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Synthesis and crystal structure of tetrakis(2,4,6-trimethylphenyl)dibismuthoxide

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Abstract

Bis(2,4,6-trimethylphenyl)chlorobismuth (**1**), synthesized by comproportionation reaction of tris(2,4,6-trimethylphenyl)bismuth and bismuth chloride, was reduced with sodium in liquid ammonia. By subsequent insertion of oxygen into the Bi–Bi bond of the intermediate dimer tetrakis(2,4,6,-trimethylphenyl)dibismuth the title compound (**2**) was formed whose crystal structure has been determined: [monoclinic, space group $P2_1/n$; $a = 12.225(1)$ Å; $b = 14.957(1)$ Å; $c = 18.531(1)$ Å; $\beta = 97.76(1)°$; $Z = 4$]. (2) shows a Bi–O–Bi bond angle of 124.6° and a short intramolecular nonbonding Bi···Bi distance of 3.665 Å, probably the inherent reason for the metallic colour of (**2**). © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Bi–Bi bond; Bond angle; Bond distance; Crystal structure; Tetrakis(2,4,6,-trimethylphenyl)dibismuth

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1. Introduction

Chalcogen insertion into bismuth–bismuth bonds has been reported and compounds with Bi–E–Bi units have been synthesized by a cleavage reaction of bismuth–bismuth bonds [1–4]:

$$R_4Bi_2 + E \rightarrow R_4Bi_2E\left(E = \frac{1}{2}O_2, \frac{1}{8}S_8, \frac{1}{x}Se_x \text{ and } \frac{1}{x}Te_x,\right.$$

R = Methyl, Ethyl, *i*-Propyl, *i*-Butyl)

However, up to now we have only found one publication dealing with the crystal structures of these compounds. In this work we report the synthesis of bis(2,4,6-trimethylphenyl)chlorobismuth (**1**), tetrakis(2,4,6-trimethylphenyl)dibismuthoxide (**2**) and the X-ray crystal structure determination of (**2**).

2. Results and discussion

Compound (**1**) can be prepared, similar to the preparation of diphenylchlorobismuth [5], by the comproportionation reaction of tris(2,4,6-trimethylphenyl)bismuth with bismuth chloride in ether. A mixture of tris(2,4,6-trimethylphenyl)bismuth and bismuth chloride in ether was stirred at r.t. for 20 h and refluxed for another 30 h. After evaporation of the solvent the resulting yellow solid was separated, washed with a solvent mixture of ether and *n*-hexane until the filtrate is colourless. Bright yellow crystals of (**1**) were dried in vacuo (yield 86%). Following this operation compound (**1**) is pure enough for the next reaction step; the NMR spectra of (**1**) exhibit only signals characteristic for its molecular structure. The crystal structure of the analogous compound 2,4,6-trimethylphenylbismuthdichloride was discussed recently [6]. Compound (**1**) is air sensitive, soluble in THF and chloroform.

$$2\ Bi[C_6H_2(CH_3)_3]_3 + BiCl_3 \underset{RT}{\overset{Et_2O}{\rightarrow}} 3\underset{(1)}{[(CH_3)_3C_6H_2]_2BiCl}$$

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Reduction of (**1**) with sodium in liquid ammonia at − 70°, subsequent evaporation of ammonia in vacuo, extraction with *n*-hexane and filtration results in an orange solution. Solvent was removed in vacuo at 0°C until a first crop of crystals appeared. Cooling to − 30°C of this concentrated solution for 30 h affords yellow and green crystals with a metallic lustre which were separated and dried in vacuo. Both types of crystals were shown to be identical (**2**) by analysis (yield 60%). (**2**) is not soluble in *n*-hexane or aromatic hydrocarbon solvents, but is readily soluble in THF and chloroform. We assume that reduction of (**1**) with sodium results at first with the formation of an intermediate, viz. tetrakis(2,4,6-trimethylphenyl)dibismuth (**3**) (not isolated), which then easily undergoes an insertion reaction with dioxygen to form a Bi–O–Bi bonded species:

$$2[(CH_3)_3\underset{(1)}{C_6}H_2]_2BiCl + 2Na \xrightarrow{NH_3/-70^{\circ}C}$$

$$\{[(CH_3)_3\underset{(3)}{C_6}H_2]_4Bi_2\}^* + 2NaCl$$

$$\{[(CH_3)_3\underset{(3)}{C_6}H_2]_4Bi_2\}^* + \frac{1}{2}O_2 \underset{-30^{\circ}C}{\overset{Solvent}{\rightarrow}} [(CH_3)_3\underset{(2)}{C_6}H_2]_4Bi_2O$$

There remains a lone electron pair on each bismuth atom in compounds containing Bi–Bi bonds; this weak Bi–Bi bond has a specific tendency to undergo electron transfer processes which subsequently lead in further reactions to Bi–Bi bond cleavage [4]. Compound (**2**) melts at 194°C at ambient pressure without thermolysis; four bulky organic ligands (viz. 2,4,6-trimethylphenyl groups) in (**2**) protect the (Bi–O–Bi) unit rendering (**2**) an air and thermally stable compound.

2.1. Crystal structure of (2)

The solid state structure of (**2**) was determined by single crystal X-ray diffraction study: a plot of the molecule and the unit cell of (**2**) are given in Fig. 1 and 2, crystallographic data are listed in Table 1.

The structure was solved by Patterson methods [7] and refined against F^2 [8] with all 4677 independent reflections to $wR_2 = 0.0853$, resulting in a conventional $R = 0.0344$ for the 3155 observed data [$I > 2\sigma(I)$]. For all non-hydrogen atoms anisotropic temperature factors could be refined. The hydrogen atoms were kept riding on calculated positions with common isotropic temperature factors. The resulting positional parameters and equivalent isotropic temperature factors can be obtained from the data basis[1].

Table 1
Crystallographic data of (2)

Formula	$C_{36}H_{44}Bi_2O$
Molecular weight (g mol^{-1})	910.71
Crystal size (mm × mm × mm)	0.1 × 0.1 × 0.3
Crystal system:	Monoclinic
Space group:	$P2_1/n$
Z	4
Unit cell dimensions	
a (Å)	12.225(1)
b (Å)	14.957(1)
c (Å)	18.531(1)
β (°)	97.76(1)
V (Å^3)	3357.4(4)
D_{calc} (g cm^{-3})	1.802
μ(Mo–K$_\alpha$) (mm^{-1})	10.5, empirical corr., Ψ-scans
Min./max. transmission	0.40/0.46
Diffractometer	CAD4, Enraf-Nonius
Radiation	Mo–K$_\alpha$, graphite monochromator
Measuring temperature (K)	293
Measuring range	2θ: 2–46°, $\pm h$, $-k$, $+l$
Scan type	ω
Numbers of reflections total/independent	4841/4677
Number of reflections observed ($I > 2\sigma(I)$)	3155
R	0.0344
wR_2	0.0853

The geometrical data within the four ligands do not vary significantly with respect to the high standard deviations in the presence of the heavy bismuth atoms; averaged values are given therefore in Table 2.

The molecules have a pseudo C_2-symmetry. Bismuth atoms display a distorted pyramidal coordination sphere, each bismuth atom is linked to two carbon atoms of a 2,4,6-trimethylphenyl ligand (average bond length 2.275 Å) and to the bridging oxygen atom

Table 2
Selected bond lengths [Å] and bond angles [°] for (**2**)

Bi1–O1	2.075(8)	Bi1–C11	2.272(10)
Bi1–C21	2.272(10)	Bi2–O1	2.064(7)
Bi2–C31	2.269(10)	Bi2–C41	2.280(10)
Bi1···Bi2	3.665(1)		
Bi1–O1–Bi2	124.6(3)	O1–Bi1–C11	95.5(3)
O1–Bi1–C21	100.6(3)	C11–Bi1–C21	98.4(3)
O1–Bi2–C31	98.0(3)	O1–Bi2–C41	99.3(3)
C31–Bi2–C41	98.3(3)		
C1–C2	1.406(9)	C2–C3	1.397(5)
C3–C4	1.372(14)	C4–C5	1.377(10)
C5–C6	1.400(2)	C6–C1	1.402(9)
C2–C1–C6	119.4(6)	C1–C2–C3	118.9(10)
C2–C3–C4	122.6(5)	C3–C4–C5	118.0(5)
C4–C5–C6	122.4(6)	C5–C6–C1	118.9(8)

Data for the four mesityl groups are averaged; the atomic numbering is indicated by the last common digit. Standard deviations arise from the averaging process.

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[1] Additional material of the crystal structure investigation can be obtained from Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen 2, Germany, under specification of deposit number CSD 408079, names of the authors and the journal reference.

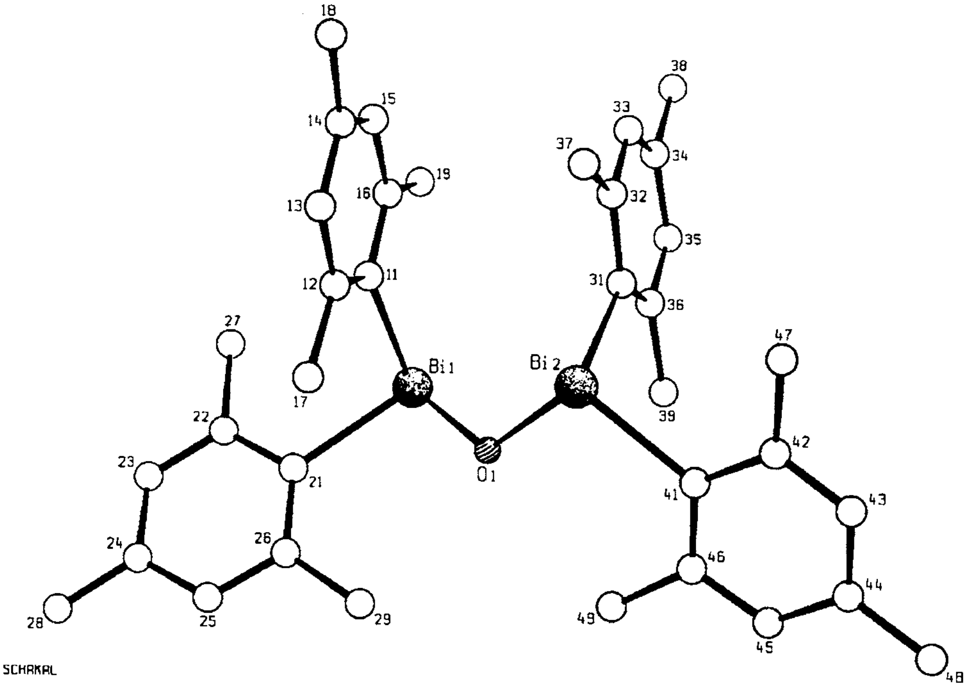

Fig. 1. Molecular structure of (**2**), Schakal plot.

(average bond length 2.070 Å). Bond angles of O(1)–Bi(1)–C(11), O(1)–Bi(1)–C(21) and C(11)–Bi(1)–C(21) are 95.5, 100.6 and 98.4°, respectively; each one is considerably smaller than tetrahedral, indicating that the free electron pair at bismuth is predominantly of 5-character (Figs. 1 and 2).

The Bi–O distances with only 2.064 and 2.075 Å are the shortest bismuth–oxygen bond lengths reported so far for bismuth compounds [9–13] (2.080–2.800 Å). The bond angle Bi(1)–O(1)–Bi(2) is 124.6° which is close to an sp^2-hybridized oxygen atom; this angle is considerably reduced to 117.1° [4] when (**2**) is co-crystallized with ethanol in a 2:1 ratio (see Table 3).

Comparing our data with those of structure (**2**)·0.5 ethanol [4] the bond distances show only small deviations as shown in Table 3.

Comparing transition metal organic compounds, e.g. binuclear compounds of the type M–O–M (M = transition metal), a single oxo-bridge (μ_2-oxide) may lead to an angle somewhat between 140 and 180°, this angle being determined by both steric and/or electronic factors [14]. McPhail et al. [15] assumed that this kind of bridging angle may be largely determined by stereochemical requirements of the ligands attached to the metal centers. Hodgson et al. [16] suggested that the size of the bridging angle may be determined mainly by ligand–ligand electronic effects.

The intermolecular, nonbonding Bi···Bi distance in (**2**) is longer than 7.00 Å, indicating that there is certainly no intermolecular 'secondary bonding' between bismuth atoms of one molecule to other neighbouring molecules.

In contrast, the intramolecular nonbonding Bi···Bi distance of 3.665 Å is considerably shorter than the sum of the van-der-Waals radii of bismuth (4.60 Å) [17]. Becker et al. [18] reported a nonbonding intermolecular Bi···Bi distance in tetrakis(trimethylsilyl)dibismuth of 3.804 Å, suggesting the existence of a 'secondary bond' between bismuth atoms of different molecules. Ashe et al. [19] published a nonbonding intermolecular Bi···Bi distance in 2,2′,5,5′-tetramethyl-1,1′-dibismaferrocene with 3.66 Å and similarly speculated on the existence of a 'secondary bond' between bismuth atoms. Clearly, in compound (**2**) the nonbonding intramolecular Bi···Bi distance is shorter than all

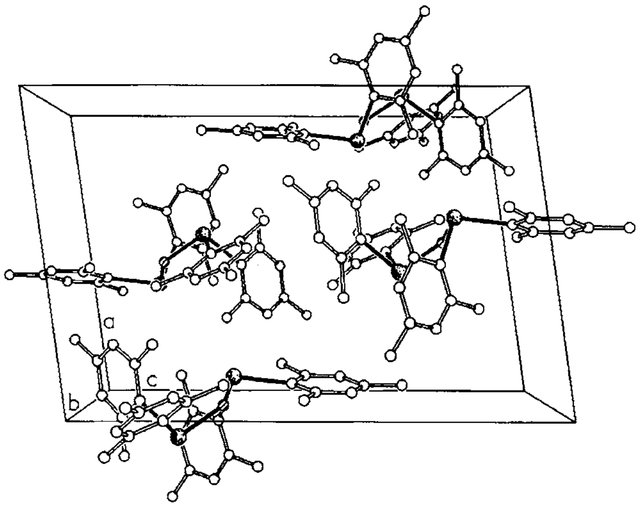

Fig. 2. Plot of the unit cell of (**2**).

Table 3
Comparison of distances and angles in Bi–X–Bi compounds

X	Bi···Bi	Bi–X	Bi–X–Bi	Bi–C	Literature
O	3.665(1)	2.075(8) 2.064(7)	124.6(3)	2.273(10)	this paper
O	3.594(2)	2.095(18) 2.117(19)	117.1(8)	2.255(29)	[4]
S		2.520(7) 2.545(6)	98.7(3)	2.274(26)	[4]
Se		2.651(1)	91.2(1)	2.275(10)	[4]

Bond lengths in (Å), angles in (°), Bi–C mean bond length, ESD's in parentheses.

other hitherto reported 'secondary bonding' Bi···Bi distances. From this we conclude, that on excitation of electrons from the nonbonding electron pairs at the bismuth centers charge density is easily transferred along the molecules in the crystal packing and leads to the metallic appearance of the crystals.

The bismuth–carbon distances range from 2.269 to 2.280 Å and compare well with already published Bi–C-distances ranging from 2.24 to 2.38 Å [20–28].

The sum of angles at bismuth is 294.5°, which is in the range of angles from 282 to 317.9° reported for pyramidal bismuth compounds [20,21,23]. Table 4 provides a comparison of parameters for some selected, but relevant bismuth compounds.

The difference in torsions of the 'left' and the 'right' hand side [Fig. 3b] documenting the deviations from C_2 symmetry is probably due to packing effects. The difference of 10° of the torsions C31–Bi2–Bil–C11 on the opposite side of the oxygen bridge and C41–Bi2–Bil–C21 on the same side may be attributed to the steric influence of the lone pairs at oxygen.

3. Experimental

All manipulations were carried out under argon atmosphere; for air sensitive compounds solvents were dried by standard methods and freshly distilled before use. NMR spectra were recorded on a Bruker AMX-500 (500 MHz) spectrometer. EI-mass spectra were recorded on a Varian MAT-CH-7A spectrometer, IR spectra on a Perkin-Elmer spectrometer. Tris(2,4,6-trimethylphenyl) bismuth (trimesitylbismuth) was prepared according to the literature [5], bismuth chloride was sublimed at 190° in vacuo at 0.01 mbar prior to use.

3.1. Synthesis of (**1**)

A solution of tris(2,4,6-trimethylphenyl)bismuth (25.00 g; 44 mmol) in diethyl ether (200 ml) was added to a stirred solution of bismuth chloride (6.96 g; 22 mmol) in diethyl ether (200 ml) in 30 min. at 0°C. A yellow precipitate was formed. The mixture was first stirred at r.t. for 20 h, then refluxed for additional 30 h. Ether was evaporated in vacuo, the residue was washed with a mixture of diethyl ether and *n*-hexane until the filtrate became colourless. The resulting bright yellow solid was dried in vacuo. Yield: 26.45 g (86%).

Found: C, 37.19; H, 3.78. $C_{18}H_{22}BiCl$ calc.: C, 44.78; H, 4.57. ^{1}H-NMR ($CDCl_3$): δ (ppm): 2.27, s, 6H, *p*-CH_3; 2.36, s, 12H, *o*-CH_3; 7.20, s, 4H, C_6H_2. ^{13}C-NMR: δ (ppm): 21.24, *p*-CH_3; 25.32, *o*-CH_3; 126.90, 132.14, 138.74, 145.71, aromatic carbons. IR spectra (Nujol, v cm^{-1}): 120 m/br, 179 w, 291 vst/br, 492 vw, 577 vw, 694 vw, 891 vw, 835 vw, 1026 vw, 1171 vw/br, 1290 m, 1403 vw/br, 1555 w/br, 1591 w, 1609 w, 1723 w/br, 2730 m/br.

Table 4
Comparison of parameters for some selected bismuth compounds

Compound	Sum of angles at bismuth (°)	Bismuth–Carbon distance (Å)	Literature
$Bi(C_6H_5)_3$	282	2.24	[21]
$Bi(C_5H_5)_3$	284	2.37	[29]
$Bi_2(C_6H_5)_4$		2.28	[25]
$[C_6H_2(CF_3)_3]_2BiCl$	294	2.34–2.36	[20]
(**2**)	295	2.27–2.28	This paper
$Bi[C_6H_2(CH_3)_3]_3$	308	2.24–2.32	[22]
$Bi[C_6H_2(CF_3)_3]_3$	318	2.36–2.38	[20]
$Bi[C_6H_2(C_6H_5)_3]_3$	317	2.34–2.38	[30]
$Bi[C_6H_2(CH_3)_3]Br_2$	287.5	2.20	[31]
	287.9	2.25	
$Bi[C_6H_2(CH_3)_3]Cl_2$	290.1	2.27	[6]

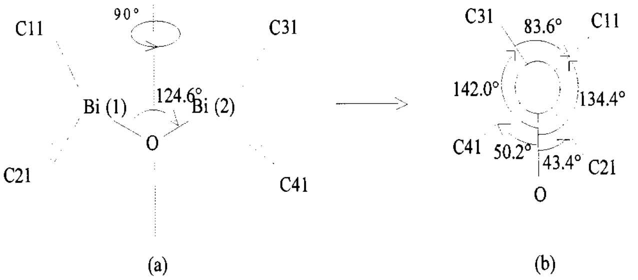

Fig. 3. Newman projection of (**2**).

*3.2. Synthesis of (**2**)*

Sodium (0.13 g; 5.8 mmol) was added to a stirred suspension of (**1**) (2.81 g; 5.8 mmol) in ammonia (50 ml) at -70°C. After 4 h stirring at this temperature ammonia was evaporated at 0°C, the solid was dried in vacuo at r.t., *n*-hexane (80 ml) was added to the solid and stirred for 30 min: insoluble residues were filtered. After filtration of the yellow liquid solvent was removed in vacuo at 0°C until the first crystals appeared. Cooling the concentrated solution to -30°C for 30 h affords yellow and green crystals which were separated and dried in vacuo. The yellow and green crystals were characterized as an identical product (**2**). Yield: 2.50 g; 1.6 mmol of 2, 56%. Melting point: 194°C.

Found: C, 47.83; H, 4.90. $C_{36}H_{44}Bi_2O$ calc.: C, 47.48; H, 4.87. ^{1}H-NMR (THF-d_8): δ (ppm): 2.44, s, 12H, *o*-CH_3, 2.48, s, 6H, *p*-CH_3, 7.25, s, 4H, C_6H_2; ^{13}C-NMR: δ (ppm): 20.60, CH_3, 22.97, CH_3, 130.44, 130.67, 136.66, 145.01, aromatic carbons. EI-MS (70 eV): m/z, ion, intensity %: 791, M-$C_6H_2(CH_3)_3$, 14.2; 537, $Bi_2[C_6H_2(CH_3)_3]$, 1 2; 565, $Bi[C_6H_2(CH_3)_3]_3$–H, 3.9; 463, $[C_6H_2(CH_3)_3BiO$, 4.1; 447, $Bi[C_6H_2(CH_3)_3]_2$, 100.0; 418, Bi_2, 1.0; 342, $C_6H_2(CH_3)_3BiO + H$, 3.4; 327, $BiC_6H_2(CH_3)_3$, 60.1; 209, Bi, 71.0; 119, $C_6H_2(CH_3)_3$, 39.3. IR (Nujol, ν cm^{-1}): 149 m/br, 174 vst, 200 vst, 329 m, 382 m, 391 m, 473 m, 493 m, 545 vw, 607 w, 698 vw, 845 vw, 1025 vw, 1157 vw/br, 1287 vw, 1553 vw, 1593 vw, 2726 vw/br, 3443 w/br.

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