

## On the Structure of Alkali Metal Triphenylstannide Salts in Solution and in the Solid State

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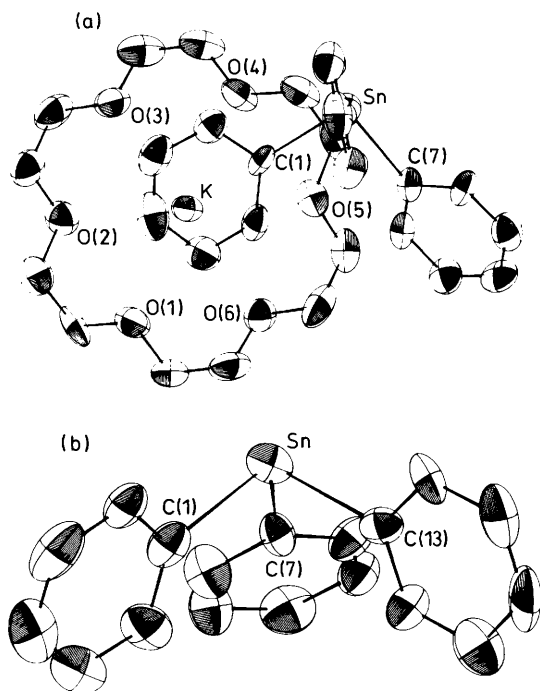
Mössbauer data are reported for the Li<sup>+</sup>, Na<sup>+</sup>, and K<sup>+</sup> salts of the triphenylstannide anion; the X-ray crystal structure of Ph<sub>3</sub>SnK(18-crown-6) shows that the triphenylstannide is a naked pyramidal ion (Sn–C 2.224 Å, C–Sn–C, 96.9°): no solvent molecules are incorporated into the structure.

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Salts of the triphenylstannide anion have not been well characterized, either in solution or in the solid state, although they are widely used in the syntheses of both organic and inorganic compounds.<sup>1</sup> These anions are easily generated in solution either by treating the parent hydride with alkali metal,<sup>2</sup> or by cleavage of hexaphenylditin, again by alkali metals.<sup>3</sup> The tin-119 Mössbauer spectrum of solid triphenyl-

stannyl-lithium has been reported and shows only a single absorption line.<sup>4</sup> We now report the single crystal X-ray structure of triphenylstannylpotassium-18-crown-6.

For the series of triphenylstannide salts, cation-anion interactions should strongly affect the <sup>119</sup>Sn Mössbauer parameters. We have therefore examined these species as frozen solutions by Mössbauer spectroscopy. Spectra of these



**Figure 1.** (a) Structure of  $\text{Ph}_3\text{SnK}(18\text{-crown-6})$ ; selected bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ): Sn–C(1) 2.239(6), Sn–C(7) 2.207(6), Sn–C(13) 2.227(6), K–O(1) 2.799(5), K–O(2) 2.768(5), K–O(3) 2.851(5), K–O(4) 2.783(6), K–O(5) 2.764(5), K–O(6) 2.848(6), C(1)–Sn–C(7) 96.8(2), C(1)–Sn–C(13) 96.1(2), C(7)–Sn–C(13) 97.7(2); (b) structure of the naked  $\text{Ph}_3\text{Sn}^-$  ion.

compounds, in frozen ether solvents, have been reported before,<sup>5,6</sup> but with different interpretations. These spectra were observed to consist of two lines of unequal intensity, the strongest at *ca.* 1.3 and the weaker at *ca.* 3.0  $\text{mm s}^{-1}$ . One interpretation<sup>5</sup> was that these two resonances arise from solvent-separated ion pairs and contact ion pairs, respectively. This suggestion did not appear reasonable since the Mössbauer spectrum of solid triphenylstannyl-lithium had been reported as having a single absorption line at *ca.* 1.3  $\text{mm s}^{-1}$  (ref. 4) and we find a shift of 1.12  $\text{mm s}^{-1}$ . A second interpretation<sup>6</sup> was that the line at 1.3  $\text{mm s}^{-1}$  arose from a contact ion pair while that at *ca.* 3.0  $\text{mm s}^{-1}$  was in reality one half of a quadrupole doublet arising from solvent-separated ion pairs, the second component of which lay beneath the resonance at *ca.* 1.3  $\text{mm s}^{-1}$ .

Here we present some recent frozen solution Mössbauer data for triphenylstannide salts in tetrahydrofuran (THF) and in liquid ammonia. † Two resonance lines were observed in all cases but, except for the  $\text{Li}^+$  and  $\text{K}^+$  salts in THF, the two lines were of equal intensity; such a doublet could arise from a tin nucleus in an asymmetric environment. The spectra from the  $\text{Li}^+$  and  $\text{K}^+$  salts in THF are similar to those previously reported<sup>5,6</sup> and we have fitted these spectra to a doublet and a single line. The isomer shifts of these single absorptions are the same within experimental error and comprise *ca.* 40% of the total spectrum. The shift of this resonance is in the  $\text{Sn}^{\text{IV}}$  region of the spectrum, *i.e.*  $< 2.0 \text{ mm s}^{-1}$ , while the shift of the

other component is slightly greater than  $2.0 \text{ mm s}^{-1}$ ; the latter is a doublet, consistent with its origin in a  $\text{Sn}^{\text{III}}$ -like species. A strong interaction between the anion and cation would give the tin four contacts; hence it would be considered as a  $\text{Sn}^{\text{IV}}$  species.

Crystallization of these compounds has proved difficult, but we were successful in isolating a crystalline product from a solution of the  $\text{K}^+$  salt in 1,2-dimethoxyethane, after the addition of 18-crown-6. The  $^{119}\text{Sn}$  Mössbauer spectrum of this product consists of two equal intensity lines which we interpret as a quadrupole doublet: it has parameters identical with those of the doublets observed from a frozen solution. Mass spectrometric analysis (fast atom bombardment) did not show a fragment attributable to a parent ion, but peaks due to the triphenyltin and 18-crown-6 moieties were observed; no fragments arising from THF were present. A single-crystal X-ray analysis showed the compound to be  $\text{Ph}_3\text{SnK}\cdot\text{C}_{12}\text{H}_{24}\text{O}_6$ . ‡

The structure consists of a pyramidal triphenyltin anion (Figure 1) with an average C–Sn distance of 2.224  $\text{\AA}$ , 0.10  $\text{\AA}$  greater than that in tetraphenyltin.<sup>11</sup> The average C–Sn–C angle ( $96.9^\circ$ ) is much less than the tetrahedral value. These data suggest that the C–Sn bonds have a lower *s* character, with the non-bonding electron pair of the stannide ion compensating for this change. The tin nucleus becomes more shielded and this is reflected in the more positive Mössbauer isomer shift in comparison with tetraphenyltin. The low symmetry at the tin nucleus explains the large quadrupole splitting of 1.86  $\text{mm s}^{-1}$ . Six oxygen atoms from the 18-crown-6 co-ordinate the  $\text{K}^+$ , with K–O distances ranging from 2.764(5) to 2.851(5)  $\text{\AA}$ . All other bond distances in the 18-crown-6 are as expected. Of considerable interest is the location of the  $\text{K}^+$  relative to the tin. These two atoms are  $>6 \text{\AA}$  apart; furthermore,  $\text{K}^+$  does not lie on the pseudo-three-fold axis of the anion. There is then no anion–cation interaction in the normal sense. Examination of the structure reveals that the  $\text{K}^+$  is sandwiched between two phenyl rings, one from each of two different anions, and it is this interaction that links the ions in the unit cell. This structure analysis clearly establishes that no solvent molecules are present.

From all these data it seems clear that the asymmetric two-line  $^{119}\text{Sn}$  Mössbauer spectra observed for frozen solutions of triphenyltin salts<sup>5,6</sup> do result from the overlap of a quadrupole doublet and a single resonance absorption. The

‡ *Crystal data:*  $(\text{C}_6\text{H}_5)_3\text{SnK}(\text{C}_{12}\text{H}_{24}\text{O}_6)$ ,  $M = 653.4$ , orthorhombic, space group  $P2_12_12_1$  (No. 19),  $a = 9.740(1)$ ,  $b = 12.811(1)$ ,  $c = 24.771(1) \text{\AA}$ ,  $U = 3090.9(1) \text{\AA}^3$ ,  $Z = 4$ ,  $D_c = 1.40 \text{ g cm}^{-3}$ ,  $T = 295 \text{ K}$ ,  $F(000) = 1341.2$  (calc. using anomalous dispersion corrections<sup>7</sup>),  $\mu(\text{Mo-K}\alpha) = 10.04 \text{ cm}^{-1}$ . The structure solution and refinement were based on 3705 observed ( $I > 0$ )<sup>8</sup> reflections (from 4346 measured intensities,  $2\theta < 45^\circ$ ) obtained with a Syntex  $P2_1$  diffractometer. Absorption corrections were not applied [estimated conceivable errors in  $F$  are *ca.* 1.12% (min) and *ca.* 1.22% (max)]. The positional parameters of the tin atoms were determined from a three-dimensional Patterson map. The remaining non-hydrogen atoms were located from subsequent electron density difference maps. The hydrogen atom positions were calculated and refined with their temperature factors fixed at  $0.08 \text{\AA}^2$ . A block diagonal refinement (consisting of the one block comprising the 'cation,' NP = 245; and a second block comprising the 'anion,' NP = 218) including anisotropic temperature factors (SHELX 76)<sup>9</sup> converged at  $R = 0.063$ ,  $R_w = 0.035$ . The weighting scheme was of the form  $w = 1/[\sigma^2(F) + gF^2]$ , where  $g = 0.000064$ . The highest peak in the difference map was  $0.77 \text{ e \AA}^{-3}$  (0.3176, 0.1795, 0.6640). The other enantiomer converged at  $R = 0.065$ ,  $R_w = 0.039$ ; Hamilton test on these  $R$  values revealed the correct handedness of the structure.<sup>10</sup>

Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

†  $^{119}\text{Sn}$  Mössbauer isomer shifts at 77 K relative to  $\text{CaSnO}_3$  at 298 K, quadrupole splittings ( $\text{mm s}^{-1}$ ), and contributions (%) for  $\text{Ph}_3\text{SnM}$  ( $M = \text{Li}^+$ ,  $\text{Na}^+$ , or  $\text{K}^+$ ) in THF or  $\text{NH}_3$ :  $\text{Li}^+$  (THF) 1.30(8), 0.0, 38, 2.15(8), 1.87(2), 62; ( $\text{NH}_3$ ) 2.03(1), 1.83(1), 100;  $\text{Na}^+$  (THF) 2.14(1), 1.86(2), 100; ( $\text{NH}_3$ ) 2.09(1), 1.86(1), 100;  $\text{K}^+$  (THF) 1.42(6), 0.0, 40, 2.16(5), 1.82(9), 60; ( $\text{NH}_3$ ) 2.05(1), 1.88(1), 100; and for  $\text{Ph}_3\text{SnK}(18\text{-crown-6})$  (solid): 2.13(2), 1.86(2).

doublet arises from the naked triphenylstannide ion, and its counter cation may or may not be solvated. The single line could result from the  $\text{Ph}_3\text{SnM}$  contact ion pair in solution, or from the precipitated salt: this remains to be determined.

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### References

- 1 A. G. Davies and J. C. Sciano, *J. Chem. Soc., Perkin Trans. 2*, 1973, 1977; W. Kuchen and H. Buchwald, *Chem. Ber.*, 1959, **92**, 227.
  - 2 S. F. A. Kettle, *J. Chem. Soc.*, 1959, 2936.
  - 3 C. A. Kraus and W. N. Greer, *J. Am. Chem. Soc.*, 1925, **47**, 2568.
  - 4 A. Yu. Aleksandrov, O. Yu. Okhlobystin, L. S. Polak, and V. S. Shpinel, *Dokl. Akad. Nauk. SSSR*, 1964, **157**, 934.
  - 5 K. A. Bilevich, V. I. Gol'danskii, V. Ya. Rochov, and V. V. Kraphov, *Akad. Nauk. SSSR., Bull. Div. Chem. Sci.*, 1969, 1583.
  - 6 T. Birchall and A. R. Perriera, *J. Chem. Soc., Dalton Trans.*, 1975, 1087.
  - 7 D. T. Cromer and J. T. Waber, 'International Tables for X-Ray Crystallography,' eds. J. A. Ibers and W. C. Hamilton, Kynoch Press, Birmingham, England, 1974, vol. IV, Table 2.3.1, p. 149.
  - 8 L. Arnberg, S. Hövmoller, and S. Westman, *Acta. Crystallogr., Ser. A*, 1979, **35**, 497; P. Seiler, W. B. Schweizer, and J. D. Dunitz, *Acta. Crystallogr., Ser. B*, 1984, **40**, 319.
  - 9 G. M. Sheldrick, SHELX: Program for Crystal Structure Determination, University of Cambridge, 1976.
  - 10 W. C. Hamilton, *Acta. Crystallogr.*, 1965, **18**, 502.
  - 11 P. C. Chieh and J. Trotter, *J. Chem. Soc. A*, 1970, 911.
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