Topics in bismuth chemistry:
From molecules to high-nuclearity metal oxoclusters

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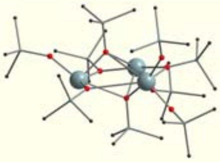
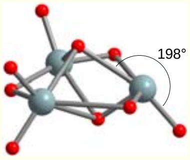
The low toxicity of the *amazingly green* element bismuth has stimulated in recent years various research projects aimed at the development of novel applications. For example, these efforts led to the commercial use of bismuth vanadate as non-toxic pigment. Additional examples of bismuth oxide-based materials are bismuth transition metal oxides used in random access memories and bismuth molybdate used as heterogeneous catalyst.[1-3] Currently, much work is devoted to the synthesis of thin films, nanoparticles and nanofibers of heterometallic, doped and pure bismuth oxide. We are interested in the potential of bismuth silanolates as molecular precursors for novel materials.[3-8] In contrast to bismuth alkoxides only few examples of silanolates and bismuth oxoclusters such as $[Bi_{18}Na_4O_{20}(OSiMe_3)_{18}]$ and $[Bi_{22}O_{26}(OSiMe_2{}^tBu)_{14}]$ are known.[4-6] Here we discuss synthetic strategies towards neodymium-substituted bismuth (oxo)silanolates and bismuth oxides. Additionally, attempts to functionalize $[Bi_{22}O_{26}(OSiMe_2{}^tBu)_{14}]$ are presented.

Synthesis and molecular structures of $[Bi(OSiMe_3)_3]$ and $[Nd(OSiMe_3)_3]$

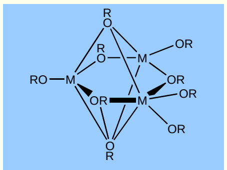
$$3\ Me_3SiOH \quad + \quad [M(O^tBu)_3] \xrightarrow[-\ 3\ ^tBuOH]{\text{toluene}} [M(OSiMe_3)_3] \quad M = Bi, Nd^{[7,8]}$$



$[Bi(OSiMe_3)_3]_3$

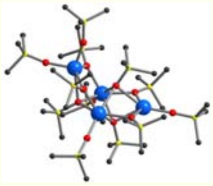


Bi–O 2.04 - 3.23 Å

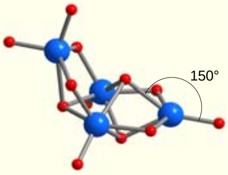


A M = Bi, Nd
R = $SiMe_3$

The basic structural motif of $[Bi(OSiMe_3)_3]$ and $[Nd(OSiMe_3)_3]$ is a common motif observed in a large number of homo- and heterometallic alkoxides such as $[Ln_3(O^tBu)_9(THF)_2]$ (Ln = La, Nd), $[M_3(O^tBu)_9(HO^tBu)_2]$ (M = Y, La) and $[Sr_2Ti(O^iPr)_8(HO^iPr)_3]$. In case of neodymium an additional $[Nd(OSiMe_3)_3]$ molecule is coordinating to fragment **A**.



$[Nd(OSiMe_3)_3]_4$

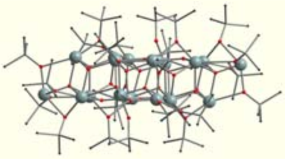


Nd–O 2.13 – 2.68 Å

➔ Similar ionic radii and coordination behaviour of Bi^{3+} and Nd^{3+} might allow the formation of heterometallic oxo-silanolate clusters.

Partial hydrolysis of bismuth silanolates

$$[Bi(OSiMe_3)_3] \xrightarrow[\text{hydrolysis}]{\text{benzene}} [Bi_{20}O_{18}(OSiMe_3)_{24}]^{[6]}$$



Co-hydrolysis of bismuth and neodymium silanolates

$$\begin{tikzcd}
22\,[Bi(OSiMe_2{}^tBu)_3] + [Nd(OSiMe_2{}^tBu)_3] \arrow[d, "\text{hydrolysis}"] & & 20\,[Bi(OSiMe_3)_3] + [Nd(OSiMe_3)_3] \arrow[d, "\text{hydrolysis}"] \\
\text{amorphous solid}\ ([Bi_{22-x}Nd_xO_{26}(OSiMe_2{}^tBu)_{14}])\,? \arrow[d, "750°C"] & & \text{amorphous solid}\ ([Bi_{20-x}Nd_xO_{18}(OSiMe_3)_{24}])\,? \arrow[d, "750°C"] \\
Bi_{1.86}Nd_{0.14}O_3,\ Bi_{12}SiO_{20} & \text{PXRD is indicative for the formation of:} \arrow[l] \arrow[r] & \text{bismuth}
\end{tikzcd}$$

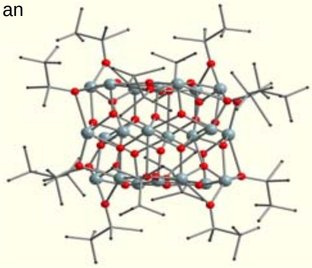
Attempts at isolating crystalline heterometallic bismuth oxoclusters upon partial hydrolysis failed so far.

The behaviour of $[Bi_{22}O_{26}(OSiMe_2{}^tBu)_{14}]$ in solution

- $[Bi_{22}O_{26}(OSiMe_2{}^tBu)_{14}]$ shows a low solubility in THF. It is insoluble in nonpolar solvents.
- A single resonance for the Me and ^tBu groups, respectively, is observed in the ^1H NMR spectrum.
- Dynamic light scattering experiments (DLS) show an average particle size of 2.5 nm.
- The diameter of the cluster in the solid state amounts to approximately 2 nm.

The cluster size of $[Bi_{22}O_{26}(OSiMe_2{}^tBu)_{14}]$ is retained in solution.

$$[Bi(OSiMe_2{}^tBu)_3] \xrightarrow[\text{hydrolysis}]{\text{benzene}} [Bi_{22}O_{26}(OSiMe_2{}^tBu)_{14}]^{[5]}$$



Is it possible to functionalize $[Bi_{22}O_{26}(OSiMe_2{}^tBu)_{14}]$?

$[Bi_{22}O_{26}(OSiMe_2{}^tBu)_{14}] + 14\ [HOOC_{12}H_{23}]$

THF → gel
toluene / suspension → amorphous solid

C%: 26.9, H%: 4.6   C%: 31.8, H%: 4.9

calcd. for $[Bi_{22}O_{26}(OOC_{12}H_{23})_{14}]$:
C%: 25.9, H%: 4.2

$[Bi_{22}O_{26}(OSiMe_2{}^tBu)_{14}] + 14\ [H_2O_3P^tBu]$

THF → solution
toluene / suspension → amorphous solid

-    C%: 10.2, H%: 2.0

calcd. for $[Bi_{22}O_{26}(HO_3P^tBu)_{14}]$:
C%: 9.7, H%: 2.0

The siloxy groups are readily exchanged by reaction of $[Bi_{22}O_{26}(OSiMe_2{}^tBu)_{14}]$ with carboxylic- or phosphonic acids. Preliminary investigations support the hypothesis that the bismuth oxo core structure is retained after reaction with organic acids.

Conclusion

We have shown previously that partial hydrolysis of bismuth silanolates readily results in large bismuth oxoclusters.[4-6] Comparison of the ionic radii, the hydrolytic stability and the coordination chemistry of metal silanolates of trivalent Bi^{3+} and Nd^{3+} supports the hypothesis that heterometallic oxoclusters should be formed by partial hydrolysis of mixtures of the respective metal silanolates. However, all attempts to synthesize neodymium-substituted bismuth oxoclusters failed so far. Preliminary results show that neodymium-substituted bismuth oxides are available from mixtures of the metal *tert*-butyldimethylsilanolates.

$[Bi_{22}O_{26}(OSiMe_2{}^tBu)_{14}]$ forms upon partial hydrolysis of $[Bi(OSiMe_2{}^tBu)_3]$. Its cluster size is retained in solution, but NMR experiments are indicative for a dynamic coordination behaviour of the siloxy groups. First experiments indicate that the substitution of the siloxy groups by organic acids is feasible. Further work is in progress.

References

[1] C. A. Paz de Araujo, J. D. Cuchiaro, L. D. McMillan, M. C. Scott, J. F. Scott, *Nature* **1995**, 374, 627.
[2] R. K. Grasselli, J. P. Burrington, *Adv. Catal.* **1981**, 30, 133.
[3] M. Mehring, *Coord. Chem. Rev.*, in press.
[4] M. Mehring, S. Paalasmaa, M. Schürmann, *Eur. J. Inorg. Chem*. **2005**, 24, 4891.
[5] D. Mansfeld, M. Mehring, M. Schürmann, *Angew. Chem. Int. Ed.* **2005**, 44, 245.
[6] M. Mehring, D. Mansfeld, S. Paalasmaa, M. Schürmann, *Chem. Eur. J.* **2006**, 12 ,1767.
[7] D. Mansfeld, M. Schürmann, M. Mehring, *Z. Anorg. Allg. Chem.* **2005**, 631, 2429.
[8] S. Paalasmaa, D. Mansfeld, M. Schürmann, M. Mehring, *Z. Anorg. Allg. Chem.* **2005**, 631, 2433.

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