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+, Na+, and K+ salts of the triphenylstannide anion; the X-ray crystal structure of Ph_3SnK(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.

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.[1] These anions are easily generated in solution either by treating the parent hydride with alkali metal,[2] or by cleavage of hexaphenylditin, again by alkali metals.[3] The tin-119 Mössbauer spectrum of solid triphenyl-

stannyl-lithium has been reported and shows only a single absorption line.[4] 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 [119]Sn Mössbauer parameters. We have therefore examined these species as frozen solutions by Mössbauer spectroscopy. Spectra of these
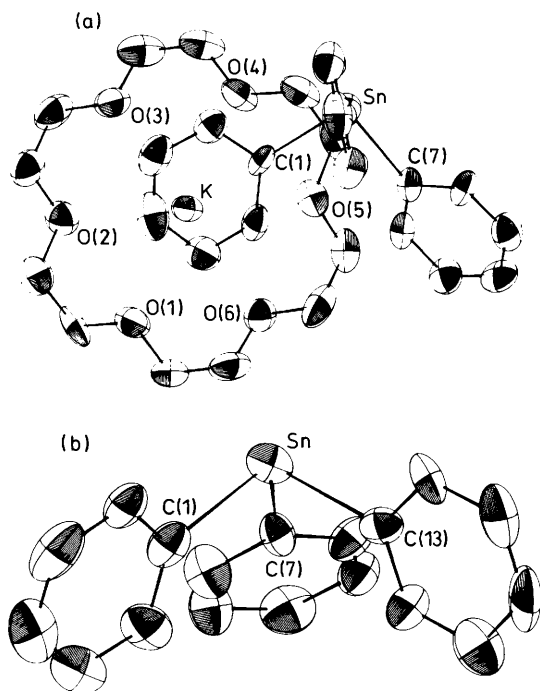
Figure 1. (a) Structure of Ph₃SnK(18-crown-6); selected bond lengths (Å) and angles (°): Sn–C(1) 2.239(6), Sn–C(7) 2.207(6), Sn–C(13) 2.227(6), K–O(1) 2.799(5), K–O(2) 2.768(5), K–O(3) 2.851(5), K–O(4) 2.783(6), K–O(5) 2.764(5), K–O(6) 2.848(6), C(1)–Sn–C(7) 96.8(2), C(1)–Sn–C(13) 96.1(2), C(7)–Sn–C(13) 97.7(2); (b) structure of the naked Ph₃Sn⁻ ion.

compounds, in frozen ether solvents, have been reported before,[5,6] 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 mm s⁻¹. One interpretation[5] was that these two resonances arise from solvent-separated ion pairs and contact ion pairs, respectively. This suggestion did not appear reasonable since the Möss-bauer spectrum of solid triphenylstannyl-lithium had been reported as having a single absorption line at *ca.* 1.3 mm s⁻¹, (ref. 4) and we find a shift of 1.12 mm s⁻¹. A second interpretation[6] was that the line at 1.3 mm s⁻¹ arose from a contact ion pair while that at *ca.* 3.0 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 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 Li⁺ and 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 Li⁺ and K⁺ salts in THF are similar to those previously reported[5,6] 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 Snᴵⱽ region of the spectrum, *i.e.* < 2.0 mm s⁻¹, while the shift of the

other component is slightly greater than 2.0 mm s⁻¹; the latter is a doublet, consistent with its origin in a Snᴵᴵ-like species. A strong interaction between the anion and cation would give the tin four contacts; hence it would be considered as a Snᴵⱽ species.

Crystallization of these compounds has proved difficult, but we were successful in isolating a crystalline product from a solution of the K⁺ salt in 1,2-dimethoxyethane, after the addition of 18-crown-6. The ¹¹⁹Sn 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 Ph₃SnK·C₁₂H₂₄O₆.‡

The structure consists of a pyramidal triphenyltin anion (Figure 1) with an average C–Sn distance of 2.224 Å, 0.10 Å greater than that in tetraphenyltin.[11] The average C–Sn–C angle (96.9°) 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 mm s⁻¹. Six oxygen atoms from the 18-crown-6 co-ordinate the K⁺, with K–O distances ranging from 2.764(5) to 2.851(5) Å. All other bond distances in the 18-crown-6 are as expected. Of considerable interest is the location of the K⁺ relative to the tin. These two atoms are >6 Å apart; furthermore, 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 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 ¹¹⁹Sn Mössbauer spectra observed for frozen solutions of triphenyltin salts[5,6] do result from the overlap of a quadrupole doublet and a single resonance absorption. The

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doublet arises from the naked triphenylstannide ion, and its counter cation may or may not be solvated. The single line could result from the Ph_3SnM contact ion pair in solution, or from the precipitated salt: this remains to be determined.

Received, 1st December 1987; Com. 1741

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