyllead carboxylates were proposed on the basis of their infrared spectra,[3,4] Beattie and Gilson[5] pointed out that the spectral data could be interpreted by assuming a bridge-type coordination between the tin and oxygen atoms. Such coordination has indeed been found in dimeric bis(trimethylsiloxy)-tetraalkyl-distannoxanes.[6] It seemed necessary, therefore, to study the infrared spectrum of a compound which leaves no ambiguity in interpretation as to its ionic or coordinated nature.

Two bis(trialkyltin) carbonates, $(R_3Sn)_2CO_3$, $R=CH_3$ (I) and $R=C_2H_5$ (II), were prepared by treating trialkyltin hydroxide with dry carbon dioxide gas. Their melting points and analytical data are: (I) mp above 200°C; Found: Sn, 61.49; C, 21.82; H, 4.69%; Calcd: Sn, 61.25; C, 21.85; H, 4.68% and (II) mp 119—142°C; Found: Sn, 50.41; C, 33.35; H, 6.24%; Calcd: Sn, 50.32; C, 33.10; H, 6.41.% Their infrared spectra (3-23μ region) were measured by a Hitachi EPI-2G grating spectrophotometer in Nujol mulls

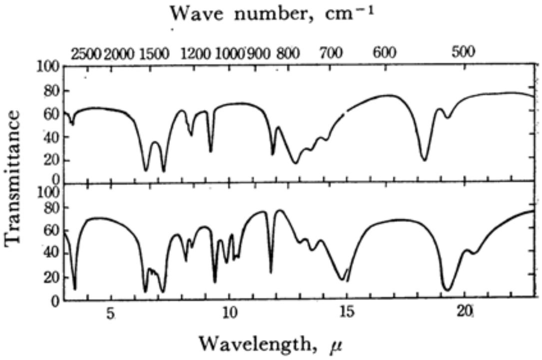

Fig. 1. Infrared spectra of bis(trialkyltin) carbonates, $(R_3Sn)_2CO_3$; (a) $R=CH_3$, (b) $R=C_2H_5$ (in KBr disks).

TABLE 1. IR SPECTRA OF BIS(TRIALKYLTIN) CARBONATES $(R_3Sn)_2CO_3$ IN KBr DISK OR (NUJOL MULL): POSITIONS OF BANDS ASSOCIATED WITH CO_3 GROUP, Sn-C AND Sn···O (in cm⁻¹)

$R=CH_3$	$R=C_2H_5$	Assignment
1553 1534	1540 1520	CO str.
1379	1370	COO antisym. str.
1072	1073	COO sym. str.
839	840	Non-planar rock.
741 705	756 723	COO bend and planar rock.
546	519	Sn-C asym. str.
518	494	Sn-C sym. str.
(381)	(385)	Sn···O coordination

---

[1] Presented at the International Symposium on Molecular Structure and Spectroscopy, Tokyo, 1962, A 308.

[2] Present address: Department of Chemistry, Faculty of Engineering Science, Osaka University, Toyonaka, Osaka.

[3] R. Okawara, D. E. Webster and E. G. Rochow, *J. Am. Chem. Soc.*, **82**, 3287 (1960).

[4] R. Okawara and H. Sato, *J. Inorg. Nucl. Chem.*, **16**, 204 (1961).

[5] I. R. Beattie and T. Gilson, *J. Chem. Soc.*, **1961**, 2585.

[6] R. Okawara, D. G. White, K. Fujitani and H. Sato, *J. Am. Chem. Soc.*, **83**, 1342 (1961).

and in KBr disks. For the ethyl compound, the spectra of carbon disulfide and carbon tetrachloride solutions were also measured. The observed spectra did not show any essential difference due to the media in which they were measured. The spectra observed in KBr disks are shown in Fig. 1. In Table 1 the observed frequencies are listed. The spectra of the 15—35μ region were measured in Nujol mulls by a Koken double-beam spectrophotometer model DS-401G equipped with a grating and CsBr optics. The data of this region are also listed in Table 1.

A free carbonate anion with D_{3h} symmetry has only three active bands in its infrared spectra.7) Interaction with another species reduces the symmetry and gives six bands.8) Each of the compounds studied here shows six bands attributable to the carbonate group, showing a reduced symmetry. The presence of two bands associated with the Sn–C stretching vibration shows the pyramidal structure of the C_3Sn skelton. A band observed in the far infrared region can be attributed to a coordination of Sn···O. Therefore, a bridge-type structure such as is shown in Fig. 2 can be assumed.9)

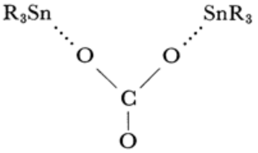

Fig. 2. The coordinated structure of bis-(trialkyltin) carbonates.

The present author wishes to express his deep gratitude to Professor Rokuro Okawara of Faculty of Engineering, Osaka University for helpful discussions. He is indebted to Dr. Ichiro Nakagawa of the University of Tokyo for far-infrared measurements and helpful discussions.

---

7) G. Herzberg, Infrared and Raman Spectra of Polyatomic Molecules, Van Nostrand, Princeton, 1945.

8) B. M. Gatehouse, S. E. Livingston and R. S. Nyholm, *J. Chem. Soc.,* **1958** 3137.

9) Recently Lohmann studied independently the infrared spectrum of the compound (II), and obtained the results essentially in accord with ours; D. H. Lohmann, *J. Organometal. Chem.*, **4**, 382 (1965).