Demethylation of the $[Me_3Sn(PhN_2O_2)]_4$ tetramer into dimeric $[Me_2Sn(PhN_2O_2)_2]_2$: a thermally induced methyl-transfer between supramolecules†‡

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The single crystals of tetrameric $[Me_3Sn(PhN_2O_2)]_4$ (1) supramolecule demethylates into single crystals of $[Me_2Sn(PhN_2O_2)_2]_2$ dimer (2) and volatile Me_4Sn, as a result of a crystal-to-crystal supramolecular structural transformation, which occurs upon heating and it is accompanied by a significant change of the molecular and crystal structures.

A classical solid-state reaction can be photochemically[1] and/or thermally[2] induced and proceed either by topochemical or non-topochemical mechanism.[3] The thermally induced methyl migration of organic compounds in the solid-state is of particular structural interest since they are all methyl-transfer isomerisation (rearrangement) reactions.[4] Interestingly, in contrast to thermally induced solid-state methyl migrations in organic molecules which have been the subject of extensive investigations,[4] the solid-state methyl transfer phenomenon in organometallic complexes have not been exploited. The methyl migrational dismutation of triorganotins has been detected in the environment, and the alkyl group removal has been attributed to the action of UV light, chemical cleavage and biological degradation by bacteria, although its chemistry has never been elucidated.[5] In addition, toxic organotins are progressively dealkylated to inorganic Sn(IV) in mammalian organs, and recently it was shown that a linear peptide derived from the membrane protein stannine is able to dealkylate the trimethyltins.[6] Interestingly, no cases of demethylation processes occurring in the solid state have been published previously for triorganotin(IV) derivatives.

In this Communication, we report the first thermally accelerated crystal-to-crystal supramolecular structural transformation of a $[Me_3Sn(PhN_2O_2)]_4$ (**1**) tetramer into self-assembled $[Me_2Sn(PhN_2O_2)_2]_2$ dimer (**2**) *via* methyl-transfer process (Fig. 1).[7] During the X-ray diffraction measurements of **1** a significant 28% decay and a shrinkage (before: 0.55 × 0.30 × 0.25 mm; after: 0.45 × 0.25 × 0.24 mm) of the single crystal was observed,[8] indicating radiation-induced crystal decay and thermal sensitivity of the sample. However, crystals of **1** stored at room temperature were stable for several weeks as confirmed by liquid phase NMR spectroscopic measurements in non-coordinating solvents (*e.g.* $CDCl_3$).[9]

To gain further insight into this process, the $\mathbf{1} \rightarrow \mathbf{2} + Me_4Sn$ methyl-transfer was carried out in open-end vials at different temperatures (*viz*. 70, 86 and in the melt at 100 °C). Typically after 7 hours of heating the single crystals of **2** began to crystallize from the melt at 100 °C (Fig. 2).

The X-ray structure determination of a well formed crystal confirmed the formation of a dimer **2**,§ and thus, the demethylation of tetramer **1**. Accordingly, the 20-membered $Sn_4O_8N_8$ macrocyclic ring system of **1** transforms into five-membered inorganic SnO_2N_2 chelate rings, which are chelated to a stannoxanic Sn_2O_2 dimerized supramolecule **2**. This supramolecular structural transformation proceeds with the disruption of the

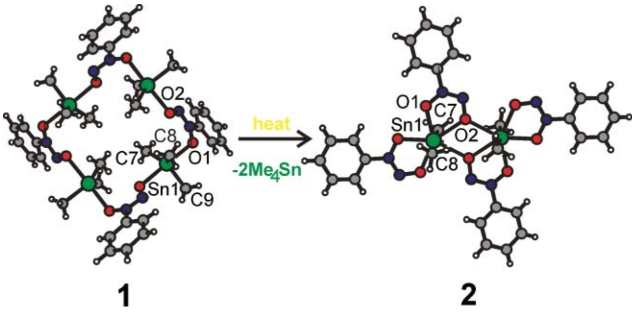
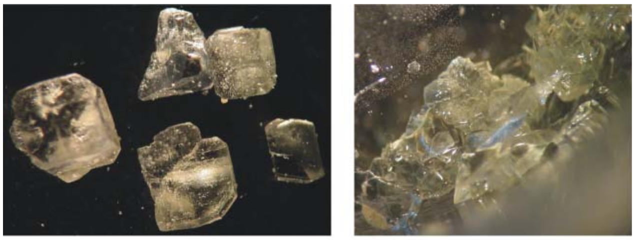


Fig. 1 Thermally induced crystal-to-crystal supramolecular structural transformation of a $[Me_3Sn(PhN_2O_2)]_4$ (**1**) tetramer into $[Me_2Sn(PhN_2O_2)_2]_2$ dimer (**2**) *via* methyl-transfer process.



(A) (B)

Fig. 2 The images of the (single) crystals of **1** before heating (**A**) and the melt-crystallised crystals of **2** after 9 hours of heating at 100 °C (**B**) as observed through a microscope. It can be seen that the supramolecular structural transformation proceeds with complete morphology change.

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† Dedicated to Professor Alajos Kálmán on the occasion of his 70th birthday.

‡ Electronic supplementary information (ESI) available: Crystallographic data of **2** along with the figure of the molecular structure. The $[A]^{-1}$ *vs* t plot used for the estimation of the k rate constant, and the aliphatic region of the ^1H-NMR spectra used for the component analysis of **1** after 70, 86 and 100 °C heating the crystals in open vials for various durations. See http://dx.doi.org/10.1039/b506728f

original crystal structure turning the initial space group $P\bar{4}2_1/c$ (**1**) into $P\bar{1}$ (**2**). In crystal lattice, the tetramers of **1** stack in columns parallel to the tetragonal *c* axis and the shortest intermolecular Sn···C distance between neighbouring columns is 4.81 Å, however, the shortest intramolecular Sn···C distance is only 4.69 Å. Both distances are appropriate for a topochemically controlled methyl migration process. Nevertheless, since the reaction proceeds faster in the melt and includes a marked change in the molecular and crystal structures a non-topochemical process is also conceivable. Further studies are necessary to clarify the discrete mechanistic details.

The single crystal of **2** has a slightly different unit cell than that of **2′** obtained from solution.[10] The high isostructurality index[11] ($I_i(23)$ = 93.7%) and the high volumetric index[12] (I_v = 98.5%) indicate that **2** and **2′** are isostructural. A comparison of the unit cell parameters show that the *a* and *b* axis of the crystals obtained from the melt (**2**) are shorter than those of **2′** (Δa = 0.009 and Δb = 0.019 Å), and the α and β angles are interchanged. Accordingly, the *a* and *b* axes must also be interchanged, which can be rationalized by the C–H···N hydrogen-bonded molecular layers of **2** and **2′** projected along their *c* axis in Fig. 3.[14] It can be seen that polymorphs **2** and **2′** can be distinguished *via* the different orientation of a given hydrogen bond with respect to the shortest *a* axis (Fig. 3A) of the triclinic crystals.[13] They are related to each other by a non-crystallographic twofold C^*_2-axis lying on the plane of the molecules tilted at *ca.* 45° to the respective *b* (**2′**) or *a* (**2**) axis. A turn of 180° around this C^*_2-axis of the molecule **2′** interchanges the *a* and *b* axes, consequently the orientation of the *c* axis is also changed, therefore the direction of the hydrogen bonding pattern becomes identical with those of **2** (Fig. 3B). Furthermore, the C–H···N bonded layers of **2** are connected together by weak C–H···π interactions,[14] and the stacking distance of identically oriented hydrogen-bonded layers in **2** is 0.05 Å shorter than that in **2′**. It is clear that this 180° turn of the hydrogen bonding patterns must generate very similar unit cell dimensions and very similar packing in the same space group to maintain the initial crystal symmetry, otherwise defects would be introduced and the collapse of the crystal lattice occurs. In other words, an 180° turn of the molecules around a non-crystallographic axis is allowed since the *a* and *b* axes are nearly equal (Δab = 0.041 Å for **2′** and 0.031 Å for **2**), therefore they are interchangeable, as are the hydrogen bonding patterns with respect to the original crystal symmetry. The interchange of the cell axes as well as the turn of the whole hydrogen bonding pattern around a non-crystallographic axis are generally mediated by solvents and/or temperature, whereas most cases occur with the disruption of the original crystal lattice.[15] To the best of our knowledge, the crystal structures of **2** and **2′** represent the second example of hydrogen-bonded isostructural polymorphs related by a non-crystallographic turn with virtually the same unit cell.[16] In our case, however, the source of the polymorphs is different and unprecedented: melt *versus* solution.

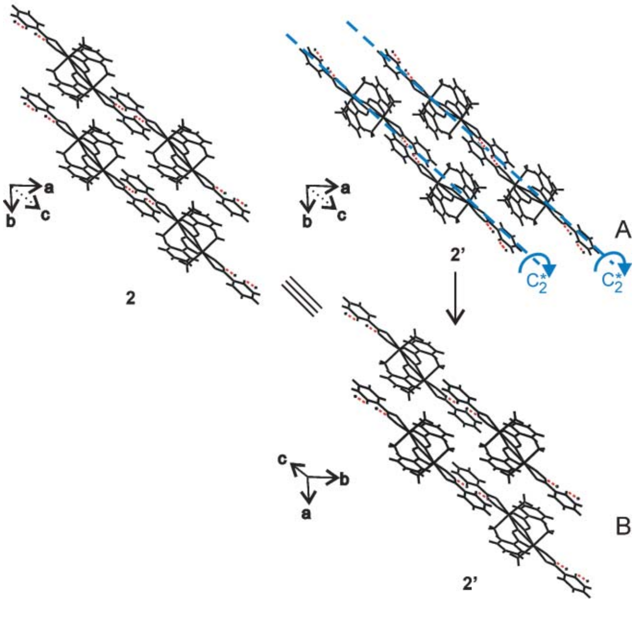

Fig. 3 Section of the crystal structures of **2** and **2′** showing the infinite C–H···N hydrogen-bonded layers. (**A**) It can be seen that the orientation of hydrogen-bonds are different with respect to the shortest *a* axis of a triclinic crystals of **2** and **2′**. (**B**) A turn of 180° around the non-crystallographic C^*_2-axis of the molecule **2′** interchanges the *a* and *b* axes, consequently the orientation of the *c* axis is also changed, therefore, the direction of the hydrogen bonding pattern becomes identical to those of **2**.

To investigate the thermal induction of the methyl transfer a series of identical crystals of **1** were placed in open-end vials and heated to 70, 86 and 100 °C, respectively. The molar ratio of the methyl-moieties was monitored by ^{1}H-NMR spectroscopy.¶

The progress with the time is shown in Fig. 4; based on these data it appears that the calculated monomeric $[Me_2Sn(PhN_2O_2)_2]_1$/$[Me_3Sn(PhN_2O_2)]_1$ ratio increased substantially with the temperature: more than nine times greater ratio was measured in the melt at 100 °C than at 86 °C after 2 hours of heating. This indicates that the melt state is providing more than just a high concentration medium for the demethylation of **1**: we suppose that bimolecular collisions of the monomers dominate. To clarify this we further characterized the kinetics of the **1** → **2** + Me_4Sn methyl-transfer by keeping the crystals melt at the characteristic temperature 100 °C for various durations (20 minutes to 4 hours). The kinetics of the transformation in the melt was also followed by liquid NMR analysis ($CDCl_3$) of the samples after cooling down the individual vials at different times. The initial reaction rates at 100 °C indicated a second order 2A → B + C type kinetics with the approximate rate constant of k = 1.61 E–4 ± 6.9 E–6 l·mol^{-1}·s^{-1} (for details see Supporting Information‡).

The appearance of the volatile by-product Me_4Sn became evident when the reaction mixtures from sealed vial melt

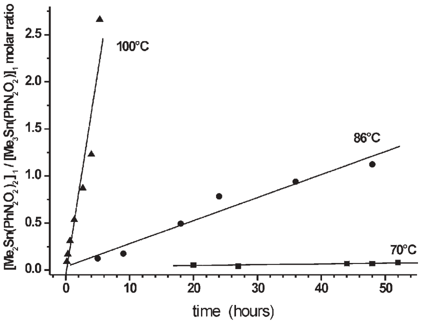

Fig. 4 Time course of the **1** → **2** + Me_4Sn methyl-transfer induced by heating at different temperatures.

experiments (86 °C) were analysed. In contrast to the open vial experiments, however, our attempt to provide reproducible kinetic data from sealed vial experiments has failed. We assume that this difference between the outcome of the two types of experiments is strongly related to the complete or partial removal of a weakly coordinating Me_4Sn species from the reaction mixture. When Me_4Sn is removed through heating in an open vial experiment the nascent product **2** is stabilized by dimerization, whereas if Me_4Sn remains more abundant in the reaction mixture, the self-assembled dimer is destabilized opening ways for other competitive degradation processes. To provide more evidence for this theory further liquid state investigations of **2** in coordinating and non-coordinating solvents are desirable.

In summary, we have observed an unprecedented supramolecular structural transformation which occurs upon heating accompanied by a significant change of the molecular and crystal structure. As a result, a unique (single) crystal phase of **2** is produced with a hydrogen bond orientation different from that in solvent-grown crystals. The demethylation of **1** proceeded considerably faster in the melt than in the solid state. It is still unclear how far the elementary steps of the ligand exchange reaction occur intra- or intermolecularly in the melt and whether this thermal reaction is topochemically controlled or not in the solid state. Additional investigations are in progress to explore and clarify the assumptions concerning the validity of a bimolecular 2A → B + C mechanism found in the melt state. One may tentatively assume that this thermally induced methyl-transfer reaction is not uncommon for triorganotin(IV) complexes and further studies are in progress to discover analogous systems.

Notes and references

§ *Crystal data* for **2**: $C_{28}H_{32}N_8O_8Sn_2$, M = 846.04, triclinic, colorless prisms, a = 9.408(3), b = 9.439(3), c = 10.739(2) Å; α = 64.31(2), β = 75.94(2), γ = 78.00(2)°; V = 827.9(4) Å^3, T = 293(2) K, space group $P\bar{1}$ (no. 2), Z = 1, μ(Mo–K$_\alpha$) = 1.568 mm^{-1}, ρ_{calcd} = 1.697 Mg m^{-3}, *F(000)* = 420, λ = 0.71073 Å, crystal size 0.55 × 0.40 × 0.20 mm. Intensity data of 12298 reflections were measured (2.49 ⩽ Θ ⩽ 32.04°) on an Enraf-Nonius CAD-4 diffractometer (ω-2Θ scans) of which 5723 were independent (R_{int} = 0.022). The intensities of the standard reflections indicated a crystal decay of 2%, which was corrected. A semi-empirical (psi-scan) absorption correction was also applied. The structure was solved by direct methods (SHELXS-97)[17] and refined by full-matrix least-squares (SHELXL-97).[17] 5723 reflections were employed in the structure refinement (210 parameters, 0 restraints). The final R values were $R1$ = 0.0543 ($I > 2\sigma(I)$) and $wR2$ = 0.1396 (all data). All non-hydrogen atoms were refined anisotropically. Hydrogen atomic positions were generated from assumed geometries. A riding model refinement was applied for the hydrogen atoms. CCDC 272081. See http://dx.doi.org/10.1039/b506728f for crystallographic data in CIF or other electronic format.

¶ ^{1}H-NMR spectra were recorded on a Varian-INOVA 400 MHz spectrometer in $CDCl_3$ (Merck Gmbh) at 25 °C. Chemical shifts were referenced to the residual protons of the deuterated solvent. In open vial reactions, **1** and **2** were the only detectable species and the $[Me_2Sn(PhN_2O_2)_2]_1/[Me_3Sn(PhN_2O_2)]_1$ molar ratio of the product and starting material was usually measured by dissolving the reaction mixture in $CDCl_3$ and integrating their respective methyl resonances. The ^{1}H-NMR spectra of **2** and **2′** were identical ($CDCl_3$).

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13 For the better comparison between the cell parameters of **2** and **2′** polymorphs, we have adopted the convention $a < b < c$ for the unit cell setting in triclinic crystal system.

14 The geometric parameters of C–H···N hydrogen-bonds are H(6A)···N(6A)^i 2.70 Å, C(6A)···N(6A)^i 3.403(6) Å, C(6A)–H(6A)···N(6A)^i 133.0°; symmetry code: (i) 1 − x, 2 − y, − z for **2** and H(2A)···N(2A)^i 2.70 Å, C(2A)···N(2A)^i 3.407(3) Å, C(2A)–H(2A)···N(2A)^i 132.9°; symmetry code: − x, 1 − y, 1 − z for **2′**, respectively. The geometric parameters of C–H···π hydrogen-bond are H(2B)···π^i 3.32 Å, C(2B)···π^i 3.560(6) Å, C(2B)–H(2B)···π^i 97.5°; symmetry code: (i) − x, 2 − y, 1 − z for **2**, where π is the centroid of the C(1A)/C(2A)/C(3A)/C(4A)/C(5A)/C(6A) phenyl-ring.

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