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Novel structural forms for imidoamides and oxoalkoxides of bismuth

Siân C. James, Nicholas C. Norman,* A. Guy Orpen, Michael J. Quayle and Ulrike Weckenmann

The University of Bristol, School of Chemistry, Bristol BS8 1TS, UK

The reaction between $BiCl_3$ and 3 equivalents of Li[NHR] (R = 2,6-$Me_2C_6H_3$) afforded the trinuclear bismuth imidoamide species $[Bi_3(\mu\text{-}NR)_4(NHR)]$ whilst $BiPh_3$ and 3 equivalents of the alcohol HOR′ (R′ = 2,6-$Cl_2C_6H_3$) gave the hexanuclear oxoalkoxide compound $[Bi_6(\mu_3\text{-}O)_3(\mu\text{-}OR)_7(OR)_5]$ both of which have been characterised by X-ray crystallography.

Alkoxides of the p-block elements continue to be of interest to synthetic inorganic chemists,[1] not least because of their importance as models for, or potential precursors to, useful element oxide materials.[2] In the particular case of bismuth such materials include both the bismuth-containing cuprate and the bismuthate superconductors,[3] ferroelectric bismuth phases such as $Bi_4Ti_3O_{12}$[4] and mixed bismuth–transition metal oxide heterogeneous oxidation and ammination catalysts.[5] However, whilst the study of bismuth(III) alkoxides,[1] and the related amides,[6] is becoming established, much less is known concerning the related oxoalkoxides and imidoamides. Structurally characterised examples of the former include the compounds $[Bi_6(\mu_3\text{-}O)_7(\mu_3\text{-}OC_6F_5)\{Bi(OC_6F_5)_4\}_3L_2]$ **1** [L = tetrahydrofuran (thf) or toluene][7] and $[Bi_6(\mu_3\text{-}O)_2(\mu_4\text{-}O)(OC_6F_5)_{12}(thf)_2]$ **2**[8] described by Whitmire and co-workers, together with the tetranuclear species $[Bi_4(\mu_3\text{-}O)_2(\mu\text{-}OBu^t)_2(OBu^t)_6]$ **3** reported by Sauer *et al.*,[9] whereas the only example of a neutral bismuth imidoamide of which we are aware is the dinuclear compound $[Bi_2(\mu\text{-}NR)_2(NHR)_2]$ **4** (R = 2,6-$Pr^i{}_2C_6H_3$) recently reported by Roesky and co-workers.[10] Herein, we describe a significantly new structural form for each of these types of bismuth compound.

The reaction between $BiCl_3$ and 3 equivalents of Li[NHR] (R = 2,6-$Me_2C_6H_3$) in thf–Et_2O afforded, after work-up and crystallisation,† an intimate mixture of orange and red crystals of which the latter proved suitable for an X-ray crystallographic study.‡ This study revealed a trinuclear complex $[Bi_3(\mu\text{-}NR)_4(NHR)]$ **5** as a CH_2Cl_2 solvate (Fig. 1). The structure has approximate C_s symmetry and comprises a unique bismuth [Bi(1)] bonded to a terminal primary amido group [Bi(1)–N(1) 2.16(2) Å] and two bridging imido groups [average Bi(1)–N 2.17 Å] each of the latter being further bonded to a second bismuth centre [Bi(2)–N(2) 2.15(2) and Bi(3)–N(5) 2.17(2) Å] which in turn are both mutually bridged by two additional imido groups with somewhat longer Bi–N bonds [average Bi(2) and Bi(3)–N 2.21 Å]. All three bismuth centres adopt the trigonal-pyramidal geometry expected for three-co-ordinate bismuth(III) [sum of angles: Bi(1) 278.3, Bi(2) 269.5, Bi(3) 265.6°] whilst the nitrogen centres are all fairly close to trigonal planar especially N(4) and N(5) [sum of angles: N(2) 345.8, N(3) 340.9, N(4) 359.7, N(5) 359.6°]. For comparison, relevant parameters associated with the bismuth centres in **4** are Bi–N (amido) 2.164(4), Bi–N (imido) 2.174(5), 2.158(4) Å and sum of angles at Bi 269°,[10] whilst those for the tris(primary amido) complex $[Bi\{NH(2,4,6\text{-}Bu^t{}_3C_6H_2)\}_3]$ **6** are Bi–N 2.18 Å (average) and sum of angles at Bi 287.9°.[11] An ionic compound containing the dianion $[Bi_2(NBu^t)_4]^{2-}$ has also recently been described[12] for which the Bi–N distances average 2.182 Å.

In terms of the mechanism of formation of compound **5**, detailed speculation is unwarranted here, but we note that both Roesky[10] and Burford[11] and co-workers have addressed this matter in relation to similar compounds; the formation of **5** *via* a tris(primary amido) species analogous to **6** according to equation (1) is one possibility.

$$BiCl_3 + 3\,Li[NHR] \longrightarrow Bi(NHR)_3 + LiCl$$
$$3\,Bi(NHR)_3 \longrightarrow [Bi_3(\mu\text{-}NR)_4(NHR)] + 4\,NH_2R \quad (1)$$

The nature of the orange crystals formed in this reaction is not yet known, but we note that in the corresponding reaction between $SbCl_3$ and 3 Li[NHR] (R = 2,6-$Me_2C_6H_3$) the main product formed is the dimer $[Sb_2(\mu\text{-}NR)_2(NHR)_2]$ **7**[13] structurally analogous to **4**[10] and to the complex $[Sb_2(\mu\text{-}NR')_2(NMe_2)_2]$ **8** [R′ = 3,4,5-$(MeO)_3C_6H_2$] reported by Wright and co-workers.[14]

The reaction between $BiPh_3$ and 3 equivalents of 2,6-dichlorophenol in refluxing toluene afforded, after work-up and crystallisation,§ yellow crystals of a compound identified

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† A solution of $BiCl_3$ (0.499 g, 1.59 mmol) in thf (10 cm^3) was added to a stirred solution of Li[NHR], prepared from 1-NH_2-2,6-$Me_2C_6H_3$ (0.59 cm^3, 4.80 mmol) and $LiBu^n$ (3 cm^3 of a 1.6 mol dm^{-3} solution in hexanes), in Et_2O (10 cm^3) at 0 °C resulting in an immediate change to red-orange and the formation of a white precipitate. After warming to room temperature all volatiles were removed by vacuum and the resulting solid redissolved in CH_2Cl_2 (30 cm^3). After a subsequent filtration, the volume was reduced to ≈ 5 cm^3 and hexanes (20 cm^3) were added as an overlayer. Solvent diffusion at −30 °C over a period of days afforded an intimate mixture of orange crystals and red crystals of compound **5**, as a CH_2Cl_2 solvate, in moderate yields (combined 0.25 g). Satisfactory analytical data for **5** were not obtained due to difficulties in removing all traces of the orange crystals. A ^1H NMR spectrum of a solution of the orange and red crystals (which were difficult to separate) showed that several species were present in solution but little structural information could be ascertained. Likewise, mass spectrometry provided little useful information.

‡ Crystal data for $[Bi_3(NR)_4(NHR)]\cdot CH_2Cl_2$ (R = 2,6-$Me_2C_6H_3$) **5**·CH_2Cl_2. $C_{41}H_{48}Bi_3Cl_2N_5$, $M = 1329.10$, rhombohedral, space group $R\bar{3}$ (no. 148), $a = 30.750(11)$, $b = 30.750(11)$, $c = 24.373(6)$ Å, $U = 19\,959(10)$ Å^3, $Z = 18$, $D_c = 1.990$ Mg m^{-3}, $\lambda = 0.710\,73$ Å, $\mu = 12.086$ mm^{-1}, $F(000) = 11\,160$, $T = 173$ K, crystal dimensions 0.4 × 0.3 × 0.2 mm. Data (25 989 total, 5791 unique, $R_{int} = 0.098$) were collected on a Siemens SMART diffractometer for a full hemisphere of reciprocal space with $2 < \theta < 22.5°$. The structure was solved by direct methods and refined by least squares, against all 5661 F^2 values with $F^2 > 3\sigma(F^2)$ corrected for absorption, to $wR2 = 0.1732$, $w = [\sigma^2(F^2) + (0.0416\,F^2)^2 + 1594\,F^2]^{-1}$ [$R1 = 0.070$ for 4101 data with $F^2 > 2\sigma(F^2)$]. Hydrogen atoms were constrained to idealised geometries and assigned isotropic displacement parameters 1.2 times the U_{iso} of their attached atoms for aromatic hydrogens and H(1), and 1.5 U_{iso} for all others. The structure was partly disordered with Bi(1) refined over two positions in the ratio 96(1):4(1). The CH_2Cl_2 solvate molecules were also disordered, one, C(99), in a general position with *ca.* $\frac{2}{3}$ occupancy and the second, C(98), disordered about a three-fold axis. Crystal quality was less than ideal.

§ Samples of $BiPh_3$ (0.500 g, 1.136 mmol) and 2,6-dichlorophenol (0.549 g, 3.368 mmol) were dissolved in toluene (40 cm^3) and heated to reflux for 48 h during which time the colour changed from colourless to yellow. Subsequent removal of all volatiles, redissolution in a mixture of thf and Et_2O (≈ 5 cm^3) and the addition of an overlayer of hexanes

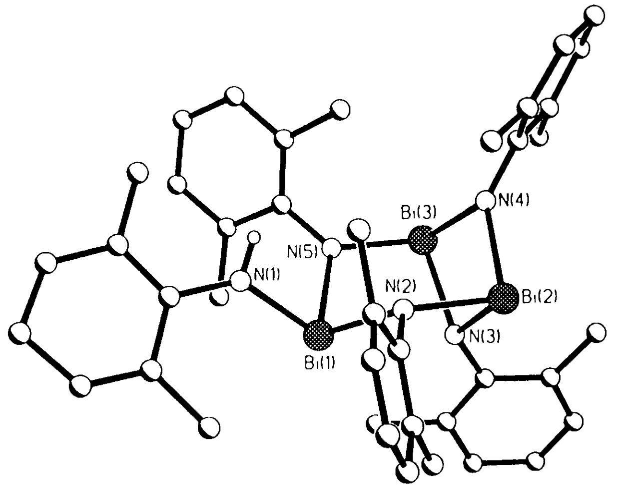
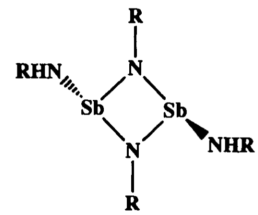


Fig. 1 Molecular structure of compound **5** showing the atom numbering scheme. Atoms are drawn as spheres of arbitrary radius. Selected bond lengths and angles: Bi(1)–N(1) 2.16(2), Bi(1)–N(2) 2.18(2), Bi(1)–N(5) 2.16(2), Bi(2)–N(2) 2.15(2), Bi(2)–N(3) 2.23(2), Bi(2)–N(4) 2.22(2), Bi(3)–N(3) 2.20(2), Bi(3)–N(4) 2.20(2) and Bi(3)–N(5) 2.17(2) Å; N(1)–Bi(1)–N(2) 92.5(8), N(1)–Bi(1)–N(5) 90.9(8), N(2)–Bi(1)–N(5) 95.9(6), N(2)–Bi(2)–N(3) 89.5(6), N(2)–Bi(2)–N(4) 100.7(7), N(3)–Bi(2)–N(4) 79.3(7), N(3)–Bi(3)–N(4) 80.2(6), N(3)–Bi(3)–N(5) 88.4(6) and N(4)–Bi(3)–N(5) 97.0(6)°



7; R = 2,6-Me$_2$C$_6$H$_3$

by X-ray crystallography* as a solvate of the hexanuclear bismuth oxoalkoxide [Bi$_6$(μ_3-O)$_3$(μ-OR)$_7$(OR)$_5$] **9** (R = 2,6-Cl$_2$C$_6$H$_3$) views of which are shown in Figs. 2 and 3 (one molecule of 2,6-dichlorophenol per molecule of **9** is also present in the crystal). The structure is complex and differs significantly from those of the other known hexanuclear species **1** and **2**.[7,8] The central core consists of a butterfly arrangement of bismuth atoms [Bi(2) to Bi(5)] with an alkoxide group bridging each edge and an oxo group [O(14)] bridging one face defined by Bi(3), Bi(4), Bi(5). In addition, the two edges Bi(2)–Bi(3) and Bi(4)–Bi(5) are each bridged by a further oxo group, O(13) and O(15) respectively, which are, in turn, bonded to the outer bismuths Bi(1) and Bi(6) such that both oxo groups are triply bridging. The edges Bi(1)–Bi(2) and Bi(5)–Bi(6) are each further bridged by alkoxide groups with Bi(2) carrying a terminal alkoxide and each of the outer bismuths [Bi(1) and Bi(6)] carrying two terminal alkoxides. Alternatively, the Bi$_6$ core may be described as a C_{2v} octahedron with edges and faces bridged as above and the vertices Bi(1), Bi(2) and Bi(6) having two, one and two terminal alkoxides respectively. The resulting co-ordination numbers and geometries of the bismuth centres are five, square-based pyramidal for Bi(2) to Bi(5) and four, disphenoidal for Bi(1) and Bi(6) and representative average bond lengths are given in the caption to Fig. 2.

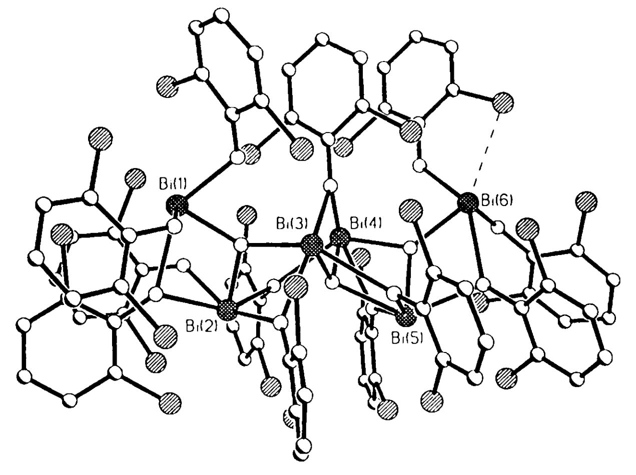


Fig. 2 Molecular structure of compound **9**. Atoms are drawn as spheres of arbitrary radius. Mean bond lengths include Bi–OR (terminal) 2.15, Bi–OR (bridging) 2.26 and Bi–O (oxo) 2.16 Å

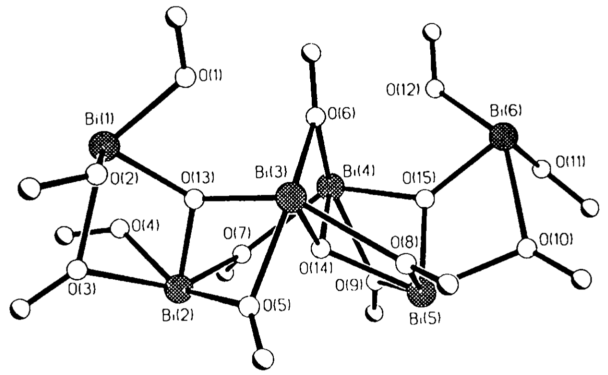


Fig. 3 Core structure of compound **9** showing only the Bi, O and *ipso*-C atoms and the atom numbering scheme

The overall oxoalkoxide charge in compound **9** is −18 consistent with each bismuth having an oxidation state of +3, and one representation of the bonding in terms of normal covalent and dative covalent bonds is shown, being based on the fact that dative bonds are generally *trans* to covalent bonds

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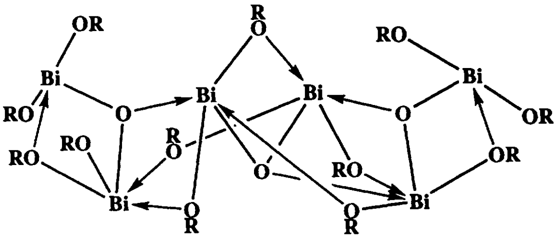
(20 cm^3) afforded yellow crystals of compound **9** (23% based on bismuth), as a solvate containing toluene, Et$_2$O and 2,6-dichlorophenol, after solvent diffusion over several weeks at −30 °C. On removal from the mother-liquor the crystals lost solvent rapidly. In the absence of toluene and Et$_2$O, **9**·1-HO-2,6-Cl$_2$C$_6$H$_3$ (C$_{78}$H$_{40}$Bi$_6$Cl$_{26}$O$_{16}$) requires C, 27.50; H, 1.20 (Found: C, 28.45; H, 1.30%). A ^{1}H NMR spectrum revealed only a broad multiplet in the aromatic region which was of little diagnostic value. The reaction between BiPh$_3$ and an acidic phenol is a useful alternative to more conventional salt metathesis reactions, a feature which has been well demonstrated by Whitmire and co-workers.[7,8]

* Crystal data for [Bi$_6$(μ_3-O)$_3$(μ-OR)$_7$(OR)$_5$]·2.0 C$_6$H$_5$Me·1.0 Et$_2$O·1.0 ROH (R = 2,6-Cl$_2$C$_6$H$_3$), **9**. 2.0 C$_6$H$_5$Me·1.0 Et$_2$O·1.0 ROH. C$_{96}$H$_{66}$Bi$_6$Cl$_{26}$O$_{17}$, M = 3667.07, monoclinic, space group $P2_1/n$ (no. 14), a = 16.579(4), b = 31.892(9), c = 22.509(5) Å, β = 109.51(2)°; U = 11 218(5) Å^3, Z = 4, D_c = 2.171 Mg m^{-3}, λ = 0.710 73 Å, μ = 10.060 mm^{-1}, $F(000)$ = 6872, T = 173 K, crystal dimensions 0.6 × 0.2 × 0.2 mm. Data (51 676 total, 19 638 unique, R_{int} = 0.101) were collected on a Siemens SMART diffractometer for a full hemisphere of reciprocal space with $2 < \theta < 25°$. The structure was solved by direct methods and refined by least squares, against all 19 570 F^2 values with $F^2 > 3\sigma(F^2)$ corrected for absorption, to $wR2$ = 0.2025, $w = [\sigma^2(F^2) + (0.0344\ F^2)^2 + 588\ F^2]^{-1}$ [$R1$ = 0.081 for 13 011 data with $F^2 > 2\sigma(F^2)$]. Hydrogen atoms were constrained to idealised geometries and assigned isotropic displacement parameters 1.2 times the U_{iso} of the attached carbon. The aryl rings of the toluene and free alcohol were constrained to regular hexagonal geometry and the Et$_2$O of solvation showed some positional disorder. Crystal quality was less than ideal. Atomic coordinates, thermal parameters, and bond lengths and angles for both structures have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/278.



in the axial positions of the disphenoidal geometry for four-coordination, and in the square-basal planar geometry in five-coordination.[15] The origin of the oxo groups is most likely due to partial hydrolysis from adventitious water although oxo formation resulting from alkoxide C–O bond cleavage is well established.[16]

In conclusion, the results described illustrate the potentially large structural variety that should be expected for imidoamide and oxoalkoxide complexes of bismuth (and antimony), an appreciation and understanding of which will be essential for efficient molecules-to-materials studies.

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