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# Structural Studies of Tin(II) and Lead(II) Dimethylamides: X-ray Crystal Structure of $[Sn(NMe_2)_2]_2$ and Isolation of Its Lead Analogue

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The X-ray crystal structure of $[Sn(NMe_2)_2]_2$ (**1**) and the synthesis of its lead analogue (**2**) are reported. For **1**, which crystallizes from *n*-hexane as colorless prisms, crystal data are as follows: triclinic, space group $P\bar{1}$ (No. 2), unit cell dimensions $a = 6.210$ (4) Å, $b = 7.094$ (5) Å, $c = 8.802$ (7) Å, $\alpha = 81.59$ (7)°, $\beta = 72.46$ (6)°, $\gamma = 76.97$ (5)°, $Z = 1$. The structure has been refined to an $R$ index of 0.035 on the basis of 1623 unique reflections. Compound **1** is a centrosymmetric dimer with the tin atoms bridged by two dimethylamido groups. Each tin atom is 3-coordinate, being also bonded to a terminal dimethylamido group. The sum of the angles surrounding each tin is 280.4° indicating the presence of a stereochemically active lone pair at each metal. For the lead analogue, **2**, suitable crystals for X-ray collection were not obtained. The compound is both heat and light sensitive and decomposes rapidly at ambient temperature. Variable-temperature $^1H$ NMR studies indicate that the structure of the lead compound in solution is similar to that of the dimeric **1**.

## Introduction

The heavier main group elements show a marked reluctance to form compounds in their highest oxidation state.[1] For example, in the group 4 elements, two rather than four outer-shell electrons are used to form complexes in which the metal oxidation state is +2. Many such compounds are known, but most of these are ionic salts. More covalent, unimolecular compounds are less easily obtained. This is thought to be due to the imposition of the low coordination number of two, resulting in six rather than eight valence electrons. These compounds are electron deficient and associate unless prevented from doing so by very large substituents. This association is of two general types and can take the form of (i) rings or chains with a metal–metal bonded skeleton or (ii) simple or complex arrays of molecules in which the metal has a high coordination number as a result of the ligands bridging two or more metal atoms.[2]

The use of very large groups has permitted the isolation of a small number of organotin(II) compounds that can exist as monomeric or dimeric species in solution or the solid phase. A small number of these structures have been described in detail. These are the monomeric $M[N(SiMe_3)_2]_2$ (M = Sn or Pb),[3] monomeric $Sn(OC_6H_2Me\text{-}4\text{-}t\text{-}Bu\text{-}2,6)_2$,[4] $Sn(\eta^5\text{-}C_5H_5)_2$,[5a] $Sn(\eta^5\text{-}C_5Me_5)_2$ (M = Sn or Pb),[5b] the dimeric $Sn[CH(SiMe_3)_2]_2$[6] (with Sn–Sn bonding), $SnN(t\text{-}Bu)SiMe_2N(t\text{-}Bu)$[7] (which can exist in both monomeric and dimeric forms in the crystal phase), and the interesting monomeric nido cluster $[C_5Me_5Sn]^+[BF_4]$.[8] No X-ray crystal structures of divalent group 4 elements with smaller organo substituents have been published. In this paper we report the first structure of a centrosymmetric dimeric tin compound with a simple dialkylamido substituent and also the synthesis of its thermally unstable lead analogue.

Table I. Crystal Data and Experimental Details for $[Sn(NMe_2)_2]_2$

| | |
|---|---|
| $M_r$ | 413.69 |
| formula | $C_8H_{24}N_4Sn_2$ |
| $a$, Å | 6.210 (4) |
| $b$, Å | 7.094 (5) |
| $c$, Å | 8.802 (7) |
| $\alpha$, deg | 81.59 (7) |
| $\beta$, deg | 72.46 (6) |
| $\gamma$, deg | 76.97 (5) |
| $V$, Å$^3$ | 358.9 (5) |
| $d_{calcd}$(85 K), g cm$^{-3}$ | 1.91 |
| $d_{measd}$(298 K), g cm$^{-3}$ | 1.8 (dec) |
| space group | $P\bar{1}$ |
| $Z$ | 1 |
| cryst dimens, mm | 0.12 × 0.18 × 0.25 |
| radiation | Mo Kα, λ = 0.71069 Å (graphite monochromator) |
| temp, K | 85 |
| $\mu_{Mo\ K\alpha}$, cm$^{-1}$ | 34.7 |
| diffractometer | Syntex P2$_1$ |
| scan type | ω |
| scan range, deg | 2 |
| $2\theta_{max}$, deg | 55 |
| range abs cor fac | 2.1-2.7 |
| no. of reflens measd | 1801 ($R$(merge) = 0.04) |
| octants collected | $h, \pm k, \pm l$ |
| no. of unique data | 1630 |
| no. of reflens with $I > 3\sigma(I)$ | 1623 |
| no. of parameters | 64 |
| $R$ | 0.035 |
| $R_w$ | 0.047 |

## Experimental Section

All manipulations were carried out in modified Schlenk apparatus under an atmosphere of dry oxygen-free nitrogen. Both diethyl ether and *n*-hexane were distilled under nitrogen from sodium/potassium benzophenone ketyl. Both $SnCl_2$ and $PbCl_2$ (Alfa) were used as purchased. $^1H$ NMR spectra were recorded on a Nicolet NT-200 spectrometer.

**$[M(NMe_2)_2]_2$ (M = Sn or Pb).** Tetrakis(dimethylamido)ditin(II) was synthesized as previously described[9] from lithium dimethylamide and tin(II) chloride in diethyl ether. The lead analogue was prepared in an identical manner at −40 °C. Instead of sublimation,[9] purification of both products, $[Sn(NMe_2)_2]_2$ (**1**) and $[Pb(NMe_2)_2]_2$ (**2**), was via recrystallization from *n*-hexane at −40 °C. Compound **1** crystallized as colorless prisms (mp 90–92 °C; lit, 91–93 °C) suitable for X-ray data collection. However, we were unable to obtain specimens of **2**

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**Table II.** Atom Coordinates (×10$^4$) for $[Sn(NMe_2)_2]_2$ (1)

| atom | *x* | *y* | *z* |
|---|---|---|---|
| Sn | 1164 (1) | 825 (1) | 1281 (1) |
| N(1) | −1708 (7) | 2075 (6) | 2982 (5) |
| C(1) | −1213 (11) | 2577 (9) | 4381 (6) |
| C(2) | −4181 (8) | 2342 (7) | 3184 (6) |
| N(2) | 9 (7) | −1862 (6) | 952 (4) |
| C(3) | −1986 (9) | −2392 (7) | 2234 (5) |
| C(4) | 1979 (10) | −3498 (7) | 874 (6) |

**Table III.** Bond Lengths (Å) and Angles (deg) for $[Sn(NMe_2)_2]_2$ (1)

| | | | |
|---|---|---|---|
| Sn-N(1) | 2.067 (4) | Sn-N(2) | 2.266 (5) |
| Sn-N(2A) | 2.265 (4) | N(1)-C(1) | 1.464 (9) |
| N(1)-C(2) | 1.463 (7) | N(2)-C(3) | 1.481 (6) |
| N(2)-C(4) | 1.477 (6) | | |
| N(1)-Sn-N(2) | 100.4 (2) | N(1)-Sn-N(2A) | 99.8 (2) |
| N(2)-Sn-N(2A) | 80.0 (1) | Sn-N(1)-C(1) | 114.3 (4) |
| Sn-N(1)-C(2) | 133.1 (4) | C(1)-N(1)-C(2) | 112.1 (4) |
| Sn-N(2)-C(3) | 115.3 (3) | Sn-N(2)-C(4) | 107.3 (3) |
| C(3)-N(2)-C(4) | 108.2 (3) | Sn-N(2)-SnA | 100.0 (1) |
| C(3)-N(2)-SnA | 107.7 (3) | C(4)-N(2)-SnA | 118.6 (3) |

suitable for X-ray studies, since it invariably crystallized as a colorless fibrous solid. Compound **2** is also thermally unstable, rapidly decomposing at room temperature. Even at −20 °C, **2** slowly turns black and a metallic mirror is deposited.

**X-ray Data Collection and Refinement.** Crystals of $[Sn(NMe_2)_2]_2$ were protected from air contamination by a layer of hydrocarbon oil. The crystal selected for data collection was attached to a mounting fiber and immediately placed on the goniometer head in the cold stream of the low temperature apparatus. A summary of crystal data and data collection parameters is given in Table I. Two check reflections, monitored every 200 reflections, gave no evidence for decay. Lorentz, polarization, and absorption corrections[10] were applied.

The structure was solved by location of the tin atom on a 3-dimensional Patterson map and computation of a Fourier map. Non-hydrogen atoms were refined by using anisotropic thermal parameters. Hydrogen atoms were included in the refinement as rigid methyl groups, recalculated with each cycle, with fixed isotropic *U*'s. The mean shift/esd in the final cycle of refinement was 0.010. A final difference map was featureless except for some spurious density (0.5–1.2 e Å$^{-3}$) in the vicinity of the Sn atom. Final positional parameters are given in Table II. Bond distances and angles are listed in Table III. Tables of calculated hydrogen atom coordinates, thermal parameters, and structure factor tables are available as supplementary material.

## Description of Structure

The structure of **1** consists of discrete centrosymmetric (crystallographically imposed) dimers of the $Sn(NMe_2)_2$ unit (Figure 1). Each dimer is a planar rhombus comprised of two tin and two dimethylamido nitrogens (Sn, SnA, N(2) and N(2A)). Each tin atom is further bonded to a nitrogen from a terminal dimethylamido group. The bridging Sn–N bond distances are essentially equal, having the values Sn–N(2) = 2.266 (5) and SnA–N(2) = 2.265 (4) Å. The plane formed by the two carbons and nitrogen of the bridging amido groups, e.g., N(2)–C(3)–C(4), is at an angle of 97° with respect to the $Sn_2N_2$ core and is tilted away from the terminal amido group. The terminal nitrogen is essentially planar, the sum of the angles at N(1) being 359.5°. The Sn–N(1) distance is 2.067 (4) Å, and the N(1)–C(1)–C(2) plane is almost perpendicular (94°) to the $Sn_2N_2$ core. The angle at nitrogen on the more crowded side of the terminal amido group is significantly (~20°) larger than the angle on the less crowded side. The presence of a stereochemically active lone pair on tin is indicated by the angle between the Sn–N(1) vector and the central $Sn_2N_2$ plane of 103.3°. The sum of the angles surrounding each tin is 280.4°. The nitrogen–carbon distances in the bridging amido groups average 0.0155 Å longer than those in the terminal groups. The Sn···SnA distance is 3.471 (2) Å.

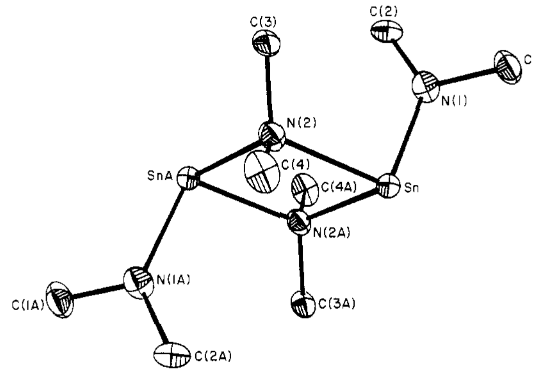
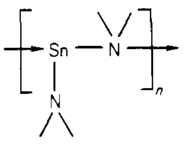


**Figure 1.** Perspective drawing of $[Sn(NMe_2)_2]_2$ (**1**) showing anisotropic thermal ellipsoids at the 40% probability level.

## Discussion

The structure of **1** is essentially the same as one of the solution structures proposed by Foley and Zeldin on the basis of dynamic $^1H$ NMR and cryoscopic studies.[9] However, our results do not support the polymeric solid-state structure tentatively proposed on the basis of Mössbauer data.[11] The current interpretation of these data had led to the proposal that structures **3** or **4** may be present in the solid state. The X-ray data clearly show the structure to be composed of discrete dimers with no significant intermolecular interactions. The structure of **1** resembles those of the cyclic tin amides $[(\overline{\mathrm{SnN(R)SiMe_2N}}(\mathrm{R}))_2]$ where R = *i*-Pr or *t*-Bu.[7] The structure of the *t*-Bu-substituted compound consists of a 1:1 mixture of monomers and dimers in its monoclinic phase and exclusively dimers in the triclinic phase.[7] When the substituent at tin is even bulkier, for example in compounds such as $M(NR_2)_2$ where M = Ge, Sn, or Pb and $NR_2$ = N(*t*-Bu)$_2$, $N(SiMe_3)_2$, or $\overline{\mathrm{NC(Me)_2(CH_2)_3C}}(\mathrm{Me})_2$, only monomeric structures are formed.[3] This is due mainly to the prevention of association by the large size of the amido substituents. So far the structures of only two simple tin(II) amides have been reported; those of the cyclic species $[(\overline{\mathrm{SnN}(t\text{-Bu})\mathrm{SiMe_2N}}(t\text{-Bu}))_2]$[7] (both monomeric and dimeric) and the monomeric $Sn(N(SiMe_3)_2)_2$.[3]



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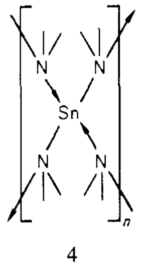

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The structure of **1** is interesting for several reasons: (i) it is the first example of a stable 3-coordinate tin(II) compound with a simple dialkylamide ligand, (ii) it shows that very bulky ligands are not required to stabilize low-coordinate, covalent tin(II), and (iii) it emphasizes the need for caution in the assignment of structures on the basis of Mössbauer data. Several of the geometric details of the structure are also worthy

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(10) All structure determination calculations were done on a Data General Eclipse computer using the SHELXTL Version 3 software package. The absorption correction was applied using program ABSORPTION, a method that obtains an empirical absorption tensor from an expression relating $F_o$ and $F_c$: Hope, H.; Moezzi, B., unpublished results.

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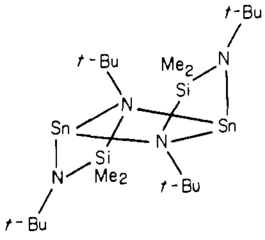
of comment. The terminal Sn–N bond length of 2.067 (4) Å is slightly shorter than known Sn(II)–N bond lengths, which average 2.09 Å.[12] This may be due to reduced crowding with the smaller $NMe_2$ groups. Another reason might be that the known Sn(II)–N bond lengths[3,7,12] involve d-acceptor silyl groups at nitrogen that may competitively reduce any potential Sn(II)–N d–p π-interaction with the p-orbital on nitrogen. The bridging Sn–N(2) bond distance, 2.266 (5) Å is, as expected, significantly longer than the terminal bond length. However, the equality of all the Sn–N lengths within the $Sn_2N_2$ core in **1** is unique. The core distances in the cyclic $[(Sn\overline{N(t\text{-}Bu)SiMe_2N}(t\text{-}Bu))_2]$ (**5**)[7] have the values 2.244 (7) and 2.389 (7) Å, with the shorter distances belonging to the $SnN_2Si$ ring unit. The longer Sn–N values bridging the two monomeric units may be the result of increased steric crowding upon dimerization and the lack of flexibility within the $SnN_2Si$ ring, which shows only very slight changes in geometry upon dimerization. The weaker nature of the association of $[(Sn\overline{N(t\text{-}Bu)SiMe_2N}(t\text{-}Bu))_2]$ is borne out by its monomeric formulation in hydrocarbon solution while **1** remains a dimer. It would be of interest, for comparison, to have structural data on $[(Sn\overline{N(i\text{-}Pr)SiMe_2N}(i\text{-}Pr))_2]_2$, which also remains dimeric in solution.



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It has been noted in the descriptive section that the Sn–N(1)–C(2) angle on the more crowded (nearest the $Sn_2N_2$) core) side of the terminal amido groups is much (~ 20°) larger than the less crowded side, Sn–N(1)–C(1). We feel that this effect is steric in origin, since the interatomic distances between the hydrogens on C(2) and the hydrogens on C(3) and C(4A) are quite short (2.16–2.36 Å). These short contacts may be sufficient to cause considerable widening of the Sn–N(1)–C(2) angle. A further aspect of the structure concerns the angles at each tin, which total 280.4°. This indicates that both tin atoms possess a stereochemically active lone pair. It should be possible to isolate compounds in which both metals behave as donor atoms related to the monodentate stannylenes already known.[13]

Finally it can be seen (Table III) that the nitrogen–carbon distances in the bridging amido groups are all longer than those in the terminal positions. This is more than likely due to the different coordination numbers and hybridization at each nitrogen atom in which the greater s-character in the terminal N(1)–C(1) bond is reflected in the shorter N(1)–C(1) bond length.

It is unfortunate that crystals of the lead analogue proved unsuitable for data collection. Structural data on low-coordinate lead compounds are practically nonexistent.[3,5b] The only structurally characterized (in the solid phase) 2-coordinate lead compound is $Pb[N(SiMe_3)_2]_2$.[3] $^1H$ NMR shows $Pb(NMe_2)_2$ to have a broad single peak at δ 2.9 in $C_6D_5Cl$ at 0 °C, that splits into two broad lines at −30 °C. It appears from its $^1H$ NMR behavior that **2** has a similar structure to **1** in solution. However, the apparently different crystallization exhibited by **2** may indicate that its structure in the solid phase differs from that of **1**. Studies on other lead(II) amides involving different alkyl substituents with the objectr of obtaining suitable crystals for X-ray studies are in progress.

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**Registry No.** 1, 55853-45-7; 2, 88130-90-9; $Sn(NMe_2)_2$, 55853-40-2; $Pb(NMe_2)_2$, 88130-91-0.

**Supplementary Material Available:** Tables of hydrogen coordinates, anisotropic thermal parameters, and structure factors (11 pages). Ordering information is given on any current masthead page.

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# Gas-Phase Structure of Dimeric Tetrafluorosulfur Chloroimide, $(ClNSF_4)_2$

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The geometric structure of $(ClNSF_4)_2$ was studied by gas electron diffraction. The four-membered SNSN ring is planar with the out-of-plane chlorine atoms in trans positions ($C_{2h}$ symmetry). The S–N bonds (1.734 (4) Å) are lengthened due to angle strain (SNS = 99.3 (0.6)°). The extremely short N–Cl bond lengths (1.638 (10) Å) are rationalized by the large SNCl bond angles (122.1 (0.7)°). Substitution effects on trans and cis S–F bond lengths of the $SF_4$ groups are discussed.

## Introduction

Four-membered ring systems with hexacoordinated chalcogen atoms are known in selenium and tellurium chemistry.[2,3] In contrast to $O{=}SF_4$, the dimeric species of the fluoro oxides of the higher homologues, $(OSeF)_2$ and $(OTeF_4)_2$, are more stable than the monomeric species. This different behavior of sulfur can be rationalized by the different size of the central atoms. Only in the case of sulfur is the formation of an O=X double bond favored, while the p(O)–d(X) interaction is strongly reduced for X = Se or Te. Tetrafluorosulfur imides show similar behavior as $O{=}SF_4$ and $RN{=}SF_4$ (R = F,[4]

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