Crystalline Binuclear *cis*- and *trans*-Chlorotin(II) Amides $[Sn(\mu\text{-}Cl)(NR_2)]_2$, the *cis*-1a ⇌ *trans*-1b Isomerisation for $[NR_2 = \overline{NCMe_2(CH_2)_3CMe_2}]$, and the X-Ray Structures of 1a and of *trans*-$[Sn(\mu\text{-}Cl)\{N(SiMe_3)_2\}]_2$†

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Crystalline binuclear chlorotin(II) amides $[Sn(\mu\text{-}Cl)(NR_2)]_2$ have been X-ray characterised as *cis*-$[NR_2 = \overline{NCMe_2(CH_2)_3CMe_2}$, **1a**] and *trans*-(R = $SiMe_3$, **2b**) conformers [Cl–Sn–Cl′ = 78.53(4) **1a** or 81.33(4)° **2b**, Sn–Cl–Sn′ 100.91(4) **1a** or 98.67(4)° **2b**, <Sn–Cl> 2.74 **1a** or 2.67 Å **2b**]; a solution of **1** in toluene undergoes rapid *cis* ⇌ *trans* exchange at ambient temperature, but distinct *cis*-**1a** and *trans*-**1b** forms coexist below 192 K (^{119}Sn NMR spectroscopy and line-shape analysis) and evidence is presented for an intramolecular mechanism for this exchange.

We report the synthesis [eqn. (1)]‡ and X-ray characterisation§ of two crystalline binuclear μ-chlorotin(II) amides $[Sn(\mu\text{-}Cl)NR_2]_2$ $[NR_2 = \overline{NCMe_2(CH_2)_3CMe_2}$ **1** or R = $SiMe_3$ **2**]. Surprisingly, while one of these is the *cis*-isomer (**1a**, Fig. 1), the other has the *trans*-configuration (**2b**, Fig. 2) (each tin atom can be regarded as having a stereochemically active lone pair of electrons). Moreover, we demonstrate that in PhMe, complex **1**, unlike **2**, undergoes *cis*-**1a** ⇌ *trans*-**1b** isomerisation sufficiently slowly for the process to be observable on the NMR timescale. The mechanism of this exchange may involve unprecedented inversion at a three-coordinate Sn^{II} centre, as discussed theoretically {on model compounds such as $[SnCl_2(NH_2)]^-$} elsewhere.[3]

$$Sn(NR_2)_2 + SnCl_2 \rightleftharpoons [Sn(\mu\text{-}Cl)NR_2]_2 \qquad (1)$$

Upon progressively cooling a $[^2H_8]$toluene solution of **1** in the cavity of an NMR spectrometer, a singlet observed initially at δ +240 (305 K) (in an $^{119}Sn\{^1H\}$ experiment) shifted rapidly and linearly with accompanying line-broadening to δ +193 at 195 K. Strong temperature dependence of $\delta(^{119}Sn)$ is well-known;[4] however, further cooling to 192 K (the coalescence temperature, T_C) led to the appearance of two distinct singlets at δ +181 and +193 in an integrated ratio of *ca.* 2 : 1; these signals were too broad to discern whether $^1J(^{119}Sn\text{–}^{117}Sn)$ was observable; the large band width of the signals may be due to the neighbouring quadrupolar ^{35}Cl and ^{14}N nuclei. These changes were entirely reversible on warming.

The chemical shift difference of *ca.* 12 ppm at T_c is exceedingly small when compared with the ^{119}Sn chemical shift dispersion normally associated with Sn^{II} complexes (*ca.* 4500 ppm).[4] We conclude that each signal arises from a species having a closely similar Sn^{II} environment, most probably the *cis*-**1a** and *trans*-**1b** conformers of the chlorotin(II) amide **1**. This notion is supported by (*i*) the isolation of crystalline *cis*-**1a** and *trans*-**2b** forms of two related dimeric μ-chlorotin(II) amides, and (*ii*) calculations which show not only that *cis*- and

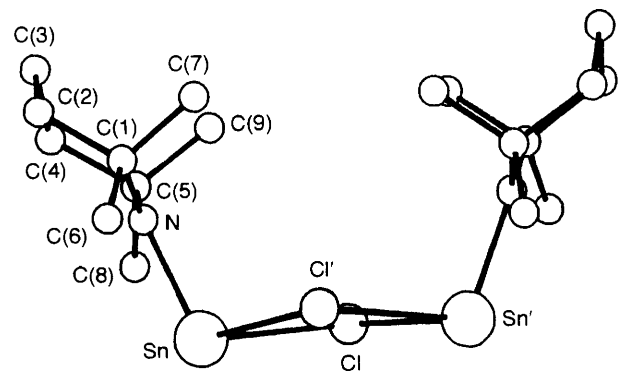

Fig. 1 The molecular structure of *cis*-$[Sn(\mu\text{-}Cl)\{\overline{NCMe_2(CH_2)_3CMe_2}\}]_2$ **1a** and atom numbering scheme. Selected bond lengths and angles: Sn–Cl 2.704(1), Sn–Cl′ 2.786(2), Sn–N 2.055(3), N–C(1) 1.486(5), N–C(5), 1.481(5) Å; Cl–Sn–Cl′ 78.53(4), Sn–Cl–Sn′ 100.91(4), Cl–Sn–N 102.3(1), Cl′–Sn–N 106.3(1), Sn–N–C(1) 119.7(3), Sn–N–C(5) 119.9(3), C(1)–N–C(5) 119.7(3)°.

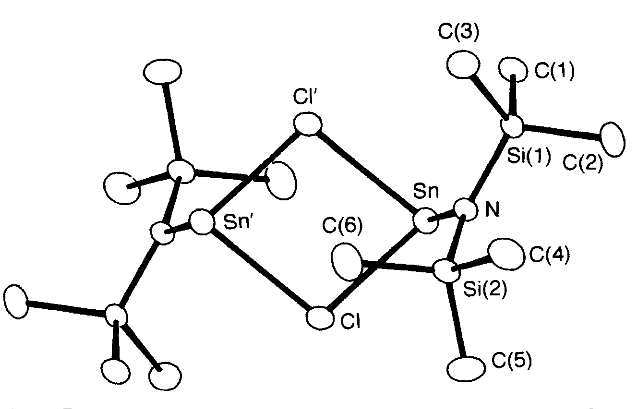

Fig. 2 The molecular structure of *trans*-$[Sn(\mu\text{-}Cl)\{N(SiMe_3)_2\}]_2$ **2b** and atom numbering scheme. Selected bond lengths and angles: Sn–Cl 2.598(1), Sn–Cl′ 2.741(1), Sn–N 2.069(3), N–Si(1) 1.729(3), N–Si(2) 1.733(3) Å; Cl–Sn–Cl′ 81.33(4), Sn–Cl–Sn′ 98.67(4), Cl–Sn–N 101.08(8), Cl–Sn–N′ 94.20(9), Sn–N–Si(1) 112.2(2), Sn–N–Si(2) 124.3(2), Si(1)–N–Si(2) 123.3(2)°.

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† No reprints available.

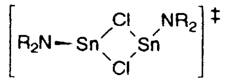
‡ *Preparation of* **1**: Red $Sn(NR_2)_2$ $[NR_2 = \overline{NCMe_2(CH_2)_3CMe_2}]^1$ (2.37 g, 5.94 mmol) in Et_2O (75 ml) was added to $SnCl_2$ (1.11 g, 5.85 mmol) in Et_2O (75 ml). After 45 h at *ca.* 25 °C, volatiles were removed *in vacuo*, and the residue extracted into C_6H_{14}. From this, orange crystals of **1** (1.79 g, 52%) were obtained at −30 °C, m.p. 125–130 °C; ^1H NMR ($[^2H_8]$PhMe, 305 K): δ 1.56s, 1.27m. Colourless $\mathbf{2}^2$ (87%), subl. 90–100 °C 10^{-3} Torr, was made similarly; ^1H NMR (C_6D_6, 305 K): δ 0.47.

§ *Crystal data* [*T* 22 °C, Enraf-Nonius CAD-4 diffractometer, no absorption corrections, full-matrix least-squares refinement with non-hydrogen atoms anisotropic, H atoms fixed, $w = 1/\sigma^2(F)$]:

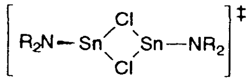
1a $C_{18}H_{36}Cl_2N_2Sn_2$, M = 588.8, monoclinic, space group $C2/c$, a = 17.346(1), b = 12.850(2), c = 11.582(1) Å, β = 114.41(1)°, U = 2350.7 Å^3, $F(000)$ = 1168; Z = 4, D_c = 1.66 g cm^{-3}; μ(Mo-Kα) = 23.7 cm^{-1}, specimen 0.2 × 0.2 × 0.15 mm, 2174 unique reflections for $2 < \theta < 25°$, 1420 reflections with $|F^2| > 3\sigma(F^2)$ used in the refinement; R = 0.028, R_w = 0.036.The dimer lies on a crystallographic two-fold rotation axis.

2b $C_{12}H_{36}Cl_2N_2Si_4Sn_2$, M = 314.5, triclinic, space group $P\bar{1}$, a = 6.434(1), b = 8.910(1), c = 12.750(1) Å, α = 101.04(1), β = 95.54(1), γ = 109.08(1)°, U = 667.9 Å^3, $F(000)$ = 312; Z = 1, D_c = 1.56 g cm^{-3}; μ(Mo-K_α) = 22.6 cm^{-1}, specimen 0.4 × 0.25 × 0.2 mm, 2452 unique reflections for $2 < \theta < 25°$, 2076 reflections with $|F^2| > \sigma(F^2)$ used in the refinement, R = 0.032, R_w = 0.042. The dimer has a crystallographic inversion centre.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.



A



B

trans-model analogues have very similar $\Delta_\mathrm{f}G^\circ$,[5] but also that $\Delta G^\ddagger$ for their interconversion is low [*via* a T-shaped, rather than a C_{2v}, tin-centred transition state; *i.e.*, an edge **A** rather than a vertex **B** (as in NH_3) inversion process].[3]

An alternative explanation for the two $\delta(^{119}Sn)$ signals at T_c for **1** as arising from a dimer $\rightleftharpoons$ 2 monomer equilibrium is discounted, because (*i*) **1** is a dimer in frozen benzene, and (*ii*) a comparison of the vastly different $\delta(^{119}Sn)$ parameters in PhMe for the only established dimer $\rightleftharpoons$ 2 monomer Sn^{II} system:[6] $(SnR'_2)_2$ [$\delta(^{119}Sn)$ + 740 and +725 at 165 K in PhMe] and SnR'_2 [$\delta(^{119}Sn)$ +2315 at 375 K] [R' = $CH(SiMe_3)_2$].[7]

When the ^{119}Sn NMR spectra of complex **1** were examined using tetrahydrofuran (THF) as solvent, there were only minor shifts (*ca.* 20 ppm) compared with the PhMe results [*e.g.*, $\delta(^{119}Sn)$ +172 at 193 K] but no signal splitting was observed down to 173 K. These features are indicative of an exceedingly weak $Sn^{II} \cdots$ THF association in the dimer, with one conformer somewhat more preferred, rather than the formation of the unknown monomeric $SnCl(NR)_n(THF)_n$ which would have been expected to have a vastly greater $\delta(^{119}Sn)$ shift to a lower frequency compared with **1**. In support we note that whereas $Sn[N(SiMe_3)_2]_2$ in C_6D_6 has $\delta(^{119}Sn)$ +771, we now find that addition of THF leads to a low frequency shift to δ +624 at 290 K.

On the basis of measurements at the coalescence temperature, $\Delta G^\ddagger_{192\,\mathrm{K}}$ for the process **1a** $\rightleftharpoons$ **1b** is estimated as 32.7 kJ mol^{-1}, whereas a full line shape analysis[8]¶ leads to $\Delta H^\ddagger$ 70 kJ mol^{-1}, $\Delta S^\ddagger$ 187 J K^{-1} mol^{-1} and $\Delta G^\ddagger$ 34.2 kJ mol^{-1}. This indicates that the isomerisation is entropy driven (favouring a dissociative process), but caution is called for since (*i*) high values of $\Delta S^\ddagger$ are an occasional artefact of the spectral analysis/line-shape simulation, and (*ii*) the difficulty of estimating line-widths in this system. An alternative intramolecular mechanism might implicate $R_2NSn^+(\mu\text{-}Cl)\text{-}Sn^-(Cl)\text{-}NR_2$ as an intermediate.

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¶ *Spectral parameters used*: $\delta(^{119}Sn)$ +192.2 (= 35 840 Hz) and +177.0 (= 33 010 Hz) at 183 K; populations (*p*) 0.67 and 0.33, respectively at 183 K; minimum line-width at half-peak height, 940 Hz, transverse relaxation time; $T_2 = 3.4 \times 10^{-4}$ s. Unresolved $^1J_{Sn\text{-}N}$ coupling was incorporated into T_2 for the purpose of the lineshape analysis.

References

1 M. F. Lappert, P. P. Power, M. J. Slade, L. Hedberg, K. Hedberg and V. Schomaker, *J. Chem. Soc., Chem. Commun.*, 1979, 369.
2 D. H. Harris and M. F. Lappert, *J. Chem. Soc., Chem. Commun.*, 1974, 895.
3 D. A. Dixon, A. J. Arduengo and M. F. Lappert, *Heteroatom Chemistry*, 1991, **2**, in the press.
4 *cf.*, B. Wrackmeyer, *Ann. Repts. NMR Spectrosc.*, 1985, **16**, 73.
5 G. Trinquier, *J. Am. Chem. Soc.*, 1990, **112**, 2130; 1991, **113**, 144.
6 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; M. F. Lappert, *Silicon, Germanium, and Tin Compounds*, 1986, **9**, 129.
7 K. W. Zilm, G. A. Lawless, R. M. Merrill, J. M. Millar and G. G. Webb, *J. Am. Chem. Soc.*, 1987, **109**, 7236.
8 D. A. Kleier and G. Binsch, DNMR 3; A Computer Program for the Calculation of Complex Exchange-broadened NMR Spectra. Modified Version for Spin Systems Exhibiting Magnetic Equivalence or Symmetry. Program 165, Quantum Chemistry Program Exchange, Indiana University, Bloomington, 1970.