APPLIED ORGANOMETALLIC CHEMISTRY
Appl. Organometal. Chem. 2004; **18**: 487–488
Main Group Metal Compounds **AOC**

Crystallographic report

Octameric sodium trimethylsilanolate hemihydrate hemi-THF solvate, $[NaOSiMe_3\cdot\frac{1}{2}H_2O\cdot\frac{1}{2}THF]_8$

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Received 14 April 2004; Revised 19 April 2004; Accepted 27 April 2004

The title compound is composed of two Na_4O_4 heterocubanes which are connected via four μ-$OSiMe_3$ groups. The oxygen atoms of the water molecules occupy two corners of an Na_4O_4 cube and additionally form hydrogen bonds to the μ-$OSiMe_3$ groups with O···O distances in the range 2.649(4)–2.714(4) Å. Copyright © 2004 John Wiley & Sons, Ltd.

KEYWORDS: crystal structure; sodium trimethylsilanolate; cluster; hydrogen bonding

COMMENT

Sodium trimethylsilanolate is a cheap starting material for the synthesis of metal silanolates via the salt metathesis route. However, commercial $NaOSiMe_3$ often contains some residual water, and thus might give rise to undesired side reactions. The most effective synthesis of anhydrous $NaOSiMe_3$ is the reaction of Me_3SiOH with sodium.[1] Alternatively, Hyde *et al.*[2] suggested the reaction of hexamethyldisiloxane with sodium amide in liquid ammonia to prepare $NaOSiMe_3$. The molecular structure of anhydrous $NaOSiMe_3$ is based on an Na_4O_4 heterocubane,[3,4] whereas the structures of the hydrate $NaOSiMe_3\cdot 3H_2O$ and of $[Na_{11}(OSiMe_3)_{10}(OH)]$ are more complex.[5,6] The affinity of sodium silanolates towards water is also documented by the Na_4O_4-heterocubane structure of $[NaOSiPh_3]_4\cdot 3H_2O$.[7] We observed single crystals of $[NaOSiMe_3\cdot\frac{1}{2}H_2O\cdot\frac{1}{2}THF]_8$ as a by-product in an attempt to prepare an organobismuth silanolate from $ArBiCl_2$ (Ar = 2, 6-dimesityl-4-*t*Bu-phenyl) and sodium trimethylsilanolate. The unique structure of the title compound (Fig. 1) is composed of two Na_4O_4 heterocubanes connected via four μ-$OSiMe_3$ groups. Each Na_4O_4 heterocubane is composed of four sodium atoms, two oxygen atoms of the μ_3-$OSiMe_3$ groups and two μ_3-oxygen atoms of water. The sodium atom Na2 is four-coordinate, whereas Na1 is five-coordinate. The Na–μ-$OSiMe_3$ and the Na–μ_3-$OSiMe_3$ distances are in the ranges 2.330(3)–2.339(3) Å and 2.250(3)–2.289(3) Å respectively, which are comparable with Na–O distances

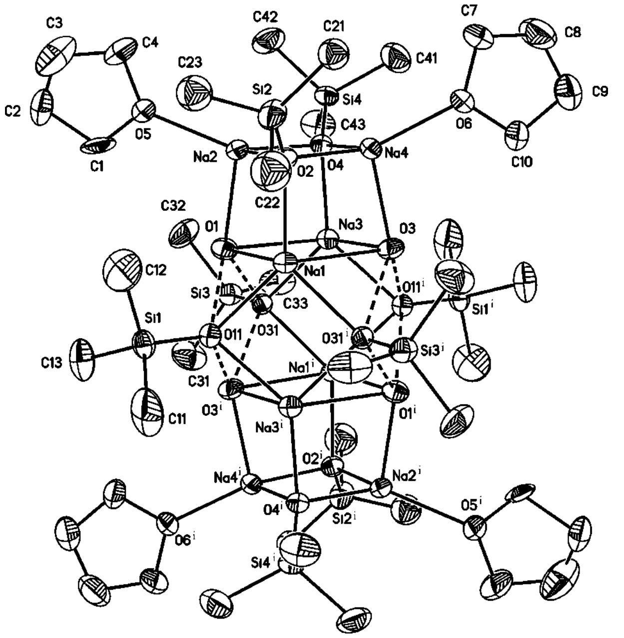

Figure 1. Molecular structure of $[NaOSiMe_3\cdot\frac{1}{2}H_2O\cdot\frac{1}{2}THF]_8$; hydrogen atoms omitted for clarity. Symmetry transformations used to generate equivalent atoms: $-x + 1/2$, $-y + 1/2$, $-z$. Selected geometric parameters: Na1–O1/O2/O3/O11/O31^{i} 2.715(4)/2.246(3)/2.727(3)/2.339(3)/2.333(3) Å; Na2–O1/O2/O4/O5 2.284(3)/2.285(4)/2.289(3)/2.300(4) Å, O1–O11 2.649(4) Å, O1–O31 2.714(4) Å, O3–O11^{i} 2.714(4) Å, O3–O31^{i} 2.668(4) Å; O11–O1–O31 104.51(13)°, O1–O11–O3^{i} 75.06(11)°, O3–O31–O1^{i} 74.76(12)°.

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of the coordinated THF molecule [2.300(4) and 2.293(4) Å]. Noteworthy, the bond distances between four-coordinate sodium atoms and the oxygen atoms of water [2.272(3) and 2.284(3) Å] are markedly shorter than those between water and five-coordinate sodium atoms [2.715(4)–2.758(4) Å]. In addition, the water molecule is coordinated via hydrogen bonding to two μ-OSiMe$_3$ groups showing O···O distances of 2.649(4)–2.714(4) Å. The title compound is most likely an intermediate along the reaction pathway of the hydrolysis of NaOSiMe$_3$. Attempts to prepare $[\mathrm{NaOSiMe_3}\cdot\frac{1}{2}\mathrm{H_2O}\cdot\frac{1}{2}\mathrm{THF}]_8$ from anhydrous sodium trimethylsilanolate by addition of water gave $[\mathrm{Na_{11}(OSiMe_3)_{10}(OH)}]$ instead.[6]

EXPERIMENTAL AND RESULTS

To a solution of (2,6-dimesityl-4-*t*Bu-phenyl)bismuth dichloride (0.23 g, 0.35 mmol) in THF (15 ml) was added at room temperature NaOSiMe$_3$ (1.0 g, 0.90 mmol) in small portions. The suspension was stirred for an additional hour and the solvent was removed *in vacuo*. The yellow residue was extracted with benzene (20 ml) and the solid filtered off. Crystallization at 6 °C gave single crystals of the title compound. ^{1}H NMR (200.1 MHz, CDCl$_3$): $\delta = 0.12$ (s, CH$_3$), 1.83 (m, CH$_2$, THF), 3.73 (m, CH$_2$, THF). The moisture-sensitive compound was transferred directly from the mother liquid to the diffractometer using the oil drop technique. Intensity data were collected at 173 K on a Nonius Kappa CCD for a colourless block of dimensions 0.14 × 0.14 × 0.16 mm^3. $C_{40}H_{108}Na_8O_{16}Si_8$, $M = 1253.90$, monoclinic, $C2/c$, $a = 25.9560(5)$, $b = 11.7472(2)$, $c = 26.2799(7)$ Å, $\beta = 105.6367(10)°$, $V = 7716.5(3)$ Å^3, $Z = 4$, 6654 unique data ($\theta_{\max}$ 25.0°), 3039 data with $I \geq 2\sigma(I)$, $R = 0.072$ (obs. data), $wR = 0.199$ (all data). Programs used: SHEXLS-97, SHELXL-97 and ORTEP. CCDC deposition number: 234630.

Acknowledgements

The Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, the Fachbereich Chemie of Dortmund University and Professor Dr K. Jurkschat are thanked for support.

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