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From Simple Alkali Metal Silanolates to Heterometallic Bismuth Oxo Clusters

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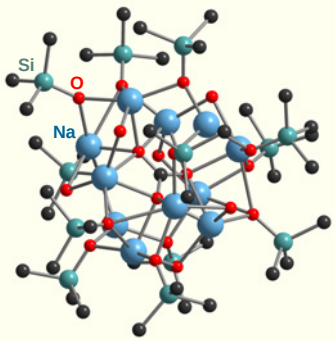
Bismuth-containing materials are associated with a variety of applications such as high-T_c superconductivity, oxide ion conduction, specialized glasses, pigments, thermoelectric devices, catalysts and ferroelectric devices.[1,2] Homo- and heterometallic bismuth alkoxides are well known precursors for heterometallic metal oxide materials, but in contrast to the alkoxides the corresponding bismuth silanolates have been studied only briefly.[3-5] In this communication we report results on our attempts to prepare bismuth trimethylsilanolate via the metathesis route using alkali metal trimethylsilanolates. Instead of pure $Bi(OSiMe_3)_3$ several alkali metal-bismuth silanolate oxo clusters were isolated. In addition we report novel clusters of partially hydrolyzed sodium trimethylsilanolate. The structures presented here demonstrate the diversity of the coordination geometry which is realized by bismuth and sodium in metal oxo clusters.

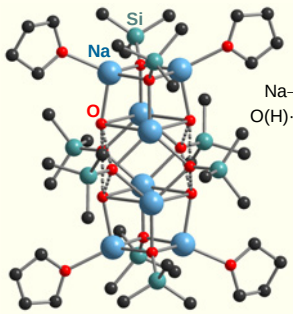
The X-ray single crystal structures of...

$Na_{11}(OSiMe_3)_3(HOSiMe_3)_9(OH)_6(CO_3)$



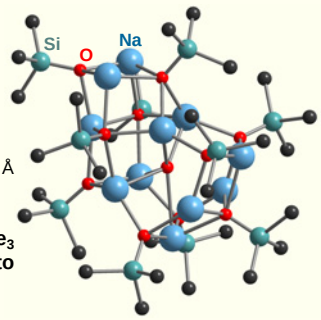
Na–O 2.24 - 2.80 Å
O(H)···O 2.43 - 2.53 Å

$Na_8(OSiMe_3)_4(HOSiMe_3)_4(OH)_4{\cdot}4THF$



Na–O 2.34 - 2.76 Å
O(H)···O 2.65 - 2.70 Å

$Na_{11}(OSiMe_3)_{10}(OH)$[6]



Na–O 2.20 - 2.82 Å
O(H)···O > 2.98 Å

... demonstrate the affinity of $NaOSiMe_3$ towards water and its tendency to aggregate upon partial hydrolysis.

$NaOSiMe_3$ - anhydrous

J. F. Hyde et al.
J. Am. Chem. Soc. **1953**, *75*, 5615

W. S. Tatlock, E. G. Rochow
J. Org. Chem. **1952**, *17*, 1555

$[NaOSiMe]_4 \cdot 4HMPA$

O. V. Konov et al.
Organomet. Chem. USSR **1991**, 4, 784

$NaOSiMe_3{\cdot}3H_2O$

I. L. Dubchak et al.
Zh. Strukt. Khim. **1982**, *23*, 63

$[NaOSiPh_3]_4{\cdot}3H_2O$

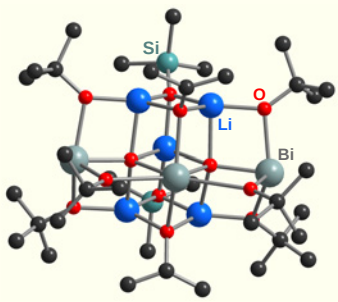
K. Dehnicke et al.
Z. Naturforsch. B **1996**, 1584

A Lithium Bismuth Oxo Cluster

3 $Bi(OtBu)_3$ + 6 $LiOSiMe_3$

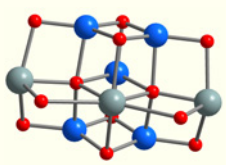
- $LiOtBu$
- 2 $Me_3SiOSiMe_3$

$Li_5Bi_3(O)_2(OSiMe_3)_2(OtBu)_8$



Bi - Li - O Core Structure

Li–O 1.88 - 2.10 Å
Bi–O 2.09 - 2.67 Å



Bismuth Trimethylsilanolate...

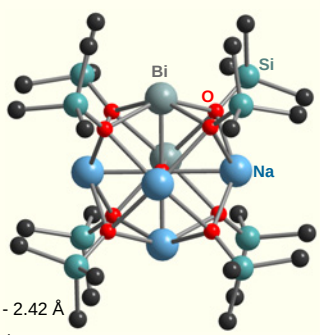
... was prepared in 1968.[4] Our attempts to synthesize $Bi(OSiMe_3)_3$ gave three heterometallic clusters instead.

$BiCl_3$ + 3 $NaOSiMe_3$

thf, moisture

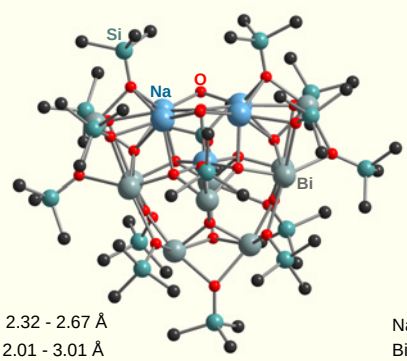
toluene

10 $NaOSiMe_3$ + 2 $BiCl_3$ — (- 6 NaCl, - $Me_3SiOSiMe_3$) → **$Na_4Bi_2O(OSiMe_3)_8$**



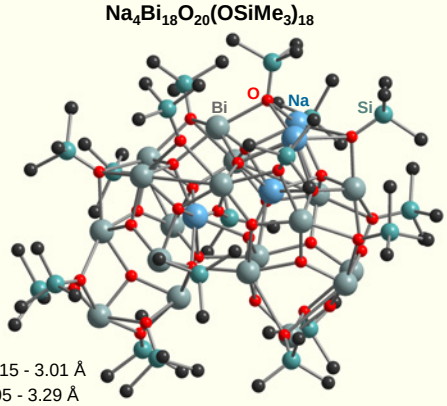
Na/Bi–O 2.29 - 2.42 Å
Na/Bi disorder

$Na_5Bi_{10}O_7(OSiMe_3)_{15}(OH)_6$



Na–O 2.32 - 2.67 Å
Bi–O 2.01 - 3.01 Å

$Na_4Bi_{18}O_{20}(OSiMe_3)_{18}$



Na–O 2.15 - 3.01 Å
Bi–O 2.05 - 3.29 Å

References
[1] C. A. Paz de Araujo, J. D. Cuchiaro, L. D. McMillan, M. C. Scott, J. F. Scott, *Nature* **2001**, *374*, 627.
[2] K. H. Whitmire, *Chemtracts - Inorg. Chem.* **1995**, *7*, 167.
[3] K. W. Terry, K. Su, T. D. Tilley, *Polyhedron* **1998**, *17*, 891.
[4] H. Schmidbaur, M. Bergfeld, *Z. Anorg. Allg. Chem.* **1968**, 85.
[5] M.-C. Massiani, R. Papiernik, L. G. Hubert-Pfalzgraf, J.-C. Daran, *Polyhedron* **1991**, *10*, 437.
[6] I. L. Dubchak, V. E. Shklover, Yu. T. Struchkov, V. M. Kopylov, P. L. Prikhod'ko, *Zh. Strukt. Khim* **1981**, 24, 59.

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