DE GRUYTER
Main Group Met. Chem. 2014; 37(3-4): 97–99

Short Communication

Gabriele Kociok-Köhn, Kieran C. Molloy* and Liam Palmer

Molecular structure of the functionalized bismuth alkoxide $Bi[OC(CH_2NMe_2)_3]_3$

Abstract: The molecular structure of the amino-functionalized bismuth alkoxide, $Bi[OC(CH_2NMe_2)_3]_3$ has been determined and embodies a six-coordinate bismuth atom with a *fac*, *fac*-BiO_3N_3 coordination sphere.

Keywords: alkoxide; bismuth; X-ray.

DOI 10.1515/mgmc-2014-0010
Received May 14, 2014; accepted June 18, 2014; previously published online July 10, 2014

Bismuth alkoxides are of importance as precursors for materials based on binary and ternary bismuth oxides (Mehring, 2007; Moniz et al., 2010, and references therein; Cosham et al., 2013). In such cases, either volatility and/or solubility are keys to precursor delivery; however, many $Bi(OR)_3$ adopt either polymeric (Massiani et al., 1990, 1991; Matchett et al., 1990) or oligomeric structures (Jones et al., 1993; Boyle et al., 1998; Kessler et al., 2002; Hatanpaa et al., 2010). Attempts to reduce the nuclearity (and hence increase volatility, solubility) of these alkoxides have largely focused on the use of bulky alkoxide (Evans et al., 1989; Hanna et al., 2001; Brym et al., 2006; Kou et al., 2009; Hatanpaa et al., 2010) or siloxide ligands (Mansfeld et al., 2004; Paalasmaa et al., 2005), though the concomitant increase in molar mass and ligand complexity may not always result in benefits. The alternative use of functionalized alkoxide ligands, which can saturate the metal coordination sphere, have been much less well studied (Matchett et al., 1990; Herrmann et al., 1993; Williams et al., 2001). We now report the structure of $Bi(tdmap)_3$ (**1**) [Htdmap=$HOC(CH_2NMe_2)_3$], which contains the highly functionalized tdmap ligand.

1 is monomeric and incorporates a six-coordinated BiN_3O_3 environment, with the ligating atoms arranged in a *fac*-O_3, *fac*-N_3 manner (Figure 1). The three Bi-O bonds are of similar lengths [Bi-O(1) 2.113(5), Bi-O(2) 2.136(5), Bi-O(3) 2.140(5) Å], while one of the Bi-N bonds is elongated with respect to the other two [Bi-N(1) 2.721(6), Bi-N(4) 2.737(7), Bi-N(7) 2.879(6) A]. Although there is little regularity to the bond angles about bismuth resulting from the presence of three five-membered $BiOC_2N$ rings, the largest angular distortions seem to involve the weakly coordinated N(7) [N(1)-Bi-N(7)113.07(18), N(4)-Bi-N(7)113.84(18)°] suggesting the presence of a stereochemically active lone electron pair in this vicinity, though this is by no means clear.

Each tdmap is κ^2-*O*,*N* bidentate, so the monomeric nature of **1** can be attributed to both N:→Bi coordination and the steric bulk of the ligand. We have observed similar low-nuclearity Group 12 complexes, e.g., $[RM(tdmap)]_2$, M=Zn (Johnson et al., 2008a), Cd (Johnson et al., 2008b), where, again, tdmap uses only one of three available donor groups in metal coordination. Such a scenario does, however, leave several pendant donor groups available for further elaboration, which may be of significance in the synthesis of single-source precursors (SSPs) for ternary bismuth oxide materials. The orientation of the non-coordinating pendant CH_2NMe_2 arms seems to be, at least in part, dictated by three weak intramolecular CH...O hydrogen bonds [H...O: 2.37–2.43 Å, C...O 2.98–3.07 Å, $\angle$C-H...O 120.4–122.1°; Figure 1], which are within the criteria used by others to identify such interactions [H...O<2.8 Å; $\angle$C-H...O>110°] (Desiraju, 1996).

The environmental differences between the three CH_2NMe_2 groups are not, however, clearly evident in the ^1H NMR spectrum, which show single resonances for the CH_2 (albeit broad) and NMe_2 groups. In the ^{13}C NMR spectrum, some splitting of the signal due to the NMe_2 groups is seen, while the CH_2 signal again remains a singlet.

1 is soluble in common organic solvents and, as such, makes it amenable to use as a SSP in AACVD experiments. While we are yet to assess the volatility of this compound, previous experience with MeM(tdmap) (M=Zn, Cd)

***Corresponding author: Kieran C. Molloy,** Department of Chemistry, University of Bath, Claverton Down, Bath BA2 7AY, UK,
e-mail: kcm68win@outlook.com
Gabriele Kociok-Köhn: Department of Chemistry, University of Bath, Claverton Down, Bath BA2 7AY, UK
Liam Palmer: Department of Chemistry, University of Bath, Claverton Down, Bath BA2 7AY, UK

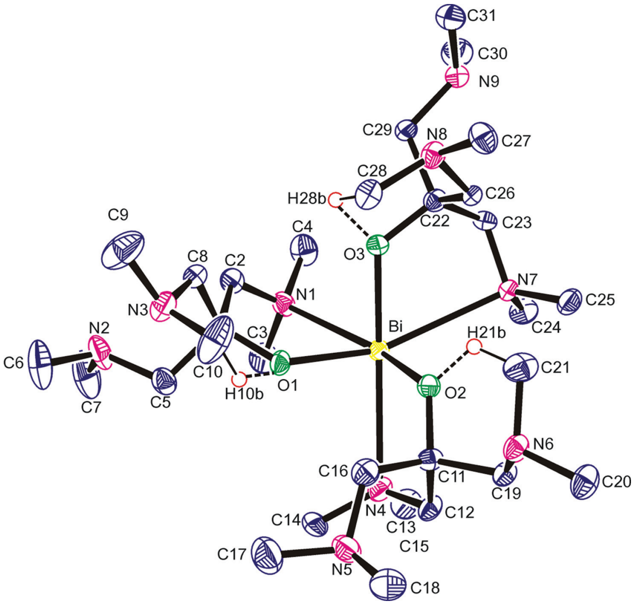

Figure 1 The asymmetric unit of **1** showing the labeling scheme used; thermal ellipsoids are at the 40% probability level. C(1) is hidden behind C(10); only key hydrogen atoms have been included for clarity. Selected geometric data: Bi-O(1) 2.113(5), Bi-O(2) 2.136(5), Bi-O(3) 2.140(5), Bi-N(1) 2.721(6), Bi-N(4) 2.737(7), Bi-N(7) 2.879(6) Å; O(1)-Bi-O(2) 90.93(19), O(1)-Bi-O(3) 88.75(19), O(1)-Bi-N(1) 69.44(19), O(1)-Bi-N(4) 84.16(19), O(1)-Bi-N(7)157.66(18), O(2)-Bi-O(3) 93.58(19), O(2)-Bi-N(1)159.6(2), O(2)-Bi-N(4) 71.86(19), O(2)-Bi-N(7) 82.91(18), O(3)-Bi-N(1) 80.87(19), O(3)-Bi-N(4)163.6(2), O(3)-Bi-N(7) 70.33(17), N(1)-Bi-N(4)110.13(19), N(1)-Bi-N(7)113.07(18), N(4)-Bi-N(7)113.84(18)°.

Table 1 Crystal data and structure refinement for **1**.

	1
Empirical formula	$C_{30}H_{72}BiN_9O_3$
Formula weight	815.95
Crystal system	Triclinic
Space group	$P\bar{1}$(no.2)
a (Å)	9.7454(3)
b (Å)	9.8244(3)
c (Å)	20.9747(4)
α (°)	84.282(2)
β (°)	83.852(2)
γ (°)	84.881(1)
V(Å³)	1980.42(9)
Z	2
ρ_{calc} (mg m^{-3})	1.368
μ(Mo-kα) (mm^{-1})	4.490
F(000)	844
Crystal size (mm)	0.33×0.33×0.20
Theta range (°)	2.94–27.62
Reflections collected	41113
Independent reflections [R(int)]	9089 [0.1681]
Reflections observed (>2σ)	7323
Data Completeness	0.985
Max. and min. transmission	0.4063, 0.2631
Goodness-of-fit on F^2	1.051
Final R_1, wR_2 indices [I>2σ(I)]	0.0608, 0.1453
R_1, wR_2 indices (all data)	0.0833, 0.1591
Largest diff. peak, hole (eÅ^3)	2.694, -4.555

suggests it may have sufficient volatility for LPCVD use, but not APCVD (Johnson et al., 2008a,b).

Experimental

Htdmap (1.70 mL, 7.57 mmol) was added to Bi[N(SiMe$_3$)$_2$]$_3$ (1.69 g, 2.44 mmol) in hexane (10 mL), causing a color change from yellow to dark orange. After heating at 65°C for 5 h, the solution was cooled to room temperature and then allowed to crystallize at -20°C. Yield 1.63 g, 81%. Analysis, found (calc. For $C_{30}H_{72}N_9O_3Bi$): C 44.1 (44.1), H 9.0 (8.9), N 14.8 (15.4)%. ^{1}H NMR (d^8-toluene): 2.32 (s, 18H, CH$_3$), 2.66 (br s, 6H, CH$_2$). ^{13}C NMR (d^8-toluene): 68.3 (OC), 68.3 (CH$_2$), 46.7, 46.5 (CH$_3$) ppm.

Crystallography

Experimental details relating to the single-crystal X-ray crystallographic study are summarized in Table 1. Data were collected on a Nonius Kappa CCD diffractometer (Enraf-Nonius B.V., Rotterdam, The Netherlands) at 150(2) K using Mo-Kα radiation (λ=0.71073 Å). Structure solution was followed by full-matrix least squares refinement and was performed using the WinGX-1.70 suite of programs (Farrugia, 1999). An absorption correction (semi-empirical from equivalents) was applied.

Supporting information

Crystallographic data for the structural analysis (in CIF format) has been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 1002818. Copies of this information may be obtained from the Director, CCDC, 12 Union Road, Cambridge, CB21EZ, UK (Fax: +44-1233-336033; e-mail: deposit@ccdc.cam.ac.uk or www.ccdc.cam.ac.uk).

References

Boyle, T. J.; Pedrotty, D. M.; Scott, B.; Ziller, J. W. Bismuth(III) coordination compounds. Synthesis, characterization, and X-ray structures of [Bi(Cl)(μ-Cl)$_2$(THF)$_2$]$_\infty$, Bi(O$_2$CMe)$_3$(Solv)$_x$ (Solv = py, x = 2 or MeIm, x = 4) and [Bi(μ-OCH$_2$CMe$_3$)-(OCH$_2$CMe$_3$)$_2$(Solv)]$_2$ (Solv = HOCH$_2$CMe$_3$ or py). *Polyhedron* **1998**, *17*, 1959–1974.

Brym, M.; Jones, C.; Junk, P. C. Rare examples of mononuclear, homoleptic antimony(III) and bismuth(III) aryloxides. *Main Group Chem.* **2006**, *5*, 13–19.

Cosham, S.; Hill, M. S.; Horley, G. A.; Johnson, A. L.; Jordan, L.; Molloy, K. C.; Stanton, D. C. Synthesis and materials chemistry of bismuth *tris*(-di-i-propylcarbamate): deposition of photoactive films. *Inorg. Chem.* **2013**, *53*, 503–511.

Desiraju, G. R. The CH...O hydrogen bond: structural implications and supramolecular design. *Acc. Chem. Res.* **1996**, *29*, 441–449.

Evans, W. J.; Hain, J. H.; Ziller, J. W. Synthesis and first *X*-ray crystal structure of a $Bi(OR)_3$ complex: tris(2,6-dimethylphenoxo) bismuth. *Chem. Commun.* **1989**, *20*, 1628–1629.

Farrugia, L. J. Wingx suite for small-molecule single-crystal crystallography. *J. Appl. Crystallogr.* **1999**, *32*, 837.

Hanna, T. A.; Keitany, G.; Ibarra, C.; Sommer, R. D.; Rheingold, A. L. Synthesis and crystal structure of a three-coordinate bismuth alkoxide with bismuth-β-phenyl secondary interactions, $Bi(OCPh_3)_3$. *Polyhedron* **2001**, *20*, 2451–2455.

Hatanpaa, T.; Vehkamaki, M.; Ritala, M.; Leskela, M. Study of bismuth alkoxides as possible precursors for ALD. *Dalton Trans.* **2010**, *39*, 3219–3226.

Herrmann, W. A.; Huber, N. W.; Anwander, R.; Priermeier, T. Monomere flüchtige alkoxide von chrom und bismut. *Chem. Ber.* **1993**, *126*, 1127–1130.

Johnson, A. L.; Hollingsworth, N.; Molloy, K. C. Kociok-Köhn, G. Organozinc aminoalcoholates: synthesis, structure, and materials chemistry. *Inorg. Chem.* **2008a**, *47*, 12040–12048.

Johnson, A. L.; Hollingsworth, N.; Kociok-Köhn, G.; Molloy, K. C. Organocadmium aminoalcoholates: synthesis, structure, and materials chemistry. *Inorg. Chem.* **2008b**, *47*, 9706–9717.

Jones, C. M.; Burkart, M. D.; Bachman, R. E.; Serra, D. L.; Hwu, S.-J.; Whitmire, K. H. Hypervalent bismuth alkoxide dimer complexes: syntheses, structures, and thermal decompositions of $[Bi(OCH(CF_3)_2)_2(\mu\text{-}OCH(CF_3)_2)(THF)]_2$ and $[Bi(OC_6F_5)_2(\mu\text{-}OC_6F_5)X_n]_2$. zY (X = Y = C_7H_8, n = 1, z = 1 or 2; X = THF, Y = C_6H_{14}, n = 2, z = 0 or 1). *Inorg. Chem.* **1993**, *32*, 5136–5144.

Kessler, V. G.; Turova, N. Y.; Turevskaya, E. P. The structure of the bismuth ethoxide ethanol solvate. A new structural type for octameric alkoxides. *Inorg. Chem. Commun.* **2002**, *5*, 549–551.

Kou, X.; Wang, X.; Mendoza-Espinosa, D.; Zakharov, L. N.; Rheingold, A. L.; Watson, W. H.; Brien, K. A.; Jayarathna, L. K.; Hanna, T. A. Bismuth aryloxides. *Inorg. Chem.* **2009**, *48*, 11002–11016.

Mansfeld, D.; Mehring, M.; Schürmann, M. From a monomeric bismuth silanolate to a molecular bismuth oxo cluster: $[Bi_{22}O_{26}(OSiMe_2\textit{t}Bu)_{14}]$. *Angew. Chem. Int. Ed.* **2004**, *44*, 245–249.

Massiani, M.-C.; Papiernik, R.; Hubert-Pfalzgraf, L. G.; Daran, J.-C. Molecular precursors of bismuth oxide. Synthesis and structure of $[Bi_2(\mu_2\text{-}OC_2H_4OMe)_4(OC_2H_4OMe)_2]_\infty$, a one-dimensional ribbon-like chain. *Chem. Commun.* **1990**, *21*, 301–302.

Massiani, M.-C.; Papiernik, R.; Hubert-Pfalzgraf, L. G.; Daran, J.-C. Molecular precursors of bismuth oxides; β-diketonates and alkoxides. Molecular structure of $[Bi_2(\mu_2,\eta^1\text{-}OC_2H_4OMe)_4(\eta^1\text{-}OC_2H_4OMe)_2]_\infty$ and of $Bi(OSiPh_3)_3(THF)_3$. *Polyhedron* **1991**, *10*, 437–445.

Matchett, M. A.; Chiang, M. Y.; Buhro, W. E. Soluble and volatile alkoxides of bismuth. The first structurally characterized bismuth trialkoxide: $[Bi(\mu\text{-}\eta^1\text{-}OCH_2CH_2OMe)_2(\eta^1\text{-}OCH_2OMe)]_\infty$. *Inorg. Chem.* **1990**, *29*, 358–360.

Mehring, M. From molecules to bismuth oxide-based materials: potential homo- and heterometallic precursors and model compounds. *Coord. Chem. Rev.* **2007**, *251*, 974–1006.

Moniz, S. J. A.; Blackman, C. S.; Carmalt, C. J.; Hyett, G. MOCVD of crystalline Bi_2O_3 thin films using a single-source bismuth alkoxide precursor and their use in photodegradation of water. *J. Mater. Chem.* **2010**, *20*, 7881–7886.

Paalasmaa, S; Mansfeld, D; Schürmann, M.; Mehring, M. Synthesis and characterization of three homoleptic bismuth silanolates: $[Bi(OSiR_3)_3]$ (R = Me, Et, *i*Pr). *Z. Anorg. Allg. Chem.* **2005**, *631*, 2433–2438.

Williams, P. A.; Jones, A. C.; Crosbie, M. J.; Wright, P. J.; Bickley, J. F.; Steiner, A.; Davies, H. O.; Leedham, T. J.; Critchlow, G. W. Crystal structure of $Bi(OCMe_2CH_2OMe)_3$ and its use in the MOCVD of Bi_2O_3 *Chem. Vap. Depos.* **2001**, *7*, 205–209.