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Cost efficient synthesis of bismuth aminoalkoxides from bismuth oxide: Molecular structure of [Bi₂(mdea)₂(mdeaH)₂](mdeaH₂)₂

Jérome Le Bris^a, Liliane G. Hubert-Pfalzgraf^a, Stéphane Daniele^{a,*}, Jacqueline Vaissermann^b

^a Université de Lyon1, IRC, 2 av. A. Einstein, 69626 Villeurbanne Cédex, France ^b Université de Paris 6, Laboratoire de Chimie Inorganique et des matériaux moléculaires, UMR, 4 place Jussieu, 75552 Paris Cédex 5, France

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Abstract

Functional Bi alkoxides were prepared by reaction between the oxide and diols such as *N*-methyldiethanolamine (mdeaH₂), diethanolamine (deaH₂) and triethanolamine (teaH₃) in refluxing toluene in high yields. Similar reactions with polyols without N-donor site lead to oxo species. The derivative obtained with *N*-methyldiethanolamine was characterised by X-ray diffraction as a dimer $[Bi_2(mdea)_2(mdeaH)_2]$ associated as chains through H-bonding with neutral diol molecules giving the title compound. Bismuth is pseudo 7-coordinate. Bi–O bond distances range from 2.150(5) to 3.093(5) Å with three short ones, whereas the transannular Bi–N bond distances are 2.737 Å av. Thermolysis and hydrolysis reactions are reported. © 2006 Published by Elsevier B.V.

Keywords: Bismuth; Functional alkoxides; Structure; Sol-gel; Aminoalkoxide; Oxide

The interest in bismuth compounds is motivated by their wide applicability in bioinorganic chemistry [1], homogeneous and heterogeneous catalysis [2] and material science [3]. Materials based on bismuth include high T_c superconductors, ferroelectrics such as Bi₄Ti₃O₁₂, but also magnetic ferroelectrics such as $BiMO_3$ (M = Mn, Fe) [4]. Bismuth is also considered nowadays as the least toxic heavy metal. Bismuth trioxide in thin films is an interesting optical material with a large energy gap, high value of refractive index and dielectric permittivity, as well as remarkable photoconductivity and photoluminescence [5]. Its various polymorphs α , β , ω , γ and δ possess distinct physical properties [6]. The technological demands require thin films or nanoparticles. The most cost efficient routes to films are chemical solution deposition techniques (CSD), namely sol-gel processing or metal-organic deposition (MOD) or vapour phase techniques such as metal-organic vapour phase decomposition (MOCVD) [7]. Although alcoholysis of bismuth nitrate pentahydrate by polyols afforded heteroleptic derivatives [8], the most common Bi(III) alkoxides have been prepared by metathesis reactions applied to halides or by alcoholysis of amides [9,10]. The metathesis route leads often to some halide or alkali metal contamination of the alkoxides - an undesirable feature for high tech materials - whereas alcoholysis of amides is quite expensive for commercial use of metal alkoxides. A number of Bi aryloxides have been reported but such compounds are quite prone to reduction and/or a source of C contamination of oxide materials. Alternate, cost efficient synthetic routes based on the reactions between anhydrous or hydrated metal oxides and polyols have been reported for a number of elements such as Si [11], Ti [12], and Pb [13]. Moreover, most reported bismuth alkoxides have a limited shelf life due to their high susceptibility to moisture and/or light. Functional bismuth alkoxides which usually show improved hydrolytic stability remain limited to a few alkoxyalkoxides such as $[Bi_2(OC_2H_4OMe)_3]_{\infty}$ [14], $(Bi(mmp)_3 [15] (mmp = OCMe_2CH_2OMe)_3 = 1$ -methoxy-2-methyl-2-proposide), $Bi(OCMe_2Et)_{3-x}(mmp)_x$ (x = 1 or

^{*} Corresponding author. Tel./fax: + 33 4 72 44 53 60.

E-mail address: stephane.daniele@catalyse.cnrs.fr (S. Daniele).

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(3)

2) [16] or aminoalkoxides $Bi(OCHRCH_2NMe_2)_3$ (R = H or Me) [14] and $Bi(tea)_3$ [17].

We wish to report herein the synthesis of Bi functional aminoalkoxides, their characterisation and preliminary data on their reactivity of the 2,2'-methyliminodiethanolate derivative.

The reactions between Bi₂O₃ and functional alcohols, namely polyols such as *N*-methyldiethanolamine (mdeaH₂), diethanolamine (deaH₂), diethyleneglycol (degH₂), triethanolamine (teaH₃) or 2,2-dimethylpropane-1,3-diol (neol- $H_2 = (OHCH_2)_2CMe_2$ (stoichiometry 1:5–1:9), in refluxing toluene lead to new bismuth derivatives (Eqs. (1)-(5)) [18]. The by-product, water, was trapped by molecular sieves. The *N*-methylethanolamine derivative **1** was established by single crystal X-ray diffraction to correspond to Bi₂- $(meda)_2(mdeaH)_2(mdeaH_2)_2$. The reactivity was similar for the various N-donor polyols $deaH_2 \sim teaH_3 \sim mdeaH_2$ and was superior to that of the polyols $degH_2 > neol-H_2$ without N-donor site. No reaction was observed between Bi₂O₃ and dimethylaminoethanol Me₂NC₂H₄OH in refluxing toluene even after 4 d. Bismuth oxide appears thus less reactive than lead(II) oxide for synthesis of metal alkoxides directly from the oxide [13]. The triethanoaminolate, $[Bi(OCH_2CH_2)_3N]_{\infty}$. was obtained previously by reacting freshly prepared Bi(OH)₃ in alcohol with teaH₃ and sodium but no yield was reported [16].

$$\begin{array}{l} Bi_2O_3 + 6mdeaH_2 \rightarrow [Bi(mdea)(mdeaH)(mdeaH_2)]_2(1) \\ + 3H_2O \end{array} \tag{1}$$

 $Bi_2O_3 + 2teaH_3 \rightarrow 2[Bi(tea)]_m(2) + 3H_2O$ (2)

 $Bi_2O_3 + 8deaH_2 \rightarrow 2/mBi(deaH)_3(deaH_2)_m(3) + 3H_2O$

 $3Bi_2O_3+6degH_2\rightarrow 2Bi_3O_2(OH)_2(degH)_3(\textbf{4})+H_2O~~(\textbf{4})$

 $Bi_2O_3 + 4neol-H_2 \rightarrow 2/mBiO(neol-H)(neol-H_2)2_m(5)$

$$+$$
 H₂O (5)

The various compounds were obtained as white solids showing no sensitivity to light, 1 and 3 hydrolyzed slowly in the presence of moisture, while 2, 4 and 5 were air stable. They were characterised by elemental analysis, FT-IR and ¹H NMR. The *N*-methyldiethanolate derivative **1** was soluble in the reaction medium in contrast to the other derivatives. The derivatives obtained with polyols without N-donor site are either oxo or oxohydroxo species. Compounds 3-5 are insoluble in usual organic solvents and water. $[Bi(tea)]_{\infty}$ was insoluble in the parent triol but soluble in water. The FT-IR spectra of all compounds except 2 show absorption bands of OH and/or NH groups around $3300-3120 \text{ cm}^{-1}$, indicating incomplete deprotonation of the various diols. Absorption bands of v_{Bi-O} vibrations were observed below 600 cm^{-1} , their value accounts in all cases for the absence of contamination by residual bismuth oxide.

The identity and the molecular structure of **1** were established by single crystal X-ray diffraction (Fig. 1) [19]. Selected bond lengths and angles are collected in Table 1.



Fig. 1. Molecular structure of the dimeric unit of 1, $Bi_2(mdea)_2(mdeaH)_2$, showing the atom labelling scheme and thermal ellipsoids at 50% probability level.

Table 1 Selected bond lengths and angles of 1

Bond lengths (Å)	Angles (°)	
Bi(1)-N(1)	2.729(5)	O(1)-Bi(1)-O(2)	95.1(2)
Bi(1) - N(2)	2.746(6)	O(1)-Bi(1)-O(2')	165.2(2)
Bi(1)–O(1)	2.150(5)	O(1)-Bi(1)-O(3)	84.8(2)
Bi(1)-O(2)	2.169(5)	O(1)-Bi(1)-N(1)	69.12(2)
Bi(1)–O(2')	2.692(5)	O(1)-Bi(1)-N(2)	81.2(2)
Bi(1)-O(3)	2.161(5)	O(1)-Bi(1)-O(4)	85.7(2)
Bi···Bi	3.976(5)	O(2)-Bi(1)-O(3)	80.8(2)
Bi(1)···O(4)	3.093(5)	O(2)-Bi(1)-O(2')	70.7(2)
		O(2)-Bi(1)-N(1)	70.7(2)
		O(2)-Bi(1)-N(2)	151.8(2)
		O(2)-Bi(1)-O(4)	149.2(2)
		O(2')–Bi(1)–O(3)	88.9(2)
		O(2')-Bi(1)-N(1)	108.2(2)
		O(2')-Bi(1)-N(2)	109.3(2)
		O(2')-Bi(1)-O(4)	38.6(2)
		O(3)-Bi(1)-N(1)	138.7(2)
		O(3)-Bi(1)-N(2)	71.1(2)
		O(3)-Bi(1)-O(4)	129.8(2)
		O(4)-Bi(1)-N(1)	53.6(2)
		O(4)-Bi(1)-N(2)	54.6(2)
		N(1)-Bi(1)-N(2)	131.6(2)
		Bi(1)-O(2)-Bi(1')	109.3(2)

Equivalent positions' = -x, 2 - y, 1 - z.

All bismuth atoms are surrounded by three short, primary bonds Bi–O, two transannular Bi–N bonds and two longer Bi–O bonds corresponding, respectively, to the association of the monomeric units into dimers with asymmetrical bridges [Bi(1)–O(2') 2.692(5) vs Bi(1)–O(2) 2.169(5) Å] as well as to the partially deprotonated diol [Bi–O(4)(H) 3.093(5) Å]. Although long, this distance is significantly shorter than the sum of the van der Waals radii (3.67 Å) and can be considered as a secondary bond as commonly observed for molecular Bi derivatives. This leads to pseudo 7-coordinated bismuth atoms with a Bi \cdots Bi distance of 3.976(5) Å and Bi–O bond distances spreading over the range 2.150(5)–3.093(5) Å. The Bi–O distances are in agreement with those observed for other Bi alkoxides where the metals have similar high coordination numbers [9,10]. With the exception of the Bi-O(4) bond, these distances are in the range of those observed for β -Bi₂O₃ where the metal has a pseudo-octahedral geometry. The transannular Bi–N bond distances (av 2.737 Å) of 1 are significantly longer than those of $[Bi(tea)]_{\infty}$ (2.551 Å av), where Bi is also 7-coordinate [17]. They are close to the values found for Bi₂(µ-ONep)₂(ONp)₄(py)₂ [10a] or for Bi(III) complexes with aminocarboxylate ligands where bismuth is, respectively, 5- and 8-coordinate [20]. The Bi ··· Bi distances are significantly longer than for the $Bi_2(\mu - OC_2H_4OM_e)_4$ - $(OC_2H_4OMe)_2$ dimer (3.6426(4) Å) displaying also strongly asymmetric bridges [9,14]. The Bi₂(mdea)₂(mdeaH)₂ dimers are further connected to each other via two neutral mdeaH₂ molecules by H bonds $[O(3) \cdots O(5)]$ and $O(1) \cdots O(6)$ 2.684 Å] forming thus polymeric chains. The H bond lengths are close to the values found in the cyclic $[Bi(OEt)_3]_8(7+x)EtOH$ (2.46(3)–2.77(3) Å) [10b]. The bites angles have values around 70°. The lone pair of the bismuth(III) centers appears stereochemically active and located between O(2) and O(4).

The solubility of 1 allowed its characterisation by ¹H NMR. The spectra in CDCl₃ at rt are quite uninformative since they display only one set of resonances for the various ligands. Compound 1 is actually fluxional. Its spectrum at -40 °C shows three resonances for the OCH₂ and NCH₂ groups both with a 3:2:1 integration ratio, two for the NMe ones (ratio 2:1). The hydroxyl protons appear as broad peaks at 4.83 and 6.09 ppm (2:1). These data indicate that the solid-state structure is retained in solution. Indeed, the quite sharp peaks of the mdeaH₂ molecules and their chemical shifts at low field with respect to those of the free diol suggest that the H-bonding association is preserved in solution.

All compounds were non-volatile, heating **1** or **4** for instance leads to the elimination of mdeaH₂ or degH₂ at 70 °C/3 × 10⁻⁴ and 100 °C/3 × 10⁻⁴ mmHg, respectively. Compound **1a** resulting from the elimination of the neutral mdeaH₂ molecules is insoluble in toluene and pyridine even by heating, probably as a result of intermolecular H-bonding due to the mdeaH ligand but remains soluble in CHCl₃ although dissolution is slow. TGA data of **1** under air indicate three decomposition steps: 130–225 °C loss of mdeaH₂ and mdeaH, 225–250 °C loss of mdea and 250–360 °C decomposition into a quite reactive oxide since it is transformed into the Bi₂O₂(CO₃) phase at 246 °C which decomposes into crystalline α -Bi₂O₃ at 600 °C, then α and ω , and finally the β -Bi₂O₃ polymorph above 900 °C.

The reaction between 1 and Ti(O*i*Pr)₄ (1:1 stoichiometry) in toluene at rt is governed by redistribution reactions as shown by ¹H NMR (Eq. (6)). The lability of the neutral mdeaH₂ molecules leads to the formation of Ti₂(mdea)(μ -O*i*Pr)₄(O*i*Pr)₅ as identified by comparison with an authentic sample [21] and of the mdeaH₂ ligand free bismuth derivative 1a. In contrast, no reaction was observed between Ti(O*i*Pr)₄ and [Bi(tea)]_∞ in toluene even after heating at 70 °C for 20 h.

$$Bi_{2}(mdea)_{2}(mdeaH)_{2}(mdeaH_{2})_{2} + Ti(OiPr)_{4}$$

$$\rightarrow 1a + 1/2Ti_{2}(OiPr)_{6}(mdea) + 2iPrOH$$
(6)

Unfortunately, no suitable crystals could be grown for **3** or the oxo clusters **4** or **5** but the presence of bismutyl species for the later is likely [22].

Appendix A. Supplementary material

Tables of coordinates, of thermal parameters, of bond lengths and angles have been deposited at the Cambridge Crystallographic Data Base Centre. CCDC 244547 contain the supplementary crystallographic data for complex 1. These data can be obtained free of charge via http:// www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or email: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.inoche.2006.09.012.

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- [18] All reactions were done under inert atmosphere using Schlenk tubes and vacuum line techniques. Solvents and reactants were purified by standard methods. Syntheses. $Bi_2(mdea)_2(mdeaH)_2(mdeaH_2)_2$ (1): 4.2 ml of mdeaH₂ (34.47 mmol) was added to a suspension of bismuth oxide (2.83 g, 6.079 mmol) in toluene (140 ml). After refluxing for 6 d (water being trapped by molecular sieves), the medium was filtered. Evaporation of the filtrate and recrystallisation in hot toluene gave crystals of 1 at rt (4.71 g, 69%). Mp: 89 °C. Calcd for BiC₁₅H₃₆N₃O₆: C, 31.98; H, 6.44; N, 7.46. Found: C, 32.05; H, 6.56; N, 7.63%. Compound 1 is hygroscopic (4 h air). FT-IR [cm⁻¹]: 3137w v_{OH} , 1610w δ_{OH} , 481w, 450w, 439w, 419m v_{Bi-O} . ¹H NMR (CDCl₃, 20 °C, ppm): 2.36 (s, 18H, CH₃N), 2.66 (t, ³J = 5.05 Hz, 24H, NCH₂), 4.20 (br, 28H, CH₂O, OH); -40 °C; 2.27 (s, 6H, CH₃N [mdeaH₂]), 2.38 (br, 12H, CH₃N [mdea, mdeaH]), 2.52 (m, 12H, NCH₂ [mdea, mdeaH]), 2.9 br (8H, NCH2 [mdeaH2]), 3.1 (br, 4H, NCH2 [mdeaH]), 3.65 (m, 12H, CH₂O [mdea, mdeaH]), 4.14 (br, 8H, CH₂O, mdeaH₂), 4.54 (br, 4H, CH₂O [mdeaH]), 4.83 (br, 2H, OH [mdeaH₂]), 6.09 (br, 2H, OH [mdeaH]). ¹³C NMR (CDCl₃, 20 °C) [ppm]: 41.55 (NCH₂), 59.83 (NCH₃, mdeaH₂), 60.82 (NCH₃), 77.31 (OCH₂). Compound (1a) FT-IR $[cm^{-1}]$: 479w, 444w v_{Bi-O} . $[Bi(tea)]_{\infty}$ (2): Same procedure as for 1 applied to 1.4 ml of H₃tea (10.46 mmol), bismuth oxide (0.97 g, 2.09 mmol) in toluene (60 ml). After 5 d, the precipitate was separated (1.29 g, 87 %). Compound 2 was insoluble in pyridine but can be recrystallized in water. Anal. Calcd for BiC₆H₁₂NO₃: C, 20.29; H, 3.40; N, 3.94. Found: C, 20.34, H, 3.47, N, 3.92%. FT-IR [cm⁻¹]: 608w, 575w, 552w, 448m, 410m v_{Bi-O}. ¹H NMR (D₂O, 20 °C): 2.64 (t, ${}^{3}J = 6$ Hz, 6H, NCH₂), 3.64 (m, 6H, CH₂O). { $Bi(deaH)_{3}(deaH_{2})$ }_m

(3): Same procedure as for 1 applied to 2 ml of deaH₃ (21.4 mmol), bismuth oxide (1.25 g, 2.66 mmol) in toluene (25 ml). After 3 d, a grey suspension was obtained. Compound 3 was insoluble in THF. CHCl₃. pyridine and acetonitrile. Anal. Calcd for BiC₁₆H₄₁N₄O₈: C, 30.67; H, 6.60; N, 8.94. Found: C, 30.16; H 6.36; N 8.69%. FT-IR $[cm^{-1}]$: 3306s, 3260s, 3233s $v_{O-H,N-H}$, 569m, 561m, 547w, 427w $v_{Bi-O,Bi-N}$. $Bi_3O_2(OH)_2(degH)_3$ (4): Same procedure as for 1 applied to 1.04 ml de H₂deg (10.93 mmol), bismuth oxide (1.02 g, 2.19 mmol) in toluene (70 ml). After 10 d, a pale yellow precipitate is obtained (1.17 g, 79 %). Anal. Calcd for Bi₃C₁₂H₂₉O₁₃: C, 14.29; H, 2.89%. Found: C, 14.31: H. 2.93%. Compound 4 was insoluble in pyridine. CHCl₃ and water. FT-IR $[cm^{-1}]$: 3368s br v_{OH} , 583w, 569m, 549m, 539m, 504w, 444w, 412m v_{Bi-O} . { $BiO(OCH_2)CMe_2(CH_2OH)$][(OHCH_2)₂C- $Me_2_2_m$ (5): Same procedure as for 1 applied to neol-H₂ (3.19 g, 30.59 mmol), bismuth oxide (1.78 g, 3.82 mmol) in toluene (70 ml). After 10 d, the grey suspension was filtered. Compound 5 was insoluble in THF, CHCl₃, acetonitrile, ethanol, nitromethane and water. Anal. Calcd for BiC15H35O7: C, 33.59; H, 6.58. Found: C, 33.90; H, 6.80%. FT-IR $[\text{cm}^{-1}]$: 3295m v_{OH} , 582w, 565w, 537w, 526w, 472m, 433m v_{Bi-O}.

- [19] A suitable crystal of 1 was obtained by crystallisation in hot toluene and was mounted on a Nonius Kappa CCD diffractometer equipped with MoK_a radiation. Accurate cell dimensions were obtained from 66 reflections collected at 150 K in the range $2 \le \theta \le 24^\circ$. The data were corrected for Lorentz and polarization effects. Computations were performed by using the PC version of CRYSTALS [23]. The structure was solved by SHELXS [24] and refined on F² by full-matrix least-squares with anisotropic displacement parameters for all nonhydrogen atoms. Hydrogen atoms were introduced in calculated positions in the last refinements with an overall isotropic displacement parameter. Crystal data for 1: BiC15H36N3O6, FW = 563.43, monoclinic, P2₁/n, a = 10.5704(8) Å, b = 16.802(2) Å, c = 11.645(1) Å, $\beta = 100.19(1)^{\circ}, \quad V = 2035.6(4) \text{ Å}^3, \quad Z = 4, \quad T = 150 \text{ K}, \quad \mu = 86.95$ cm^{-1} , 21199 reflections were measured (5839 were unique) $R^{a} = 0.0457$, wR = 0.1146, R = 0.0824, $wR^{b} = 0.128$ (all data), for 227 parameters. GOF = 0.9016.
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