Preparation and X-Ray Characterisation of the First Heteroleptic Hydrocarbon-soluble Tin(II) Pseudohalide, $Sn(NCS)[N(SiMe_3)_2]$[*]

Richard W. Chorley, Peter B. Hitchcock and Michael F. Lappert
School of Chemistry and Molecular Sciences, University of Sussex, Brighton BN1 9QJ, UK

Treatment of equivalent portions of $Sn(NCS)_2$ and $Sn(NR_2)_2$ ($R = SiMe_3$) in Et_2O yielded the toluene-soluble, crystalline, colourless $Sn(NCS)(NR_2)$, which X-ray crystallography shows to be a V-shaped monomer [N–Sn–N 94.1(2), Sn–N–CS 171.0(5)°] with weak intermolecular bonding to neighbouring units [Sn ··· S′ 3.047(2) and Sn ··· S″ 3.316(2) Å; S′ ··· Sn ··· S″ 178.4(1)°].

We recently reported the synthesis and X-ray characterisation of the chlorotin(II) amides *trans*-$\{Sn(\mu\text{-}Cl)[N(SiMe_3)_2]\}_2$ and *cis*-$\{Sn(\mu\text{-}Cl)[NCMe_2(CH_2)_3CMe_2]\}_2$.[1] We have now extended this work to the toluene- and diethyl ether-soluble isothiocyanatotin(II) amide $Sn(NCS)[N(SiMe_3)_2]$ **1**, obtained by the conproportionation (1)[†]

$$Sn(NCS)_2 + Sn[N(SiMe_3)_2]_2 \longrightarrow \underset{\mathbf{1}}{2Sn(NCS)[N(SiMe_3)_2]} \quad (1)$$

The chemistry of inorganic pseudohalides has been extensively studied;[4] there has been particular interest in using spectroscopic techniques to determine the mode of bonding of the potentially ambidentate pseudohalide moiety. The molecular structures of various tin complexes containing the NCS^- ligand have been determined by X-ray diffraction; they have invariably proved to be isothiocyanates, *i.e.* they are primarily *N*- rather than *S*-bonded. Tin(II) isothiocyanates which have been studied in this way include $Sn(NCS)_2$,[5] and the isostructural series Sn(NCS)X (X = F, Cl, Br or I);[6] these possess complex structures similar to those of Group 14 element dihalides such as $PbCl_2$, $SnBr_2$, SnClI and SnI_2. Each tin atom in $Sn(NCS)_2$, for example, is surrounded by nine NCS^- ligands, the primary co-ordination comprising Sn–N contacts of 2.20(2) and 2.27(1) Å and a Sn–S bond of 2.837(4) Å; there are longer range Sn ··· S contacts including those at 3.111(5) and 3.355(5) Å.

By contrast, X-ray crystallography[‡] (Fig. 1) of compound **1** indicates that the presence of a bulky amido group gives rise to a much less complicated tin environment, the co-ordination number being the smallest reported for a tin isothiocyanate. The primary bonding involves two Sn–N bonds, and there are two longer Sn ··· S intermolecular contacts. The tin atom of each $Sn(NCS)[N(SiMe_3)_2]$ unit may be regarded as possessing a stereochemically active lone pair of electrons, each unit adopting a V-shaped bent singlet conformation, with N–Sn–N 94.1(2)°, a value similar to those in many monomeric SnX_2 compounds,[9] but smaller than in $Sn[N(SiMe_3)_2]_2$ (104.7° in the solid state by X-ray crystallography,[10] 96.0° in the gas phase by electron diffraction[11]), presumably owing to the lower steric demand of the NCS^- ligand compared with $N(SiMe_3)_2^-$. The N–Sn–Cl angles in *trans*-$\{Sn(\mu\text{-}Cl)[N(SiMe_3)_2]\}_2$ are 94.2(1) and 101.1(1)°.[1]

As for almost all tin isothiocyanates, the Sn–N–C–S linkage is nearly linear, and the Sn–NC, N–C and C–S bond lengths are unexceptional [*cf.* data for $Sn(NCS)_2$:[5] ⟨Sn–N⟩ 2.23(2), ⟨N–C⟩ 1.15(2), ⟨C–S⟩ 1.63(2) Å]. The amido Sn–N distance of 2.079(5) Å is similar to those in $Sn[N(SiMe_3)_2]_2$, 2.096(1) and 2.088(6) Å.[10] The trimethylsilyl groups are arranged so that the Si_2NSn atoms are coplanar and make an angle of only 18° with the NSnNCS plane, in contrast to $Sn[N(SiMe_3)_2]_2$ where the amido groups are almost orthogonal to the SnN_2 plane.[10]

The monomer units in the crystal are held by close intermolecular Sn ··· S contacts, each tin atom interacting with the sulfur atom of the isothiocyanato ligand of two neighbouring $Sn(NCS)[N(SiMe_3)_2]$ units. These S atoms are positioned at distances of 3.047(2) (S′) and 3.316(2) (S″) Å near an axis perpendicular to the N–Sn–N plane, and on either side of it, S′ ··· Sn ··· S″ 178.4(1)°. Thus, if both Sn ··· S interactions are considered to be important, the resulting σ-orbital geometry around tin approaches trigonal bipyramidal (with one

---

[*] No reprints available.

[†] *Preparation of Compound* 1.—Orange $Sn[N(SiMe_3)_2]_2$[2] (1.94 g, 4.41 mmol) was added to a slightly cooled and stirring suspension of $Sn(NCS)_2$[3] (1.05 g, 4.47 mmol) in dry Et_2O (70 cm^3). After 16 h the reaction mixture was filtered and the pale yellow filtrate cooled to *ca.* −6 °C for 22 h. From this, large colourless crystals (1.46 g, 49%) of compound **1** were obtained; these were freed from the supernatant liquor, washed with cold pentane and dried in a flow of argon gas. The compound appeared to decompose on heating above *ca.* 120 °C, and after storing for a few weeks developed a red colour. It was characterised by microanalysis (Found: C, 23.8; H, 5.1; N, 8.2. $C_7H_{18}N_2SSi_2Sn$ requires C, 24.9; H, 5.4; N, 8.3%); spectroscopy {NMR ($[^2H_8]$toluene, ambient temperature): ^1H, δ 0.20 (s); ^{13}C, δ 4.59 (s); ^{119}Sn, δ −300 (s) and −306 (s). IR (Nujol mull): 2070s, 1251s, 1180m, 1050w, 930s, 872s, 839s, 754s and 567m cm^{-1}} and X-ray diffraction (Fig. 1).

[‡] *Crystal data* (*T* 22 °C, Enraf-Nonius CAD-4 diffractometer, DIFABS[7] absorption correction; structural solution by the SHELXS 86[8] heavy-atom method).—$C_7H_{18}N_2SSi_2Sn$ **1**, *M* = 337.2, monoclinic, space group $P2_1/c$, $a = 14.765(6)$, $b = 8.463(4)$, $c = 12.059(5)$ Å, $\beta = 104.61(3)°$, $U = 1458.0$ Å^3, $Z = 4$, $D_c = 1.54$ g cm^{-3}, μ(Mo-Kα) = 20.3 cm^{-1}, specimen 0.7 × 0.7 × 0.3 mm, 2752 unique reflections for $2 < \theta < 25°$, 2104 reflections with $|F^2| > 3\sigma(F^2)$ used in the refinement; $R = 0.064$, $R' = 0.080$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, Issue 1, 1992, pp. xx–xxv.

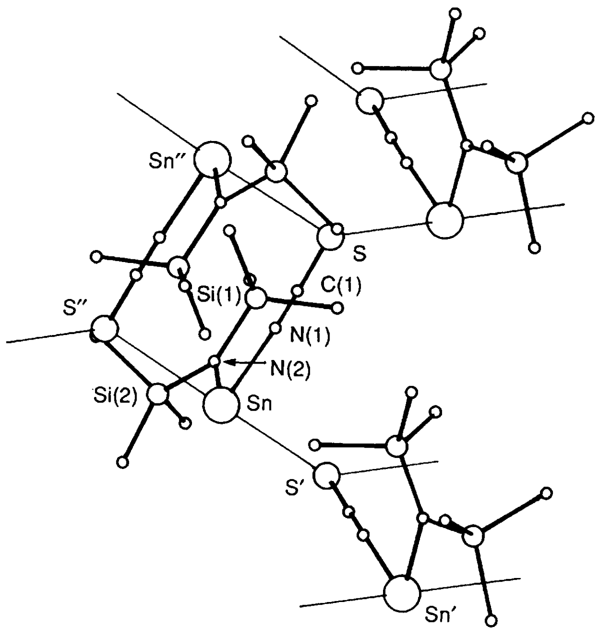
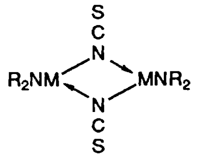
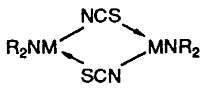


Fig. 1 The molecular structure of $Sn(NCS)[N(SiMe_3)_2]$ **1** and atom numbering scheme. Selected bond lengths and angles are Sn–N(1) 2.250(6), Sn–N(2) 2.079(5), N(1)–C(1) 1.140(8), S–C(1) 1.618(7), Sn···S″ 3.316(2), Sn···S′ 3.047(2) and Å, N(1)–Sn–N(2) 94.1(2), Sn–N(1)–C(1) 171.0(5), N(1)–C(1)–S 178.5(6) and S′–Sn–N(1) 97.0(2)°



1′



1″

equatorial site occupied by the lone pair and the two sulfur atoms taking the axial positions). As Sn···S′ is significantly shorter than Sn···S″, a better description probably involves only the Sn···S′ interaction, with a consequential distorted-tetrahedral geometry at tin.

Extended-Hückel calculations, using idealised SCN^- and $Sn(NCS)[N(SiH_3)_2]$ model fragments to simulate neighbouring monomers of compound **1**, gave an approximate bond energy of only 30 kJ mol^{-1} for the Sn···S′ interaction [*cf.*[12] the Sn–S bond energy of 217 kJ mol^{-1} in $SnMe_3(SBu^n)$].

The low co-ordination number for tin in compound **1** is unexpected. Thus, other divalent tin compounds containing less than two sterically demanding ligands adopt at least a distinct dimeric structure. For example, $\{Sn(\mu\text{-}Cl)(NR_2)\}_2$ [$NR_2 = N(SiMe_3)_2$ or $NCMe_2(CH_2)_3CMe_2$],[1] $[Sn(\mu\text{-}OBu^t)X]_2$ [X = Cl,[13a] OBu^t,[13b] or $N(SiMe_3)_2$[14]] and $SnX\{2\text{-}[C(SiMe_3)_2]C_5H_4N\}$ [X = Cl or $N(SiMe_3)_2$][15] have three-co-ordinate tin atoms. Even $Sn[CH(SiMe_3)_2]_2$, with two bulky substituents, is dimeric in the solid state, with tin–tin bonding.[16] In principle, **1** might also have adopted a dimeric structure **1′** or **1″**. The former would have required the thiocyanato nitrogen atom in each monomer unit to have a lone pair of electrons available for co-ordination to the tin atom of a second unit. However, the near-linearity of the Sn–N–C angle (171°) implies that no such lone pair is available.

The ambient-temperature ^{119}Sn NMR spectrum of compound **1** comprised two singlets of equal intensity, δ −300 and −306, which did not coalesce at 333 K. The very small difference in these chemical shifts suggests that each signal arises from a species in solution having a closely similar tin(II) environment, possibly *cis* or *trans* isomers of **1″**, by analogy with such isomerism in $\{Sn(\mu\text{-}Cl)[NCMe_2(CH_2)_3CMe_2]\}_2$.[1] This aspect is being further investigated.

Acknowledgements

We thank the SERC and Koninklijke/Shell-Laboratorium, Amsterdam, for a studentship (to R. W. C.), Dr. P. W. Lednor for his interest, the EC (Stimulation Contract: ST 200335) and the Leverhulme Trustees for support, and Dr. R. L. Johnston for considerable assistance in performing the extended-Hückel calculations.

References

1 R. W. Chorley, P. B. Hitchcock, B. S. Jolly, M. F. Lappert and G. A. Lawless, *J. Chem. Soc., Chem. Commun.*, 1991, 1302.
2 D. H. Harris and M. F. Lappert, *J. Chem. Soc., Chem. Commun.*, 1974, 895.
3 B. R. Chamberlain and W. Moser, *J. Chem. Soc. A*, 1969, 354.
4 *The Chemistry of Pseudohalides*, eds. A. M. Golub, H. Köhler and V. V. Skopenko, Elsevier, Amsterdam, 1986.
5 A. G. Filby, R. A. Howie and W. Moser, *J. Chem. Soc., Dalton Trans.*, 1978, 1797.
6 Z. Al Oraibi, W. Granier, S. Vilminot and L. Cot, *C. R. Hebd. Seances Acad. Sci., Ser. C*, 1978, **287**, 361; S. Vilminot, W. Granier, Z. Al Oraibi and L. Cot, *Acta Crystallogr., Sect. B*, 1978, **34**, 3306.
7 N. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, 1983, **39**, 158.
8 G. M. Sheldrick, in *Crystallographic Computing 3*, eds. G. M. Sheldrick, C. Krüger and R. Goddard, Oxford University Press, 1985, pp. 175–189.
9 *cf.* T. Fjeldberg, A. Haaland, B. E. R. Schilling, M. F. Lappert and A. J. Thorne, *J. Chem. Soc., Dalton Trans.*, 1986, 1551.
10 T. Fjeldberg, H. Hope, M. F. Lappert, P. P. Power and A. J. Thorne, *J. Chem. Soc., Chem. Commun.*, 1983, 639.
11 M. F. Lappert, P. P. Power, M. J. Slade, L. Hedberg, K. Hedberg and V. Schomaker, *J. Chem. Soc., Chem. Commun.*, 1979, 369.
12 J. C. Baldwin, M. F. Lappert, J. B. Pedley and J. S. Poland, *J. Chem. Soc., Dalton Trans.*, 1972, 1943.
13 (*a*) C. Zybill and G. Müller, *Z. Naturforsch., Teil. B*, 1988, **43**, 45; (*b*) T. Fjeldberg, P. B. Hitchcock, M. F. Lappert, S. J. Smith and A. J. Thorne, *J. Chem. Soc., Chem. Commun.*, 1985, 939.
14 M. J. McGeary, K. Folting and K. G. Caulton, *Inorg. Chem.*, 1989, **28**, 4051.
15 L. M. Engelhardt, B. S. Jolly, M. F. Lappert, C. L. Raston and A. H. White, *J. Chem. Soc., Chem. Commun.*, 1988, 336.
16 P. J. Davidson, D. H. Harris and M. F. Lappert, *J. Chem. Soc., Dalton Trans.*, 1976, 2268; D. E. Goldberg, P. B. Hitchcock, M. F. Lappert, K. M. Thomas, A. J. Thorne, T. Fjeldberg, A. Haaland and B. E. R. Schilling, *J. Chem. Soc., Dalton Trans.*, 1986, 2387.

Received 20*th January* 1992; *Communication* 2/00305H