A supramolecular motif in the solid-state structure of a difunctional thallium(i) amide defined by weak Tl···Tl attractions

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The crystal structure of the difunctional thallium(i) amide CH_2 $[CH_2N(Tl)SiMe_3]_2$ 1 reveals a pattern of aggregation based on weak attractive metal–metal interactions, a situation which appears to be influenced by the degree of exposure of the thallium centres; this is evidenced by the solid-state structure of the more shielded analogue $CH_2[CH_2N(Tl)SiBu^tMe_2]_2$ 2 which features no significant Tl···Tl contacts.

The utilization of intermolecular interactions which generate specific supramolecular motifs has greatly enhanced the systematic approach to both the understanding and the design of highly organized molecular arrays in solids.[1] Intermolecular hydrogen bonding as well as ionic or dipolar interactions have been the most widely employed 'directional forces' in this context.[2] More recently, the attractive interactions between heavy closed-shell metal centres (with d^{10} or $d^{10}s^2$ configuration) and the way they affect the intermolecular aggregation in solids have been investigated.[3] While compounds of monovalent gold have provided the most spectacular objects of study in this context, the neighbouring metals in the Periodic Table, in particular thallium(i), seem to be equally capable of aggregation through (mainly dispersive) metal–metal attraction.[4] The nature of these weak metal–metal interactions in thallium(i) compounds has been the subject of some debate,[5,6] although there is little doubt about their role in molecular aggregation.

The accessibility of the thallium(i) amides *via* metal exchange with well established alkali-metal analogues[7] prompted us to study their structural chemistry in more detail, in particular, with regard to the modes of aggregation defined by metal–metal interactions. That dispersive thallium(i)···thallium(i) attractions may indeed strongly influence the solid-state structures of polyfunctional thallium(i) amides was recently demonstrated by the drastic distortions of the ligand framework which the tripodal Tl–amide $MeSi[SiMe_2N(Tl)-Bu^t]_3$ displays in its crystal structure.[8] In this case, a highly flexible ligand system permitted rather unpredictable molecular shapes and thus molecular units aggregating in the crystal. In order to study intermolecular structural motifs in a meaningful and more systematic way, we chose a simpler difunctional Tl amide the molecular structure of which did not allow for significant geometrical rearrangement.

Stirring a solution of $CH_2[CH_2N(Li)SiMe_3]_2$ (dioxane)$_2$ with TlCl in dioxane at room temp. for 3 h led to a complete metal exchange. The work up of the crude product mixture by extraction with toluene afforded a deep-orange solution from which a red, highly air-sensitive, crystalline solid could be obtained at −30 °C (yield 70%), the analytical data of which were consistent with its formulation as $CH_2[CH_2N(Tl)SiMe_3]_2$ 1 (Scheme 1). The results of variable-temperature NMR studies and cryoscopic measurements in benzene indicated that the compound is monomeric in solution.† It may also be sublimed at 60 °C and 10^{-2} mbar without decomposition. A single-crystal X-ray structure analysis, however, revealed a truly remarkable pattern of molecular packing in the crystal (Fig. 1).‡

As indicated in Scheme 1, the monomeric unit of the difunctional thallium amide has the expected molecular structure in which the two amido-N atoms and the two thallium(i)

centres form a puckered four-membered ring, the metal atoms occupying rather exposed positions thus generating the poten-
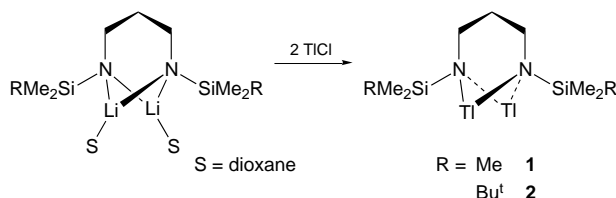
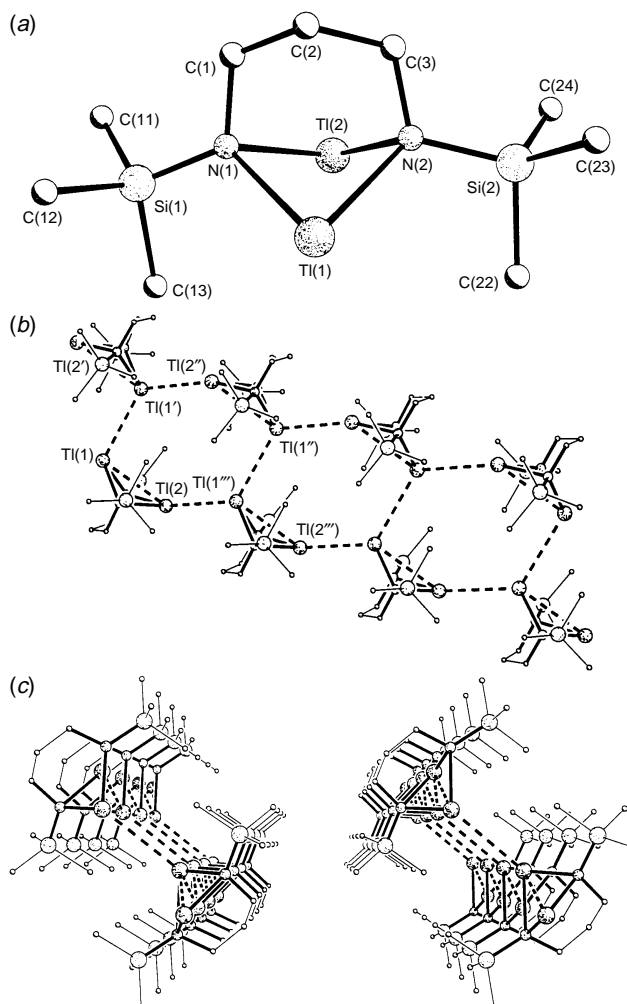**Scheme 1** Synthesis of **1** and **2** by Li/Tl exchange

Fig. 1 Crystal structure of **1**. Molecular structure (*a*) and aggregation in the crystal viewed along the crystallographic *b* axis (*b*) and *a* axis (*c*). Selected bond lengths (Å) and interbond angles (°) of the molecule: Tl(1)···Tl(2) 3.490(3), Tl(1)–N(1) 2.469(14), Tl(1)–N(2) 2.408(13), Tl(2)–N(1) 2.475(12), Tl(2)–N(2) 2.457(13); N(1)–Tl(1)–N(2) 74.8(4), N(1)–Tl(2)–N(2) 73.9(4), Tl(1)–N(1)–Tl(2) 89.8(4), Tl(1)–N(2)–Tl(2) 91.7(4).
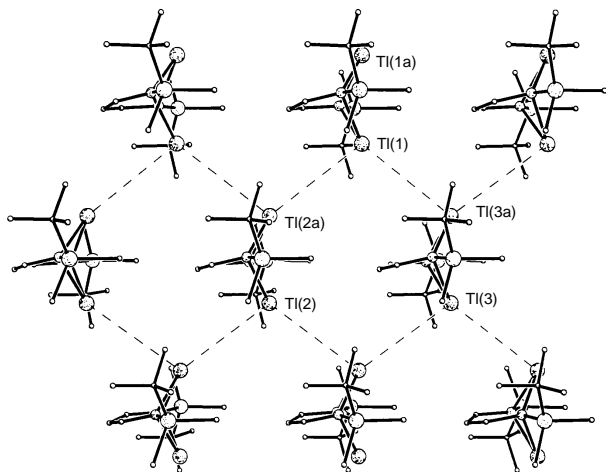
Fig. 2 Packing of **2** in the crystal viewed along the *c* axis. Selected bond lengths (Å) and interbond angles (°) of the molecule: Tl(1)···Tl(1′) 3.4800(7), Tl(1)–N(1) 2.405(7), Tl(1)–N(1′) 2.481(7); N(1)–Tl(1)–N(1′) 74.7(3), Tl(1)–N(1)–Tl(1′) 90.8, intermolecular Tl···Tl > 4.70.

tially 'sticky ends' for aggregation [Fig. 1(*a*)]. The fairly short Tl···Tl distance of 3.490(2) Å is probably a consequence of the bridging ligands tying the two metals together rather than due to significant bonding interaction although it is rather close to the interatomic distances found in α-thallium (3.408 and 3.457 Å).[9]

In the solid the molecular units of **1** aggregate *via* Tl···Tl contacts to form infinite, double-stranded bands [Fig. 1(*b*),(*c*)]. The two strands consist of monomers facing each other and occupying translationally displaced positions generating a one-dimensional grid consisting of distorted hexagons of metal–metal contacts. In the resulting planar bands one of the two metal atoms in the monomers not only forms a direct contact to its neighbour within a strand [Tl···Tl 3.775(3) Å] but also across to the opposite strand [Tl···Tl 3.697(3) Å].

In order to assess the importance of the relative exposure of the thallium(i) centres in the structure of **1** for the aggregation in the solid the structurally analogous Tl–amide CH₂[CH₂N(Tl)Si-Bu^tMe₂]₂ **2** containing the bulkier silyl substituent Bu^tMe₂Si at the amido functionalities was synthesized using the identical procedure outlined for **1** (yield 74%).† The crystal structure of **2** has revealed a packing in the solid which appears to be entirely dictated by the molecular shape rather than metal–metal contacts as found for **1** (Fig. 2).‡

The shortest intermolecular Tl···Tl distances of over 4.7 Å are testimony to the absence of significant metal–metal interaction in the crystal. With the exception of the somewhat greater shielding of the Tl₂N₂-unit in the molecule the overall molecular shapes of **1** and **2** are closely related. This is to be seen in the context of a notion put forward by von Schnering who pointed out that aggregations *via* heavy metals in a molecule may in fact arise from the requirements of crystal packing dictated by the shape of the whole molecule, a situation aptly described as the 'umbrella effect'.[10] The fact that the molecules containing the more exposed metal atoms display structural motifs characterized by metal–metal contacts, while those less favoured in doing so by nature of their more shielded molecular structure do not, supports the relevance of such weak interactions between the heavy metals in the structure of compound **1**.

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Footnotes

† *Selected spectroscopic data*. **1**: ¹H NMR (C₆D₆, 295 K); δ 0.13 [s, 18 H, Si(CH₃)₃], 1.70 (m, 2 H, CH₂C), 4.32 (br, t, 4 H, ³J_HTlH 54.8 Hz, CH₂N).

¹³C{¹H} NMR (C₆D₆, 295 K); δ 0.8 [t, ³J_TlC 59.3 Hz, Si(CH₃)₃], 37.7 (CH₂C), 51.0 (t, ²J_TlC 82.5 Hz, CH₂N). **2**: ¹H NMR (C₆D₆, 295 K); δ 0.05 [s, 12 H, Si(CH₃)₂], 1.02 [s, 18 H, C(CH₃)₃], 1.72 (br m, 2 H CH₂C), 4.37 (br t, ³J_TlH 52 Hz, 4 H, CH₂N). ¹³C{¹H} NMR (C₆D₆, 295 K); δ −3.5 [t, ³J_TlC 102 Hz, Si(CH₃)₂], 22.4 [s, (CH₃)₃C], 28.4 [t, ⁴J_TlC 50 Hz, C(CH₃)₃], 37.4 (s, CH₂C), 52.4 (t, ²J_TlC 86 Hz, CH₂N). Correct C, H, N, Tl analyses were obtained.

‡ *Crystal data*: **1**; [C₉H₂₄N₂Si₂Tl₂]∞, crimson, crystal dimensions 0.4 × 0.3 × 0.2 mm, *M* = 625.22, triclinic, space group *P*1̄, *a* = 6.557(5), *b* = 11.520(7), *c* = 12.838(8) Å, α = 116.29(4), β = 91.28(4), γ = 104.82(3)°, *U* = 830.2(10) Å³, *Z* = 2, *D*_c = 2.501 Mg m⁻³, μ = 19.509 mm⁻¹, *F*(000) = 564, 4523 reflections collected (10 ≤ 2θ ≤ 45°) at 192(2) K, 2132 independent reflections used in the structure refinement [*R*_int = 0.108]; *R*₁ = 0.066 [*I* > 2σ(*I*)], *wR*₂ = 0.175 (all data), 142 parameters, largest difference peak, hole = 3.14, −3.20 e Å⁻³;

2; [C₁₅H₃₆N₂Si₂Tl₂]∞, orange crystal dimensions 0.4 × 0.4 × 0.4 mm, *M* = 709.38, monoclinic space group *C*2/*c*, *a* = 12.7223(3), *b* = 7.3019(2), *c* = 24.2444(4) Å, β = 99.9330(3), *U* = 2218.47 Å³, *Z* = 4, *D*_c = 2.124 Mg m⁻³, μ = 14.614 mm⁻¹, *F*(000) = 1320, 13545 reflections collected (6 ≤ 2θ ≤ 52°) at 133(2) K, 2237 independent reflections used in the structure refinement [*R*_int = 0.137]; *R*₁ = 0.054 [*I* > 2σ(*I*)], *wR*₂ = 0.136 (all data), 115 parameters and 23 restrains, largest difference peak, hole = 2.82, −3.93 e Å⁻³. The data were collected on a Stoe-Siemens AED four-circle diffractomer (**1**) and on a Stoe-Siemens-Huber diffractometer fitted with a Siemens CCD detector (**2**) (graphite-monochromated Mo-Kα radiation, λ = 0.710 73 Å) equipped with a modified version of the Siemens/Nicolet LTIIa low-temperature device.[11] The structures were solved by direct methods (SHELXS-90)[12] and refined by full-matrix least-squares methods against *F*² (SHELXL-96).[13] The central methylene group in **2** was refined by suppressed constraints of the special position required from the twofold axis All data were absorption corrected and the non-H atoms were refined anisotropically. Definition of R values: *wR*₂ = [Σ[*w*(*F*ₒ² − *F*_c²)²]/Σ[*w*(*F*ₒ²)²]]^½, *R*₁ = Σ||*F*ₒ| − |*F*_c||/Σ|*F*ₒ|. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/367.

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