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Crystallographic report

A polymorph of undecasodium decatrimethylsilanolate hydroxide: $[Na_{11}(OSiMe_3)_{10}(OH)]$

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The title compound is a polymorph of $[Na_{11}(OSiMe_3)_{10}(OH)]$ and was crystallized from a toluene solution containing $NaOSiMe_3$ and water. The molecular structure is best described as being composed of two subunits, a square antiprism built from eight sodium atoms and an Na_4O_4 heterocubane, both sharing a sodium atom. Copyright © 2004 John Wiley & Sons, Ltd.

KEYWORDS: crystal structure; sodium trimethylsilanolate; cluster; OH^- encapsulation

COMMENT

The high affinity of sodium silanolates towards water is well documented.[1–6] Here, we report an additional example which is a polymorph of $[Na_{11}(OSiMe_3)_{10}(OH)]$.[4] Notably, the corresponding sodium alkoxide $[Na_{11}(OCMe_3)_{10}(OH)]$[7] shows a similar molecular structure but it is not isostructural with $[Na_{11}(OSiMe_3)_{10}(OH)]$. The molecular structure of the title compound (Fig. 1) is best described as being composed of two subunits, a square antiprism built from eight sodium atoms (Na1–Na8) and an Na_4O_4 heterocubane (Na8–Na11). The sodium atom Na8 is part of both fragments $[Na_8(OH)(OSiMe_3)_6]^+$ and $[NaOSiMe_3]_4$. Four silanolate groups are μ_3-coordinated (O2, O3, O8 and O9) to four of the eight triangular faces of the square antiprism with Na–O distances in the range 2.244(4)–2.282(4) Å. The outer square face built from Na1–Na4 is μ_4-capped with a silanolate. A μ_4-OH is located inside the square antiprism, being coordinated to Na5–Na8. A hydrogen bond between the OH group and the μ_4-$OSiMe_3$ group [O1–O11 2.972(4) Å] stabilizes the square antiprism. The oxygen atom O4 is placed on the Na5–Na6 edge and additionally coordinates to the sodium atom Na9 of the heterocubane. The heterocubane fragment is built from Na8–Na11, O5–O7 and O10. Three of four silanolate groups are μ_4-coordinated and connect the square antiprism and the heterocubane. The oxygen atom O6 is μ_3-coordinated to Na9–Na11 and consequently exhibits the shortest Na–O bond distances being in the

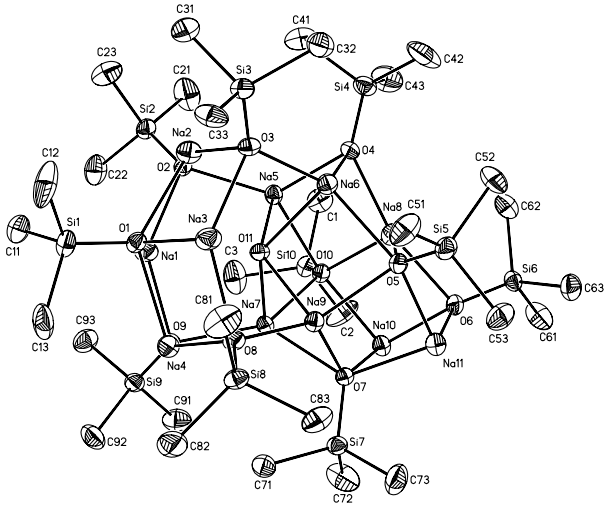

Figure 1. Molecular structure of $[Na_{11}(OSiMe_3)_{10}(OH)]$; hydrogen atoms omitted for clarity. Selected geometric parameters: Na1–O1/O2/O9 2.387(4)/2.255(4)/2.247(4) Å; Na2–O1/O2/O3 2.427(4)/2.254(4)/2.244(4) Å; Na3–O1/O3/O8 2.352(4)/2.245(4)/2.258(4) Å; Na4–O1/O8/O9 2.438(4)/2.244(4)/2.248(4) Å; Na5–O2/O4/O10/O11 2.282(3)/2.264(4)/2.449(4)/2.364(3) Å; Na6–O3/O4/O5/O11 2.267(4)/2.249(3)/2.389(4)/2.383(4) Å; Na7–O7/O9/O10/O11 2.393(3)/2.263(3)/2.289(3)/2.322(4) Å; Na8–O5/O7/O8/O11 2.280(3)/2.384(4)/2.270(3)/2.329(3) Å; Na9–O4/O5/O6/O10 2.238(4)/2.626(4)/2.324(4)/2.477(4) Å; Na10–O6/O7/O10 2.206(4)/2.376(3)/2.324(3) Å; Na11–O5/O6/O7 2.308(4)/2.198(4)/2.347(4) Å; O1–O11 2.972(4) Å.

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range 2.198(4)–2.324(4) Å. A similar subunit is found in the corresponding sodium *tert*-butanolate cluster, but only two *tert*-butanolate groups are μ_4-coordinated and two *tert*-butanolate groups are μ_3-coordinated, thus reflecting the lower Lewis basicity of alkoxides compared with their corresponding silicon analogues.

EXPERIMENTAL AND RESULTS

To a solution of $NaOSiMe_3$ (4.50 g, 40 mmol) in benzene (500 ml) was added water (300 µl). The resulting suspension was stirred overnight at room temperature and the solid material filtered off. The solvent was removed *in vacuo* and the residue crystallized from toluene (20 ml) at −6 °C to give single crystals of the title compound **1**. Compound **1** is moisture sensitive and was directly transferred 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 $0.12 \times 0.14 \times 0.14$ mm^3. $C_{30}H_{90}Na_{11}O_{11}Si_{10}$, $M = 1160.81$, monoclinic, $P2_1/n$, $a = 12.8802(2)$, $b = 25.0280(5)$, $c = 21.4652(5)$ Å, $\beta = 94.7615(7)°$, $V = 6895.8(2)$ Å^3, $Z = 4$, 11 978 unique data (θ_{max} 25.0°), 4736 data with $I \geq 2\sigma(I)$, $R = 0.066$ (obs. data), $wR = 0.137$ (all data). Programs used: SHEXLS-97, SHELXL-97 and ORTEP. CCDC deposition number: 234631.

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