Short Communication

Molecular Structure of a Monomeric Bismuth Trisalkoxide by Gas Electron Diffraction

Arne Haaland,[a],* Hans Peter Verne,[a] Hans Vidar Volden,[a] R. Papiernik[b] and Liliane G. Hubert-Pfalzgraf[b]

[a]Department of Chemistry, University of Oslo, PO Box 1033 Blindern, N-0315 Oslo 3, Norway and [b]Laboratoire de Chimie Moléculaire, Associé au CNRS, Université de Nice, Parc Valrose, 06108 Nice, Cédex 2, France

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The synthesis of bismuth tris(*tert*-butoxide), $Bi(OCMe_3)_3$, has been reported by Evans et al.,[1] and independently by Hubert-Pfalzgraf and coworkers.[2,3] Both groups reported that they had carried out investigations by X-ray crystallography, but had been unable to obtain complete structure characterization. Bismuth alkoxides such as $Bi(OEt)_3$ and $Bi(OCMe_3)_3$ are, however, volatile, and the latter has been used as a source of bismuth oxide for access to Bi-containing high-T_c superconductors through MOCVD.[4] This has enabled us to achieve the structural caracterization of $Bi(OCMe_3)_3$ in the gas phase by electron diffraction.

$Bi(OCMe_3)_3$ was synthesized as described in Ref. 3. The gas electron diffraction data were recorded on a Balzers Eldigraph KDG-2 instrument[5] with a metal inlet system and a nozzle temperature of about 125°C. Exposures were made with nozzle to plate distances of about 50 and 25 cm. Structure refinements were based on four photographic plates from each set. Optical densities were recorded on the Snoopy densitometer and processed by standard procedures.[6] Atomic scattering factors were taken from Ref. 7. Backgrounds were drawn as least-squares adjusted polynomials to the difference between total intensities and calculated molecular intensities for the best model. The final modified molecular intensities are displayed in Fig. 1.

Structure refinements were based on a molecular model of C_3 symmetry (PLUTON)[8] as shown in Fig. 2. Both the Me_3CO groups and H_3CC fragments were assumed to have C_{3v} symmetry. The structure is then determined by the Bi–O, O–C, C–C and C–H bond distances, the valence angles ∠ OBiO, ∠ BiOC and ∠ OCC, and two dihedral angles. The first dihedral angle, τ(Bi–O), is defined by the direction of the threefold symmetry axis, a

Bi–O bond and the adjoint O–C bond, the second, τ(O–C), by a O–C bond and the adjoining Bi–O and C–C bonds. The valence angle ∠ CCH was fixed at 110.4°.

The four unknown bond distances, three valence angles and two dihedral angles were refined by least-squares calculations on the intensity data along with ten root mean square vibrational amplitudes. The best values thus obtained are listed in Table 1. Since the refinements were carried out with a diagonal weight matrix, the estimated standard deviations calculated by the program have been multiplied by a factor of 3 to include the added uncertainty due to data correlation[9] and expanded to include an estimated scale uncertainty of 0.1 %. Experimental and calculated radial distribution curves are compared in Fig. 3.

Structure refinements were also carried out on a molecular model of C_s symmetry. The dihedral angles τ(Bi–O) and τ(O–C) of two ligands are equal, but have opposite signs. These angles were refined, while the dihedral angles of the third ligand was fixed at 0 to 180°. The C_s model could, however, not be brought into satisfactory agreement with the experimental intensities: the R-factors obtained were above 0.40, as compared to 0.062 for the best C_3 model.

The Bi–O bond distance, the first to be determined in a gaseous molecule, 206.7(4) pm, is 9 pm longer than calculated from Pauling's version of the Schomaker–Stevenson rule (197.6 pm),[10] but in good agreement with the value (207.6 pm) obtained by the Modified Schomaker–Stevenson rule,[11] eqn. (1).

$$R(A-B) = r_A + r_B - c \, |\chi_A - \chi_B|^{1.4} \tag{1}$$

As in many other metal alkoxides, the valence angle at oxygen is very large: 129.5(11)°. We believe the angle should be rationalized as due to geminal repulsion between the Bi and the tertiary C atom (and between the

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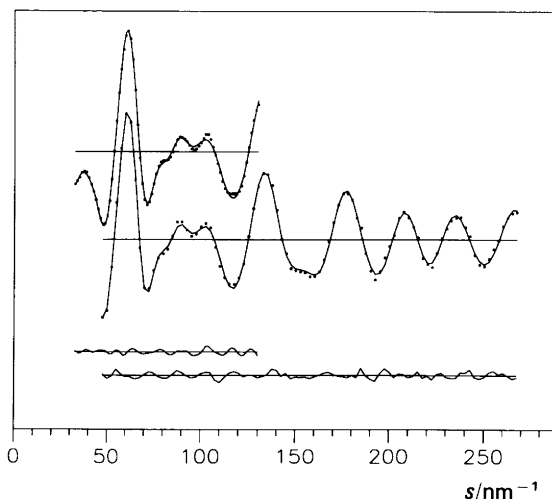* To whom correspondence should be addressed.

Fig. 1. Experimental (dots) and calculated (lines) modified molecular intensity curves for Bi(OCMe₃)₃. Below: difference curves.

Bi atom and the terminal methyl groups) rather than in terms of BiO π-bonding.

The present study confirms that the metathesis of bismuth trichloride with sodium *tert*-butoxide yields an authentic trisalkoxide, in contrast to alcoholysis of bismuth diphenylamide, which yields an oxoalkoxide, Bi₄O₂(OCMe₃)₈.[12]

In Fig. 4 we compare the coordination polyhedron of Bi in our alkoxide with the coordination polyhedra of Bi in other alkoxides, aryloxides of siloxides which have been studied by X-ray crystallography. The aryloxide Bi(OC₆H₃Me₂ − 2,6)₃), **CN3b**, is monomeric in the solid phase.[1] The mean Bi–O bond distance, 209.1(5) pm, the mean ∠ OBiO angle, 92(2)°, and the mean ∠ BiOC angle, 123(4)°, are not significantly different from their counterparts in Bi(OCMe₃)₃.[1] The Bi atom in the siloxide
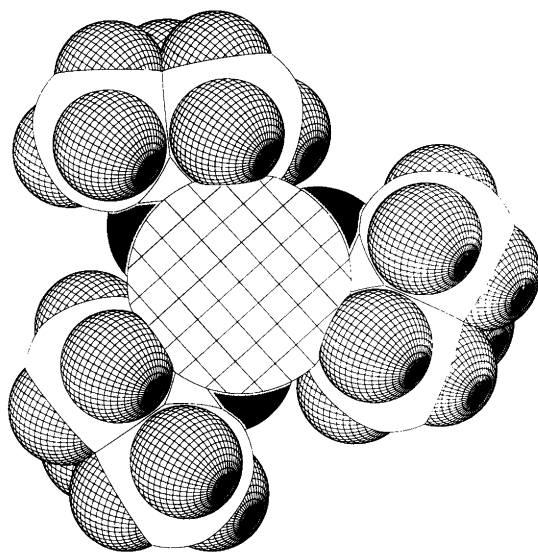
Table 1. Interatomic distances (r_a), root mean square vibrational amplitudes (l) (both in pm), valence angles and dihedral angles (τ) (both in °) of Bi(OCMe₃)₃.[a]

	r_a	l
Bond distances:		
Bi–O	206.7(4)	5.5(4)
O–C	145.7(14)	12(3)
C–C	151.5(6)	6.7(6)
C–H	111.9(5)	9.3(8)
Nonbonded distances:[b]		
Bi⋯C^t	319.7(15)	10.6(16)
Bi⋯C^p	345(4)	20(5)
Bi⋯C^p	417(13)	28(12)
Bi⋯C^p	437(9)	37(5)
O⋯C^p	251.3(6)	5.8(10)
C^p⋯C^p	237.0(6)	4.7(14)

Valence angles:		Dihedral angles:	
∠ OBiO	90.4(10)	τ(Bi–O)	59(4)
∠ BiOC	129.5(11)	τ(O–C)	13(15)
∠ OCC	115.5(5)	τ(C^t–C^p)	[±60, 180]^c
∠ C^{p}C^{t}H	[110.4]^c		

$$R = [\Sigma w(l_{obs} - l_{calc})^2 / \Sigma w l_{obs}^2]^{1/2} = 0.062$$

[a] Estimated standard deviations in parentheses in units of the last digit. [b] C^t = tertiary carbon atom; C^p = primary carbon atom. [c] These parameters were not refined.

Bi(OSiPh₃)₃, Ph = phenyl, crystallized with 3 mol of THF, **CN6**, is six-coordinate.[3] The three Bi–O(Si) bonds may be described as 'primary bonds' or as 'normal bonds', the Bi–O(THF) bonds as 'secondary' or 'dative'.[13,14] The difference between the normal (primary) bond distance and the dative (secondary) bond distance is about 90 pm. The valence angle between normal bonds is 78.3(3)°, the valence angle between dative bonds is 93.0°. The coor-
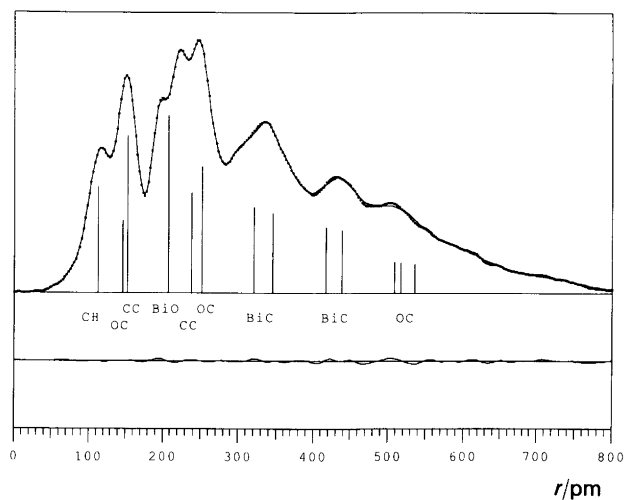

Fig. 2. Molecular model of Bi(OCMe₃)₃, point group C_3.

Fig. 3. Experimental (dots) and calculated (lines) radial distribution curves for Bi(OCMe₃)₃. Artificial damping constant $k = 25$ pm². Below: difference curve.

207 pm O

Bi

O   O

CN3A Bi(OCMe₃)₃

209 pm O

Bi

O   O

CN3b Bi(OC₆H₃Me₂-2.6)₃

209 pm O   257 pm

214 pm   O

Bi

O   O

214 pm   221 pm

CN4 |Bi(OC₆F₅)₃·(C₆H₅Me)|₂ 2C₆H₅Me

206 pm   269 pm

(THF)O   O   O

258 pm   Bi

O   O

212 pm   218 pm

CN5a |Bi(OCH(CF₃)₂)₃THF|₂

207 pm   253 pm

O.   O   O

251 pm   Bi

O   O

222 pm   223 pm

CN5b |Bi(OCH₂CH₂OMe)₃|∞

204 pm   295 pm

(THF)O   O   O(THF)

Bi

O   O

O(THF)
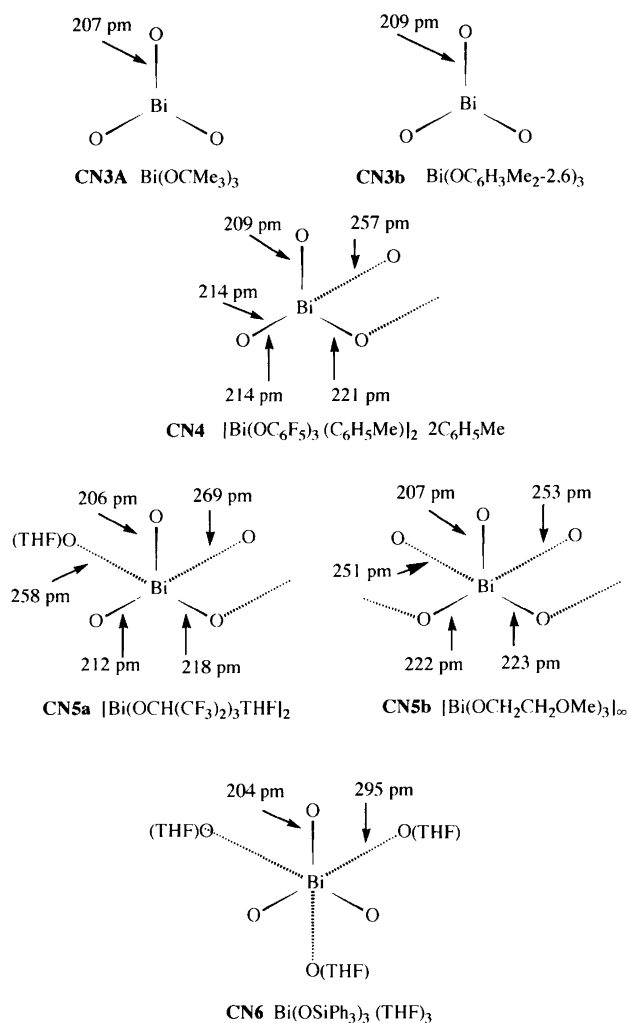
CN6 Bi(OSiPh₃)₃·(THF)₃

Fig. 4. Coordination polyhedra of Bi in some alkoxides, aryloxides and siloxides. Normal bonds are indicated by full, dative bonds by broken lines.

dination polyhedron may thus be described as distorted octahedral.

The coordination polyhedra of [Bi(OCH(CF₃)₂)₃ THF]₂,[15] **CN5a**, and [Bi(OCH₂CH₂OMe)₃]∞, **CN5b**,[3] where the cordination number of the Bi atom is 5, may be derived from the coordination polyhedron of **CN6** by removing one of the datively bonded O atoms.

In Bi(OC₆F₅)₃ crystallized with two moles of toluene, [Bi(OC₆F₅)₃(C₆H₅Me)]₂2C₆H₅Me, **CN4**,[15] each Bi atom is coordinated by four oxygen atom and a toluene ring. The Bi to ring centroid distances, 296(4) pm, are, however, so large that the bismuth atoms may be regarded as effectively four-coordinate, and the coordina-

tion polyhedron may be derived from that of **CN6** by removing two of the datively bonded O atoms.

The normal Bi–O bonds in these compounds range from 204 to 223 pm. The longer bonds are found when the normally bonded O atom is engaged in a dative bond to another Bi atom, or when there is a dative bond opposite to the normal. The dative bonds range from 251 to 295 pm.

Very recently Whitmire et al.[16] have published the crystal structures of (C₂H₅)₂BiOAr, Ar = Ph or C₆F₅. The structures are polymeric, with the OAr groups bridging two Bi atoms at equal distances, Bi–O(Ph) = 238.2(7) and Bi–O(C₆F₅) = 241.0(7) pm. We suggest that these distances should be described as 1 : 1 resonance hydrids between normal and dative Bi–O bonds.

References

1. Evans, W. J., Hain, J. H. and Ziller, J. W. *J. Chem. Soc., Chem. Commun.* (1989) 1628.
2. Massiani, M.-C., Papiernik, R., Hubert-Pfalzgraf, L. G. and Daran, J.-C., *J. Chem. Soc., Chem. Commun.* (1990) 301.
3. Massiani, M.-C., Papiernik, R.. Hubert-Pfalzgraf, L. G. and Daran, J.-C. *Polyhedron 10* (1991) 437.
4. Yamane, H. Kurzawa, H. and Hirai, T., *Chem. Lett.* (1988) 1515.
5. Bastiansen, O., Graber, R. and Wegmann, L., *Balzers High Vac. Rep. 25* (1969) 1.
6. Andersen, B., Seip, H. M., Strand, T. G. and Stølevik, R. *Acta Chem. Scand. 23* (1969) 3224.
7. Schäfer, L., Yates, A. C. and Bonham, R. A. *J. Chem. Phys. 55* (1971) 3055.
8. Spek, A. L. In: Sayre, D., Ed., *Computational Crystallography*, Clarendon, Oxford 1982, p. 528.
9. Seip, H. M., Strand, T. G. and Stølevik, R. *Chem. Phys. Lett. 3* (1969) 617.
10. Pauling, L. *The Nature of the Chemical Bond*, 3rd edn., Cornell University Press, Ithaca, NY 1960.
11. Blom, R. and Haaland, A. *J. Mol. Struct. 128* (1985) 21.
12. Sauer, N. N., Garcia, E. and Ryan, R., *Mater. Res. Soc. Proc. 180* (1990) 921.
13. Alcock, N. W. *Adv. Inorg. Chem. Radiochem. 15* (1972) 1.
14. Haaland, A. *Angew. Chem., Int. Ed. Engl. 28* (1989) 992.
15. Jones, C. M., Burkart, M. D. and Whitmire, K. H. *Angew. Chem., Int. Ed. Engl. 31* (1992) 451.
16. Whitmire, K. H., Huchison, J. C., McKnight, A. L. and Jones, C. M. *J. Chem. Soc., Chem. Commun.* (1992) 1021.