# Elucidation of Medium Effects on Molecular Structure by Solid-State and Solution $^{13}$C NMR. Identification and X-ray Structure of the Orthorhombic Modification of Dimethyltin(IV) Bis(N,N-diethyldithiocarbamate)

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**Abstract:** Solid-state and solution $^{13}$C NMR has been used to investigate medium effects on the molecular structures of Me$_2$Sn(acac)$_2$ (acac = acetylacetonate) and Me$_2$Sn(S$_2$CNEt$_2$)$_2$. The magnitude of the Me–Sn–Me angle in different phases is obtained from analysis of the tin–carbon $J$ coupling [|$^1J$($^{119}$Sn,$^{13}$C)|] data. The Me–Sn–Me angle of Me$_2$Sn(acac)$_2$ changes from 180° in the solid state (known from X-ray) to about 158° in benzene and 161° in CDCl$_3$ (estimated from the solution |$^3J$($^{119}$Sn,$^{13}$Cl)| values). Two explanations, that a single molecule (with Me–Sn–Me = ca. 160°) exists in solution or that rapid cis–trans equilibrium occurs, are consistent with the result. The solid-state NMR data for a sample of Me$_2$Sn(S$_2$CNEt$_2$)$_2$ conflict with the molecular structures of two X-ray characterized crystalline modifications [one of which contains two symmetry-independent molecules of Me$_2$Sn(S$_2$CNEt$_2$)$_2$]. The suggestion that this is a third crystalline form was confirmed by X-ray analysis. The new, orthorhombic modification (space group *Pbca*) of SnS$_4$N$_2$C$_{12}$H$_{26}$ has $a$ = 9.929 (2) Å, $b$ = 31.176 (5) Å, $c$ = 12.852 (1) Å, $Z$ = 8; $R$ was refined to 0.020. The solid-state NMR-derived estimate of the Me–Sn–Me angle, 136°, was confirmed by X-ray analysis [135.6 (2)°]. In solution, Me$_2$Sn(S$_2$CNEt$_2$)$_2$ appears to adopt a conformation similar to that of the orthorhombic modification described here.

We have explored[2–4] the potential of solid-state NMR for use in the development of new, accurate relationships between NMR and structural parameters. Investigations of the solid-state NMR of structurally characterized polycrystalline methyltin(IV) compounds revealed[3] that the magnitude of tin–carbon spin coupling, |$^1J$($^{119}$Sn,$^{13}$C)|, is linearly correlated with the size of the Me–Sn–Me angle according to eq 1, where |$^1J$| is the magnitude of

$$|^1J| = 11.4(\theta) - 875 \tag{1}$$

$^1J$($^{119}$Sn,$^{13}$C) (in Hz) and $\theta$ is the Me–Sn–Me angle (in degrees). The close adherence to this relationship of experimental data for most[5] tetramethyltin and tetra-, penta-, and hexacoordinated di- and trimethyltin(IV) compounds makes it extremely useful for deducing $\theta$ of structurally uncharacterized methyltin(IV) compounds.[6,7]

Because tin–carbon $J$ coupling can be measured in both the solid state and in solution, eq 1 may be used to estimate the Me–Sn–Me angle of methyltin(IV) species in either medium.[4] In this way it may provide a simple, accurate probe for determining the influence of different environments (solution, melt, solid) on molecular structure. In this paper we report solid-state and solution $^{13}$C NMR studies on two dimethyltin(IV) compounds which illuminate and quantify changes in their molecular conformations in different media. The existence and structural features of a new

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(2) Manders, W. F.; Lockhart, T. P. *J. Organomet. Chem.* **1985**, *297*, 143.

(3) Lockhart, T. P.; Manders, W. F.; Zuckerman, J. J. *J. Am. Chem. Soc.* **1985**, *107*, 4546.

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(5) To date, the only significant exceptions we have found are for the structurally rare *cis*-dimethyl octahedral compounds Me$_2$Sn(oxinate)$_2$ and Me$_2$Sn(N-acetylhydroxylamine)$_2$ ($\theta$ = 110.7° and 109.1°, respectively) for which |$^1J$| is some 200 Hz larger than predicted [ref 3 and unpublished results].

(6) Lockhart, T. P.; Manders, W. F. *J. Am. Chem. Soc.* **1985**, *107*, 5863.

(7) Lockhart, T. P.; Manders, W. F.; Schlemper, E. O. *J. Am. Chem. Soc.* **1985**, *107*, 7451.

**Table I.** Solid-State and Solution $^{13}$C NMR Data for Me$_2$Sn(S$_2$CNEt$_2$)$_2$ and Me$_2$Sn(acac)$_2$

| compd | medium | Me–Sn chemical shift,[a] ppm | [$^1J$($^{119}$Sn,$^{13}$C)], Hz |
|---|---|---|---|
| Me$_2$Sn(S$_2$CNEt$_2$)$_2$ | orthorhombic cryst | 16.47, 15.17 | 675 |
| | solution: | | |
| | CDCl$_3$ | 15.3 | 668[b] |
| | C$_6$D$_6$ | 16.0 | 675 |
| | acetone-d$_6$ | 15.7 | 682 |
| Me$_2$Sn(acac)$_2$ | monoclinic cryst | 11.4 | 1175 |
| | solution: | | |
| | CDCl$_3$ | 7.8 | 966[c] |
| | C$_6$D$_6$ | 8.9 | 929 |

[a] Internal chemical shift standards: Me$_4$Si (0 ppm) for solutions, Delrin (89.1 ± 0.3 ppm) for solid Me$_2$Sn(acac)$_2$, linear polyethylene (33.63 ± 0.03 ppm) for Me$_2$Sn(S$_2$CNEt$_2$)$_2$. [b] Reported as 664 Hz in ref 15. [c] Mitchell, T. N. *J. Organomet. Chem.* **1973**, *59*, 189.

crystalline modification of dimethyltin bis(N,N-diethyldithiocarbamate), Me$_2$Sn(S$_2$CNEt$_2$)$_2$, revealed by solid-state NMR, are confirmed by a subsequent X-ray diffraction study.

## Results

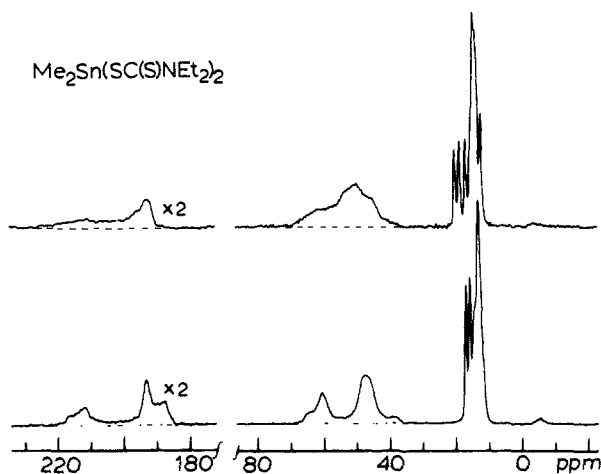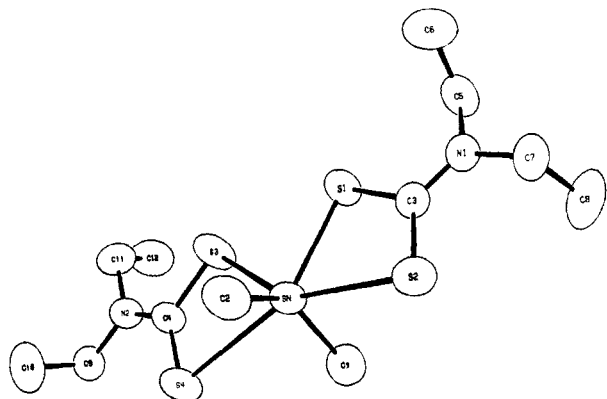Solid-state and solution $^{13}$C NMR data for Me$_2$Sn(acac)$_2$ (acac = acetylacetonate) and Me$_2$Sn(S$_2$CNEt$_2$)$_2$ are given in Table I. The solid-state spectra of pure orthorhombic and a mixture of orthorhombic, monoclinic, and triclinic modifications of Me$_2$Sn(S$_2$CNEt$_2$)$_2$ are shown in Figure 1. For the orthorhombic material (bottom of figure) two narrow resonances (16.47, 15.17 ppm) are observed for the two inequivalent methyls bonded to tin. The fused $^{117}$Sn and $^{119}$Sn satellites appear equidistant from the uncoupled Me$_2$Sn resonances. The $^{13}$C resonances of the dithiocarbamate ligand are significantly influenced by interaction with quadrupolar $^{14}$N: the directly bonded carbamate and methylene carbons (184–215 and 42–66 ppm, respectively) are unsymmetrically split; the methyl group of the ligand (11.94 ppm) is broadened to a width at half-height of about 30 Hz. The presence of the additional modifications of Me$_2$Sn(S$_2$CNEt$_2$)$_2$ (which were identified by single-crystal X-ray unit cell determinations) is evident in the upper

*Elucidation of Medium Effects on Molecular Structure*

*J. Am. Chem. Soc., Vol. 108, No. 14, 1986* 4075



Me$_2$Sn(SC(S)NEt$_2$)$_2$

**Figure 1.** Solid-state $^{13}$C NMR spectra of polycrystalline Me$_2$Sn-(S$_2$CNEt$_2$)$_2$. Upper spectrum, mixed crop of orthorhombic, monoclinic, and triclinic crystalline modifications of Me$_2$Sn(S$_2$CNEt$_2$)$_2$ (resolved methyltin resonances at 19.71, 18.25, 16.47, 11.94 ppm). Lower spectrum, orthorhombic modification (methyltin resonances at 16.47 and 15.17 ppm). $^{117,119}$Sn satellites visible in lower spectrum. In both spectra, broad, unsymmetrical doublets are observed for ligand $^{13}$C's coupled to $^{14}$N.

**Table III.** Final Atomic Parameters for the Orthorhombic Modification of Me$_2$Sn(S$_2$CNEt$_2$)$_2$$^{a,b}$

| atom | $x$ | $y$ | $z$ | $B$ (Å$^2$) |
|---|---|---|---|---|
| Sn | 0.35149 (2) | 0.12447 (1) | 0.04083 (2) | 3.940 (5) |
| S$_1$ | 0.3738 (1) | 0.20050 (3) | −0.01535 (6) | 4.71 (2) |
| S$_2$ | 0.4054 (1) | 0.18525 (3) | 0.21045 (6) | 5.03 (2) |
| S$_3$ | 0.3074 (1) | 0.11366 (3) | −0.15008 (7) | 6.09 (2) |
| S$_4$ | 0.3132 (1) | 0.03202 (3) | −0.03206 (6) | 5.92 (2) |
| N$_1$ | 0.4425 (2) | 0.26069 (7) | 0.1181 (2) | 3.66 (5) |
| N$_2$ | 0.2645 (3) | 0.03771 (7) | −0.2344 (2) | 4.26 (6) |
| C$_1$ | 0.5491 (4) | 0.1025 (1) | 0.0689 (3) | 5.69 (9) |
| C$_2$ | 0.1607 (4) | 0.1158 (1) | 0.1122 (3) | 5.90 (9) |
| C$_3$ | 0.4115 (3) | 0.21987 (9) | 0.1091 (2) | 3.57 (6) |
| C$_4$ | 0.2921 (4) | 0.05780 (9) | −0.1457 (2) | 4.38 (7) |
| C$_5$ | 0.4541 (4) | 0.2900 (1) | 0.0287 (2) | 4.61 (7) |
| C$_6$ | 0.3254 (4) | 0.3130 (1) | 0.0053 (3) | 6.4 (1) |
| C$_7$ | 0.4702 (3) | 0.2798 (1) | 0.2209 (2) | 4.48 (7) |
| C$_8$ | 0.6165 (4) | 0.2775 (1) | 0.2471 (3) | 6.6 (1) |
| C$_9$ | 0.2549 (3) | −0.00895 (9) | −0.2394 (3) | 4.63 (7) |
| C$_{10}$ | 0.1145 (4) | −0.0252 (1) | −0.2222 (4) | 7.6 (1) |
| C$_{11}$ | 0.2441 (4) | 0.0602 (1) | −0.3338 (2) | 5.42 (8) |
| C$_{12}$ | 0.3696 (5) | 0.0656 (1) | −0.3948 (3) | 7.2 (1) |

$^a$ Estimated standard deviations for the the last digit in parentheses. $^b$ Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab\cos\gamma\,B(1,2) + ac\cos\beta\,B(1,3) + bc\cos\alpha\,B(2,3)]$.



**Figure 2.** Molecular structure of the orthorhombic modification of Me$_2$Sn(S$_2$CNEt$_2$)$_2$ showing atomic numbering scheme.

**Table II.** Influence of Medium on Structure of Me$_2$Sn(S$_2$CNEt$_2$)$_2$ and Me$_2$Sn(acac)$_2$

| compd | medium | Me–Sn–Me angle, deg |
|---|---|---|
| Me$_2$(Sn$_2$CNEt$_2$)$_2$ | triclinic cryst | 142.3 (2)$^a$ |
| | monoclinic cryst | |
| | molecule 1 | 142.8 (3)$^a$ |
| | molecule 2 | 136.9 (3)$^a$ |
| | orthorhombic cryst | 135.6 (6),$^b$ 136$^c$ |
| | solution: | |
| | CDCl$_3$ | 135$^c$ |
| | C$_6$D$_6$ | 136$^c$ |
| | acetone-$d_6$ | 137$^c$ |
| Me$_2$Sn(acac)$_2$ | crystalline (monoclinic) | 180.0$^d$, 180$^c$ |
| | solution: | |
| | CDCl$_3$ | 161$^c$ |
| | C$_6$H$_6$ | 158$^c$ |

$^a$ From ref 16. $^b$ This work. $^c$ Estimated from NMR data with eq 1. $^d$ From ref 10.

**Table IV.** Interatomic Distances and Bond Angles for the Orthorhombic Modification of Dimethyltin(IV) Bis($N,N$-diethyldithiocarbamate)$^a$

| Bond Distances (Å) | | | |
|---|---|---|---|
| Sn–S$_1$ | 2.488 (1) | C$_5$–C$_6$ | 1.495 (6) |
| Sn–S$_2$ | 2.938 (1) | C$_7$–N$_1$ | 1.475 (3) |
| Sn–S$_3$ | 2.515 (1) | C$_7$–C$_8$ | 1.494 (5) |
| Sn–S$_4$ | 3.054 (1) | C$_4$–S$_3$ | 1.749 (3) |
| Sn–C$_1$ | 2.109 (5) | C$_4$–S$_4$ | 1.680 (3) |
| Sn–C$_2$ | 2.123 (4) | C$_4$–N$_2$ | 1.329 (4) |
| C$_3$–S$_1$ | 1.750 (3) | C$_9$–N$_2$ | 1.459 (4) |
| C$_3$–S$_2$ | 1.693 (3) | C$_9$–C$_{10}$ | 1.499 (6) |
| C$_3$–N$_1$ | 1.315 (4) | C$_{11}$–N$_2$ | 1.471 (4) |
| C$_5$–N$_1$ | 1.473 (4) | C$_{11}$–C$_{12}$ | 1.481 (6) |

| Bond Angles (deg) | | | |
|---|---|---|---|
| S$_1$–Sn–S$_2$ | 65.46 (3) | Sn–S$_3$–C$_4$ | 96.7 (1) |
| S$_1$–Sn–S$_3$ | 81.95 (3) | Sn–S$_4$–C$_4$ | 80.3 (1) |
| S$_1$–Sn–S$_4$ | 145.20 (3) | S$_1$–C$_3$–S$_2$ | 118.4 (2) |
| S$_2$–Sn–S$_3$ | 147.37 (3) | S$_3$–C$_4$–S$_4$ | 119.6 (2) |
| S$_2$–Sn–S$_4$ | 149.20 (2) | S$_1$–C$_3$–N$_1$ | 117.7 (2) |
| S$_3$–Sn–S$_4$ | 63.43 (3) | S$_2$–C$_3$–N$_1$ | 123.9 (2) |
| C$_1$–Sn–C$_2$ | 135.6 (2) | S$_3$–C$_4$–N$_2$ | 117.3 (2) |
| C$_1$–Sn–S$_1$ | 106.1 (1) | S$_4$–C$_4$–N$_2$ | 123.1 (2) |
| C$_1$–Sn–S$_2$ | 85.0 (1) | C$_3$–N$_1$–C$_5$ | 123.4 (3) |
| C$_1$–Sn–S$_3$ | 106.6 (1) | C$_3$–N$_1$–C$_7$ | 121.0 (3) |
| C$_1$–Sn–S$_4$ | 82.0 (1) | C$_4$–N$_2$–C$_9$ | 121.4 (3) |
| C$_2$–Sn–S$_1$ | 109.1 (1) | C$_4$–N$_2$–C$_{11}$ | 123.3 (3) |
| C$_2$–Sn–S$_2$ | 85.7 (1) | N$_1$–C$_5$–C$_6$ | 112.8 (3) |
| C$_2$–Sn–S$_3$ | 104.4 (2) | N$_1$–C$_7$–C$_8$ | 111.3 (3) |
| C$_2$–Sn–S$_4$ | 84.3 (1) | N$_2$–C$_9$–C$_{10}$ | 113.0 (3) |
| Sn–S$_1$–C$_3$ | 94.7 (1) | N$_2$–C$_{11}$–C$_{12}$ | 113.5 (4) |
| Sn–S$_2$–C$_3$ | 81.2 (1) | C$_5$–N$_1$–C$_7$ | 115.6 (3) |
| | | C$_9$–N$_2$–C$_{11}$ | 115.3 (3) |

$^a$ Estimated standard deviations for the last digit in parentheses.

spectrum where new methyltin and dithiocarbamate ligand $^{13}$C resonances are visible.

Although the $^{117}$Sn and $^{119}$Sn satellites were not resolved for Me$_2$Sn(S$_2$CNEt$_2$)$_2$, $|^1J(^{119}$Sn,$^{13}$C)| can be calculated by multiplying the separation of the fused $^{117}$Sn and $^{119}$Sn satellites by 1.023 (the gyromagnetic ratios of the spin $^1/_2$ isotopes $^{117}$Sn and $^{119}$Sn are 1:1.046) because their natural abundances are similar (7.6 and 8.6%, respectively). Table II lists the Me–Sn–Me angle for both

compounds in their various crystalline modifications and in solution as determined by X-ray and estimated from solid-state and solution NMR data with use of eq 1.

Atomic coordinates and isotropic equivalent thermal parameters from the X-ray structure determination of the orthorhombic modification of Me$_2$Sn(S$_2$CNEt$_2$)$_2$ are given in Table III. Selected bond distances and angles of the orthorhombic modification are listed in Table IV, and the molecular structure showing the atomic numbering scheme is depicted in Figure 2. Selected bond distances and angles of the three known modifications of Me$_2$Sn(S$_2$CNEt$_2$)$_2$ are given in Table V and a comparison of their

**Table V.** Comparison of Selected Intramolecular Bond Angles and Distances in Four Crystalline Forms of $Me_2(S_2CNEt_2)_2$[a]

| | | crystalline form | | |
| --- | --- | --- | --- | --- |
| | | monoclinic[b] | | |
| | triclinic[b] | molecule 1 | molecule 2 | orthorhombic[c] |
| bond distances (Å) | | | | |
| Sn–C | 2.113 (4), 2.103 (4) | 2.13 (1) | 2.15 (1), 2.12 (1) | 2.109 (5), 2.123 (4) |
| Sn–S (short)[d] | 2.527 (9) | 2.520 (2) | 2.518 (6) | 2.502 (13) |
| Sn–S (long)[d] | 2.943 (25) | 2.947 (2) | 2.968 (36) | 2.996 (58) |
| bond angles (deg) | | | | |
| C–Sn–C | 142.3 (2) | 142.8 (3) | 136.9 (3) | 135.6 (2) |
| $S_1$–Sn–$S_2$ | 65.0 (1) | 64.6 (2) | 64.6 (2) | 65.46 (3) |
| $S_2$–Sn–$S_4$ | 147.7 (1) | 146.8 (2) | 149.3 (2) | 149.20 (2) |
| $S_4$–Sn–$S_3$ | 64.6 (1) | 64.6 (2) | 64.1 (2) | 63.43 (3) |
| $S_3$–Sn–$S_1$ | 82.2 (1) | 84.0 (2) | 82.0 (2) | 81.95 (3) |

[a] Estimated standard deviations for the last digit in parentheses. [b] From ref 16. [c] This work. [d] Average of two long and two short Sn–S distances per molecule (average deviation from mean in parentheses).

**Table VI.** Comparison of Intermolecular Distances (Å) in the Triclinic, Monoclinic, and Orthorhombic Modifications of $Me_2Sn(S_2CNEt_2)_2$[a]

| triclinic modification | | monoclinic modification | | orthorhombic modification | |
| --- | --- | --- | --- | --- | --- |
| $S_1$–$C_5$ | 3.86 (1) | $S_1$–$C_6$ | 3.63 (1) | $S_1$–$C_7$ | 3.575 (3) |
| $S_1$–$C_{11}$ | 3.83 (1) | $S_1$–$C_9$ | 3.72 (1) | $S_1$–$C_8$ | 3.983 (5) |
| $S_2$–$C_1$ | 3.62 (1) | $S_2$–$C_7$ | 3.96 (1) | $S_1$–$C_8$ | 3.950 (5) |
| $S_2$–$C_2$ | 3.96 (1) | $S_3$–$C_9$ | 3.67 (1) | $S_2$–$C_6$ | 3.873 (5) |
| $S_2$–$C_6$ | 3.97 (1) | $S_4$–$C_1$ | 3.79 (1) | $S_4$–$C_9$ | 3.889 (4) |
| $C_2$–$C_{10}$ | 3.98 (1) | $C_2$–$C_8$ | 3.96 (1) | $S_4$–$C_{11}$ | 3.883 (4) |
| $C_3$–$C_7$ | 3.93 (1) | $C_3$–$C_7$ | 3.79 (1) | $S_4$–$C_{12}$ | 3.958 (5) |
| Sn–$S_2$ | 3.86 (1) | $C_3$–$C_8$ | 3.88 (1) | $N_1$–$C_8$ | 3.705 (5) |
| $S_2$–$S_2$ | 3.60 (1) | $S_3$–$S_{2'}$ | 3.66 (1) | $C_1$–$C_6$ | 3.923 (7) |
| $S_3$–$S_3$ | 3.97 (1) | $S_1$–$C_{7'}$ | 3.73 (1) | $C_1$–$C_{10}$ | 3.957 (7) |
| $S_3$–$C_5$ | 3.98 (1) | $S_2$–$C_{1'}$ | 3.66 (1) | $C_1$–$C_{11}$ | 3.824 (6) |
| $S_3$–$C_{11}$ | 3.78 (1) | $S_3$–$C_{7'}$ | 3.90 (1) | $C_2$–$C_9$ | 3.928 (6) |
| $S_4$–$C_9$ | 3.83 (1) | $S_4$–$C_{8'}$ | 3.92 (1) | $C_3$–$C_8$ | 3.901 (6) |
| $N_1$–$C_6$ | 3.99 (1) | $C_2$–$S_{2'}$ | 3.77 (1) | $C_6$–$C_8$ | 3.955 (6) |
| $N_2$–$C_9$ | 3.91 (1) | $C_5$–$S_{1'}$ | 3.66 (1) | $C_7$–$C_8$ | 3.536 (6) |
| $C_4$–$C_9$ | 3.93 (1) | $C_4$–$C_{5'}$ | 3.85 (1) | $C_9$–$C_{10}$ | 3.640 (6) |
| $C_8$–$C_{12}$ | 3.96 (1) | $C_6$–$C_{1'}$ | 3.75 (1) | | |
| $C_9$–$C_9$ | 3.74 (1) | $C_9$–$C_{7'}$ | 3.82 (1) | | |
| | | $C_{12}$–$C_{3'}$ | 3.85 (1) | | |
| cell vol/ molecule (Å³) | 490.7 | | 496.4 | | 497.3 |

[a] Estimated standard deviations for the last digit in parentheses.

intermolecular contacts in Table VI.

## Discussion

The structure of $Me_2Sn(acac)_2$ in solution has been the subject of debate, arguments in support of both *trans*-dimethyl[8] and *cis*-dimethyl[9] octahedral geometries having been presented. The $|^1J|$ of crystalline $Me_2Sn(acac)_2$, where the Me–Sn–Me angle is known to be 180.0°,[10] is 1175 Hz, the largest that we have observed to date.[2–4,6,7] In solution, $|^1J|$ decreases more than 200 Hz, indicating Me–Sn–Me angles of about 161° in $CDCl_3$ and 158° in benzene (Table II); thus our data strongly confirm dipole moment and IR studies which indicated a nonlinear Me–Sn–Me angle in solution. Interestingly, extended-Hückel MO calculations[11] indicate a broad, local minimum on the $Me_2Sn(acac)_2$ energy surface for θ between 140 and 160° (other minima occur at 90 and 180°). However, an alternate interpretation of the decrease in the Me–Sn–Me angle is that it reflects rapid equilibration of cis and trans conformations on the NMR time scale

in solution. This would also produce a single value of $|^1J|$, intermediate between those associated with the linear and bent Me–Sn–Me geometries. Although low-temperature NMR studies have failed to provide evidence for more than a single form in solution,[12] solution and solid-state IR studies[13] and the apparent anisotropy measured in light scattering experiments[14] provide evidence for the coexistence of both *trans*- and *cis*-dimethyl isomers of $Me_2Sn(acac)_2$ in solution.

It is of interest to note that $|^1J|$ of $Me_2Sn(acac)_2$ was taken as the prototypical *trans*-dimethyltin(IV) in earlier attempts[15–17] to explore the relationship between $|^1J|$, measured in solution, and the Me–Sn–Me angle of hexacoordinated dimethyltin(IV) compounds. The large decrease in the Me–Sn–Me angle (or the presence of a second isomeric form) in solution, however, vividly illustrates the vulnerability to unanticipated and unquantifiable medium effects of attempts to develop NMR/structure correlations in solution.

Two crystalline modifications of $Me_2Sn(S_2CNEt_2)_2$ were known[16] prior to the present study. However, the solid-state NMR spectrum of the $Me_2Sn(S_2CNEt_2)_2$ crystals we isolated (Figure 1; $|^1J|$ = 675 Hz, estimated θ = 136°) was inconsistent with either of them: in the triclinic modification θ = 142.3 (2)°, and in the monoclinic modification there are two independent molecules, with θ = 142.8 (3) and 136.9 (3)°.[16] In addition, on the basis of symmetry considerations, three $^{13}C$ resonances are likely for methyl bonded to tin in the monoclinic form, rather than the two observed. Our X-ray analysis of these crystals confirms that they are, indeed, a new, third crystalline form (orthorhombic) of $Me_2Sn(S_2CNEt_2)_2$ containing molecules structurally distinct from the three others known. The estimated Me–Sn–Me angle, 136°, from solid-state NMR is in close agreement with that found by X-ray, 135.6 (2)°. The suggestion from the solid-state $^{13}C$ NMR spectrum that the two methyls bonded to tin are not identical in the orthorhombic modification is also verified by the X-ray structure.

The structural features of the orthorhombic modification of $Me_2Sn(S_2CNEt_2)_2$ are generally similar to those of the monoclinic and triclinic forms[16] and to two other dimethyltin bis(dithiocarbamates), $Me_2Sn(S_2CNMe_2)_2$[18] and $Me_2Sn[S_2CN(CH_2)_4]_2$,[7] that have been structurally characterized. The dithiocarbamate ligands in $Me_2Sn(S_2CNEt_2)_2$ are anisobidentically chelated to tin, with one longer and one shorter Sn–S bond (av = 2.996 (58) and 2.502 (13) Å, respectively). The long Sn–S distances are significantly less than the sum of the van der Waals radii (4.0 Å),[19] and the coordination number of tin is unambiguously assigned

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*Elucidation of Medium Effects on Molecular Structure*

*J. Am. Chem. Soc., Vol. 108, No. 14, 1986* 4077

as six. The overall geometry at tin is, however, highly distorted from trans octahedral: the C–Sn–C angle is only 135.6 (2)°, and the tin and four $NCS_2$ sulfur atoms of the dithiocarbamate ligands are nearly coplanar but are badly distorted from square-planar geometry (cis S–Sn–S angles range from 63.43 (3) to 147.37 (3)°). The similarity of the solution and crystal Me–Sn–Me angles of $Me_2Sn(S_2CNEt_2)_2$ indicates unambiguously that the distorted octahedral conformation of these molecules is not imposed by lattice effects.

Given the remarkable polymorphism of this compound, it is of interest to compare the structures found in the various crystalline forms and in solution. Lattice effects must play some role in determining the molecular structure of the different crystalline modifications of $Me_2Sn(S_2CNEt_2)_2$, but in solution the compound is free of solid-state packing constraints on molecular structure.[20] Though energetically favorable interactions with solvent molecules could, in principle, play a major role in determining the solution conformation of $Me_2Sn(S_2CNEt_2)_2$, the similarity of the estimated $\theta$ in $CDCl_3$, benzene, and acetone suggests that such specific interactions are insignificant relative to internal electronic and steric factors. The preference for a small Me–Sn–Me angle in solution, therefore, suggests that this conformation is the lowest energy form in the absence of solid-state lattice effects.

It seems reasonable to suppose that the tightest packing in the solid state, which maximizes van der Waals attractions, is likely to require at least modest bond reorganization. Given the polymorphism of $Me_2Sn(S_2CNEt_2)_2$, this appears to be energetically feasible. Following this argument, the triclinic form, which has the smallest cell volume per molecule (Table VI), should be the most stable. The orthorhombic form, which appears to be more closely related to the structure in solution (Table II), has the largest cell volume; this suggests that it is subjected to the least bond reorganization during crystallization and may be the *kinetic* fusion product.

Of course the lowest energy reference conformation would be revealed in the structure of the field-free, gas-phase form of the ground-state molecules. Unfortunately, the complexity of the title compound deters such a determination. These unconstrained molecules could enter an inert-gas matrix or innocent solvent with their lowest energy conformations relatively intact. However, solvents capable of forming strong van der Waals interactions, those forming efficient solvent cages, or those containing donor atoms, especially atoms so juxtaposed as to be capable of chelation, crown, or cryptand behavior, or molten salts, would progressively distort the reference conformation. Condensation into the solid would presumably impose additional constraints on structure. But the reference conformation could survive transfer to the solid state intact if the competition between the minimization of internal energy of the molecules and the energy of the lattice reaches a compromise favoring the former. This could occur if the reference conformation is capable of efficient packing, maximizing attractive intermolecular interactions, for example, by adopting modes involving the mutual interpenetration of the individual units. Thus, a high-density solid could in principle contain molecules in the gas-phase conformation, whose distortion to a higher energy conformation would produce a phase of lower density. This is the opposite view to the one taken above and appears to us to be less likely.

The effort to obtain crops of pure monoclinic and triclinic $Me_2Sn(S_2CNEt_2)_2$ brings into focus one difficulty that may be encountered in solid-state NMR structural studies. A mixed crop containing different crystalline forms can prevent a satisfactory structural analysis unless either the resonances or satellites of interest are well-resolved, or it is possible to separate chemically or manually the 0.2–0.4 g of each crystalline type required for NMR. In contrast, since X-ray structure determination requires a single, small crystal of each type, a mixed crop may yield suitable crystals for analysis of each type in the mixture. The solid-state NMR spectrum in Figure 1 (top) illustrates this point: in addition

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**Table VII.** Crystal and Data Collection Parameters for the Orthorhombic Modification of Dimethyltin(IV) Bis($N,N$-diethyldithiocarbamate)[a]

| | |
|---|---|
| formula | $SnS_4N_2C_{12}H_{26}$ |
| fw | 445.30 |
| space group | *Pbca* |
| system | orthorhombic |
| $a$, Å | 9.929 (2) |
| $b$, Å | 31.176 (5) |
| $c$, Å | 12.852 (1) |
| $V$, Å$^3$ | 3978.3 |
| $Z$ | 8 |
| $d_{calcd}$, g/cm$^{-3}$ | 1.487 (1) |
| $d_{obsd}$(flotation) | 1.48 (1) |
| crystal size, mm | hexagonal plate, 0.16 × 0.33 × 0.35 |
| abs coef ($\mu$), cm$^{-1}$ | 16.8 |
| radiation | Mo K$\alpha$ ($\lambda$ = 0.7107) |
| diffractometer | Enraf-Nonius CAD-4 |
| temp, °C | 22 (1) |
| data range | |
| $2\theta$ = 2–24° | $hkl$ and $\bar{h}\bar{k}\bar{l}$ |
| $2\theta$ = 24–45° | $hkl$ |
| orientation monitors | after every 200 reflections[b] |
| intensity monitors | every 7200 s of X-ray exposure (no sign. decay) |
| absorption corr range | 0.84–1.0 |
| reflections measured | 3522 |
| independent reflections | 2600 |
| independent reflections above $2\sigma$ used in refinement | 2086 |
| extinction coeff | $g$ = 5.0 (6) × 10$^{-8}$ |
| max. shift/error on last cycle | 0.20 |
| max. diff density, e/Å$^3$, after last cycle | 0.5 |
| $R$ | 0.020 |
| $wR$ | 0.029 |
| goodness of fit | 1.05 |

[a] Estimated standard deviation for the last digit in parentheses. [b] Three orientation standards checked every 200 reflections; all 25 reflections used for cell dimensions recentered if angular change is >0.06°.

to those of the orthorhombic modification, resonances of monoclinic and triclinic $Me_2Sn(S_2CNEt_2)_2$ (known to be present in the sample from single-crystal X-ray unit cell determinations) are evident in the spectrum but cannot be assigned with confidence to specific crystalline modifications; neither can the Me–Sn–Me angles of the modifications be estimated because of overlap of the satellites and the presence of the broad $^{13}CH_2N$ resonance which obscures part of the satellite region. On the other hand, it is clear that such solid-state NMR spectra can be useful for revealing the presence of a mixture of forms in a crystalline sample of a single compound.[21]

## Conclusions

The power and accuracy of the $|^1J|$/angle NMR relationship reported previously[3] has been demonstrated by the speciation and correct prediction of the Me–Sn–Me angle in a new crystalline modification of $Me_2Sn(S_2CNEt_2)_2$. Because values of $|^1J|$ can be measured in solution as well as in the solid state, a sensitive and informative tool is available for determining the influence of different media—crystalline modifications and solutions—on the Me–Sn–Me angle of dimethyltin(IV) compounds. As illustrated for $Me_2Sn(acac)_2$, the $|^1J|$/angle equation with solution NMR data tells whether a molecular conformation in solution has changed from that present in the crystalline compound (known by X-ray or NMR). For $Me_2Sn(S_2CNEt_2)_2$, knowledge of the Me–Sn–Me angle in solution and the solid state provides infor-

(21) Other examples, of varying levels of documentation, are given in the following: (a) Lockhart, T. P.; Manders, W. F. *Inorg. Chem.* **1986**, *25*, 583. (b) Diesveld, J. W.; Menger, E. M.; Edzes, H. T.; Veeman, W. S. *J. Am. Chem. Soc.* **1980**, *102*, 7935. (c) Balimann, G. E.; Groombridge, C. J.; Harris, R. K.; Packer, K. F.; Say, B. J.; Tanner, S. F. *Phil. Trans. R. Soc. London A* **1981**, *299*, 643. (d) Hill, H. D. W.; Zens, A. P.; Jacobus, J. *J. Am. Chem. Soc.* **1979**, *101*, 7090.

mation on the influence of solid-state lattice forces on its structure.

**Experimental Section**

**Materials.** Me₂Sn(acac)₂ was recrystallized from benzene as reported in the paper describing its X-ray structure.[10] Small, colorless hexagonal plates of Me₂Sn(S₂CNEt₂)₂[16] (orthorhombic modification) were obtained by slow, room temperature evaporation of a chloroform–ethanol solution of the compound. Mixed crops of monoclinic and triclinic crystals in addition to the orthorhombic form were sometimes obtained; though we have varied recrystallization solvents, temperature, and the rate of crystallization, we have been unable to find a procedure for obtaining these other forms pure.

**NMR Spectroscopy.** Solid-state ¹³C NMR spectra were obtained on ca. 0.4 g of polycrystalline dimethyltin(IV) compounds at 15.08 MHz with 60-MHz high-power proton decoupling. Magic-angle spinning at 2300 Hz in an Andrew-type rotor and spin-locking cross-polarization with the ¹H and ¹³C fields matched at 57 kHz for 2 ms were used to obtain high-resolution solid-state spectra. Dwell times of 50 μs and repetition rates of 3 s were possible for the tin dithiocarbamate, while Me₂Sn(acac)₂ required repetition rates of 10 s; <1K scans were sufficient for chemical shift determination while 3–20K were required to obtain |¹J|. Chemical shifts (+/− 0.3 ppm) are relative to the internal secondary standard, delrin (89.1 ppm). Solution ¹³C NMR spectra run at 100 MHz on a Bruker WM-400 spectrometer were ca. 5% by weight methyltin(IV). Line widths at half-height were <5 Hz and chemical shifts, referenced

to Me₄Si (0 ppm), are +/− 0.1 ppm.

**Structure Determination and Refinement.** Crystal and data collection parameters for the orthorhombic modification of Me₂Sn(S₂CNEt₂)₂ are given in Table VII. The structure was solved by conventional Patterson and Fourier methods and refined by full-matrix least-squares methods minimizing the function $\sum w(|F_o| - |F_c|)^2$ where $w^{-1} = (\sigma^2_{counting} + (0.040F_o)^2)/4F_o^2$. Also 2086 reflections with $F_o^2 > 2\sigma(F_o^2)$ were used to refine 277 variables [x, y, z, 6 β's for non-hydrogen atoms; x, y, z for hydrogen atoms, and an isotropic extinction parameter ($g = 4.99 \times 10^{-8}$)]. The final agreement factors were $R = 0.020$, $R_w = 0.029$, and $S = 1.05$. The final difference Fourier synthesis showed no residuals greater than 0.5 e/A³. Atomic scattering factors, including $f'$ and $f''$, were taken from the *International Tables for X-ray Crystallography*, Vol. 4. Tables of anisotropic thermal parameters and $F_o$ and $F_c$ (×10) values are available as supplemental material.

**Supplementary Material Available:** Tables of anisotropic thermal factors and $F_o$ and $F_c$ (×10) values (8 pages). See any current masthead page for ordering information.

# Solid-State Structural Chemistry of Lariat Ether and BiBLE Cation Complexes: Metal Ion Identity and Coordination Number Determine Cavity Size[†1]

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**Abstract:** X-ray crystal structure data are presented for K⁺ complexes of N-allylmonoaza-18-crown-6 (**1**) monohydrate [K⁺⊂5-allyl·H₂O I⁻], N,N'-bis(3-oxabutyl)diaza-18-crown-6 (**2**) [K⁺⊂1-22-1 I⁻], N-(3-oxabutyl)monoaza-15-crown-5 (**3**) [K⁺⊂4-1 I⁻], N-(3,6-dioxaheptyl)monoaza-15-crown-5 (**4**) [K⁺⊂4-2 I⁻], and N,N'-bis(2-hydroxyethyl)diaza-18-crown-6 (**5**) [K⁺⊂H1-22-1H I⁻] along with the related complexes reported in preliminary form: [Na⁺⊂H1-22-1H I⁻] and the K⁺ complex of N-(3-oxabutyl)monoaza-18-crown-6 (**6**) [K⁺⊂5-1 I⁻] (*J. Am. Chem. Soc.* **1983**, *105*, 6717–6718) as well as the Na⁺ complex of N-(ethoxycarbonylmethyl)monoaza-15-crown-5 (**7**) [Na⁺⊂4-1E Br⁻] (*J. Am. Chem. Soc.* **1984**, *106*, 7244–7245). The crystals of K⁺⊂5-allyl·H₂O I⁻ are monoclinic, space group C2/m with four molecules in the unit cell dimensions a = 13.254 (3) Å, b = 19.673 (3) Å, c = 9.111 (1) Å, and β = 112.72 (2)°. R = 0.052 for 1416 observed reflections. The crystals of K⁺⊂1-22-1 I⁻ are monoclinic, space group C2/c with four molecules in the unit cell dimensions a = 15.823 (4) Å, b = 9.076 (4) Å, c = 17.132 (3) Å, and β = 92.90 (2)°. R = 0.027 for 2614 observed reflections. The crystals of K⁺⊂4-1 I⁻ are monoclinic, space group P2₁/n with four molecules in the unit cell dimensions a = 8.813 (2) Å, b = 13.283 (2) Å, c = 16.604 (2) Å, and β = 102.59 (2)°. R = 0.033 for 2398 observed reflections. The crystals of K⁺⊂4-2 I⁻ are monoclinic, space group P2₁/n with four molecules in the unit cell dimensions a = 11.199 (2) Å, b = 16.297 (2) Å, c = 12.047 (2) Å, and β = 104.48 (2)°. R = 0.025 for 2899 observed reflections. The crystals of K⁺⊂H1-22-1H I⁻ are monoclinic, space group C2/c with four molecules in the unit cell dimensions a = 13.696 (2) Å, b = 16.441 (2) Å, c = 11.739 (2) Å, and β = 117.02 (1)°. R = 0.029 for 2352 observed reflections. The crystals of Na⁺⊂H1-22-1H I⁻ are monoclinic, space P2₁ with two molecules in the unit cell dimensions a = 8.027 (5) Å, b = 15.618 (4) Å, c = 9.228 (4) Å, and β = 107.61 (4)°. R = 0.028 for 1820 observed reflections. The crystals of K⁺⊂5-1 I⁻ are orthorhombic, space group P2₁2₁2₁ with four molecules in the unit cell dimensions a = 10.733 (1) Å, b = 12.806 (2) Å, and c = 15.762 (3) Å. R = 0.020 for 1530 observed reflections. The crystals of Na⁺⊂4-1E Br⁻ are monoclinic, space group P2₁/c with four molecules in the unit cell dimensions a = 12.868 (2) Å, b = 9.037 (1) Å, c = 16.513 (3) Å, and β = 102.89 (1)°. R = 0.045 for 1757 observed reflections. Comparisons made with these structures and complexes of chorands and cryptands show that neither "hole-size" nor "cavity-size" concepts provide satisfactory explanations for the data. Instead, experimentally determined metal-ion-to-donor distances coincide with the effective ionic radius defined by Shannon for various ions of differing coordination numbers. For these flexible ligands, the guest cation organizes the host's donor group array.

The rational design of alkali metal cation ionophores requires an appreciation of both the molecular-architecture-chemical-

function relationship and synthetic execution. Lehn[2] has provided the blueprints for compounds having supramolecular topography,

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