

Molecular Structures of the Main Group 4 Metal(II) Bis(trimethylsilyl)-amides $M[N(\text{SiMe}_3)_2]_2$ in the Crystal (X-Ray) and Vapour (Gas-phase Electron Diffraction)[†]

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The group 4 metal(II) bis(trimethylsilyl)amides, $M[N(\text{SiMe}_3)_2]_2$, are V-shaped monomers both in the crystal ($M = \text{Sn}$ or Pb) at 140 K and the vapour ($M = \text{Ge}$, Sn , or Pb) at *ca.* 380 K, with $\angle \text{NMN}$ in the vapour being 101(1.5), 96, or 91(2)° for $M = \text{Ge}$, Sn , or Pb respectively [but 104.7(2) ($M = \text{Sn}$) or 103.6(7)° ($M = \text{Pb}$) in the solid].

There is considerable current interest in the synthesis and characterisation of the heavier group 4 metal analogues of the carbenes.^{1,2} We have already shown that the use of bulky monodentate C-, N-, or O-centred ligands leads to coloured,

thermochromic, diamagnetic bivalent compounds of Ge, Sn, and Pb which are monomers in cyclohexane or benzene solution. Typical examples of such MX_2 molecules are those with $\text{X} = \text{CH}(\text{SiMe}_3)_2$, $\text{N}(\text{SiMe}_3)_2$, or $\text{OC}_6\text{H}_2\text{Me-4-Bu}^t_{2,6}$ (OAr). Available structural data relate to both (i) the crystalline phase (X-ray) for $\text{Sn}[\text{CH}(\text{SiMe}_3)_2]_2$, a centrosymmetric Sn-Sn dimer,³

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and the V-shaped monomers $\text{Ge}\{\text{NCMe}_2[\text{CH}_2]_3\text{CMe}_2\}_4$ or $\text{M}(\text{OAr})_2$ ($\text{M} = \text{Ge}$ or Sn),⁵ and (ii) the vapour [by gas phase electron diffraction, g.e.d.; both are V-shaped monomers for SnX_2 , $\text{X} = \text{CH}(\text{SiMe}_3)_2$ or $\text{N}(\text{SiMe}_3)_2$].

We now present structural data for the series $\text{M}[\text{N}(\text{SiMe}_3)_2]_2$, and show that these compounds ($\text{M} = \text{Sn}$ or Pb) are V-shaped monomers in both the vapour (also $\text{M} = \text{Ge}$) and the crystal (at 140 K). The result for the solid phase is surprising because it was widely held that the solid tin(II) amide might well have a similar structure to that of the isoelectronic dialkyl,⁸ and was thus described as 'at least dimeric'² or, on the basis of a ¹¹⁹Sn Mössbauer study, as having 'a nonassociated, probably dimeric structure'.⁹

Other features of interest relate to (i) the trends in the NMN angle as a function of M, (ii) comparisons between the data for the vapour and the condensed state; the more important parameters are listed in Table 1, and (iii) the long $\text{M}^{\text{IV}}\text{-N}$ lengths in contrast with corresponding¹⁰ $\text{M}^{\text{IV}}\text{-N}$ lengths (*cf.*, ref. 6).

As for (i), we note a monotonic decrease (especially in the vapour) in $\angle \text{NMN}$ with increasing atomic number of M similar to that found for many other compounds of main group elements $\text{M}'\text{X}_n$, and ascribable to the tendency (Bent's rule) for s-orbital character to accumulate in the M' non-bonding orbital as the electronegativity difference of M' and the ligand X^- increases. Of course steric effects may also play an important role for the metal(II) amides. Thus, as the Pb-N bond is much longer than Ge-N , interactions between the two $\text{N}(\text{SiMe}_3)_2$ ligands are much more significant for the latter and are clearly minimised by widening the $\angle \text{NMN}$ angle. The larger $\angle \text{NSiC}$ angle for $\text{M} = \text{Ge}$ [115.9(8)] than $\text{M} = \text{Pb}$ [112(1)°], and the greater torsional displacements for the methyl groups (30–40° from staggered positions), are also regarded as strain-relieving factors (data from g.e.d.). In the crystal a similar effect is demonstrated by comparison of (a) the angle between each of the two MNSi_2 planes [111.5 ($\text{M} = \text{Sn}$) and 104.5° ($\text{M} = \text{Pb}$)], and (b) the SiNSi angle (*ca.* 123 for $\text{M} = \text{Sn}$ and *ca.* 126° for $\text{M} = \text{Pb}$).

With regard to (ii), we note that the NMN bond angle is much more sensitive to the nature of M in the vapour than the solid and moreover is significantly smaller. This is very unexpected. The differences are most plausibly attributed to the differences in ligand orientation. Packing of molecules with the gas phase symmetry would be inefficient; consequently, the ligands tilt, as observed, giving rise to close *intra*-molecular contacts. The ensuing strain is relieved by opening up the NMN angle. The torsional displacements of the $\text{N}(\text{SiMe}_3)_2$ groups are much smaller in the solid state than in the vapour; with gas phase $\angle \text{NMN}$ values this would give very close contacts between the 'inner' SiMe_3 groups, and hence larger $\angle \text{NMN}$ would be preferred. From the g.e.d. data, MN torsion angles and $\angle \text{NMN}$ are strongly correlated. As different MN torsion angles are found in the gas from those in the crystal, the MN torsion potential appears to be rather soft.

Table 1. Some structural parameters for the group 4 metal(II) amides $\text{M}[\text{N}(\text{SiMe}_3)_2]_2$.

M in $\text{M}[\text{N}(\text{SiMe}_3)_2]_2$	$\langle \text{M-N} \rangle$ Crystal	Bond length (Å)		$\angle \text{NMN}$ Angle (°)	
		Gas	Crystal	Gas	
Ge	^a [1.88] ^b	1.89(1)	^a [111.4(5)] ^b	101(1.5)	
Sn	2.09(1)	2.09(1) ^c	104.7(2)	96°	
Pb	2.24(2)	2.20(2)	103.6(7)	91(2)	

^a Not available. ^b Data in parentheses relate to $\text{Ge}\{\text{NMe}_2[\text{CH}_2]_3\text{CMe}_2\}_2$, from ref. 4. ^c Data from ref. 7.

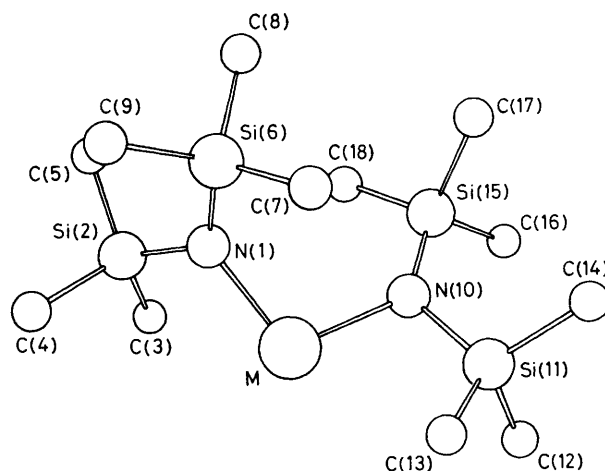


Figure 1. X-Ray crystal structure of $\text{M}[\text{N}(\text{SiMe}_3)_2]_2$ ($\text{M} = \text{Sn}$ or Pb) at 140 K. Selected bond lengths (Å) and angles (°) (data for $\text{M} = \text{Pb}$ in square brackets): $\text{M-N}(1)$ 2.096(1) [2.260(18)]; $\text{M-N}(10)$ 2.088(6) [2.222(19)]; $\text{N}(1)\text{-Si}(2)$ 1.742(6) [1.724(23)]; $\angle \text{N}(1)\text{-M-N}(10)$ 104.7(2) [103.6(7)]. Sum of angles at (i) $\text{N}(1) = 358.3$ [358.2] and (ii) $\text{N}(10) = 356$ [358.7].

The g.e.d. data (for experimental details, see ref. 11) for both molecules $\text{M}[\text{N}(\text{SiMe}_3)_2]_2$, $\text{M} = \text{Ge}$ or Pb , are consistent with monomers of C_2 -symmetry defined by four bond distances (M-N , N-Si , Si-C , and C-H), four valence angles ($\angle \text{NMN}$, $\angle \text{MNSi}$, $\angle \text{NSiC}$, and $\angle \text{SiCH}$) and three torsional angles describing the torsion around the M-N , N-Si , and Si-C bonds. Least-squares refinement afforded the parameters shown for the gases in Table 1, as well as the following mean values (lengths in Å, angles in degrees; Ge first and Pb in square brackets) Si-N 1.743(6) [1.75(1)], Si-C 1.883(6) [1.880(6)], $\angle \text{MNSi}$ 121.1(7) [119.6(8)], and $\angle \text{NSiC}$ 115.9(8) [112(1)]. The $\text{N}(\text{SiMe}_3)_2$ groups are essentially perpendicular to the NMN -plane, one Si-C bond approximately eclipses the M-N bond, and the methyl groups are twisted 30–40° ($\text{M} = \text{Ge}$) or *ca.* 20° ($\text{M} = \text{Pb}$) from staggered positions. There was no significant deviation from planarity around the nitrogen atoms for $\text{M} = \text{Ge}$, and this was assumed to be the case for $\text{M} = \text{Pb}$.

For the crystals a further point of interest is that in both structures the $\text{M-N}(1)\text{-Si}(6)$ and $\text{M-N}(10)\text{-Si}(15)$ angles are wider than the $\text{M-N}(1)\text{-Si}(2)$ and $\text{M-N}(10)\text{-Si}(11)$ angles; for $\text{M} = \text{Sn}$ the difference is *ca.* 11° and for $\text{M} = \text{Pb}$ the difference is *ca.* 8.5° (see Figure 1). The NSi_2 angles are *ca.* 123 for Sn and 126° for Pb . It seems that the wider M-N-Si angles correspond to the most crowded environment (the back side, opposite the lone pair) and the NSi_2 angles probably reflect the lower steric requirement for lead.

Crystal data (at 140 K): $\text{C}_{12}\text{H}_{36}\text{N}_2\text{Si}_4\text{Sn}$ [$\text{C}_{12}\text{H}_{36}\text{N}_2\text{Si}_4\text{Pb}$], $M = 439.5$ [528.0], orthorhombic, space group $\text{Pnaa}[Pbca]$, $a = 12.94(2)$ [13.33(3)], $b = 16.72(1)$ [15.75(3)], $c = 20.65(2)$ [22.1(5)] Å, $Z = 8$. The structures were solved by heavy atom methods from 3986 [2027] 'observed' (out of the 5150 [4063] independent) reflections measured on a diffractometer with $\text{Mo-K}\alpha$ radiation and $F > 6\sigma(F)$ measured to $2\theta = 55$ [50°], $R = 0.062$ [0.071].[‡]

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[‡] The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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