Synthesis and First *X*-Ray Crystal Structure of a Bi(OR)$_3$ Complex: Tris(2,6-dimethylphenoxo)bismuth

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$BiCl_3$ reacts with three equivalents of NaOR (R = CMe_3, $C_6H_3Me_2$-2,6) to form Bi(OR)$_3$, which for R = $C_6H_3Me_2$-2,6 was found by *X*-ray crystallography to have distorted pyramidal geometry.

The recent discovery that mixed-metal oxides such as $YBa_2Cu_3O_{7-x}$,[1] $Bi_2Sr_2Ca_2Cu_3O_{10}$,[2] and $TlBa_2Ca_3Cu_4O_{11}$[3] are superconducting at temperatures above 90 K has stimulated research on the preparation of high purity samples of these materials.[4] Hydrolysis of alkoxide complexes *via* sol-gel processes offers one route to homogeneous samples of high purity oxides and also provides synthetic routes to new oxides not available by high temperature solid-state methods.[5] Although alkoxide complexes of the metals found in the superconductors listed above have been known for many years,[6] few examples of these metal alkoxides, with the exception of copper alkoxides,[7] have been structurally defined by *X*-ray crystallography. Recent *X*-ray studies of yttrium alkoxides have shown that (i) trimetallic[8] and pentametallic[9] complexes readily form with simple alkoxide ligands[10] and (ii) halide and oxide ligands readily incorporate into these polymetallic frameworks. Since fully-defined, high purity metal alkoxides are essential to the preparation of pure oxides, it is important to confirm the composition and structure of the basic types of these metal alkoxides by *X*-ray crystallography. Relatively few examples of bismuth alkoxides have been reported in the literature.[11] In this report, we present synthetic and spectroscopic data on two Bi(OR)$_3$ systems as well as the first *X*-ray structure of such a complex.

$BiCl_3$ (6.34 mmol) was reacted with three equivalents of $NaOCMe_3$ (19.0 mmol) in 50 ml of tetrahydrofuran (THF) for 24 h. Removal of solvent from the reaction mixture followed by hexane extraction of the solid and removal of the hexane left Bi(OCMe$_3$)$_3$, (**1**), as a white powder in 80% yield. Compound (**1**) was characterized by complete elemental analysis, ^1H n.m.r., ^{13}C n.m.r., and i.r. spectroscopies.† The n.m.r. spectra showed a single environment for the $OCMe_3$ ligands at room temperature. Single *X*-ray quality crystals of (**1**) were grown from hexane at −34 °C (hexagonal; $a = b = 16.9065(28)$ Å, $c = 9.5398(33)$ Å, $U = 2361.75$ Å^3), but complete solution and refinement of the crystal structure has not been achieved. Isolated bismuth atoms are observed, which is indicative of a monomeric solid-state.

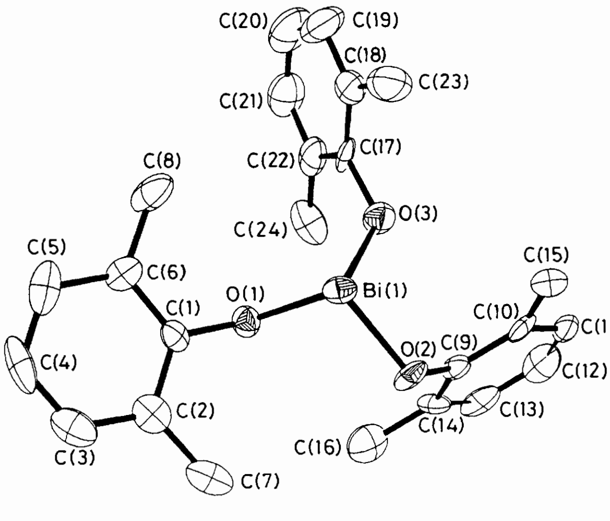

Figure 1. Molecular structure of Bi($OC_6H_3Me_2$-2,6)$_3$ with thermal ellipsoids drawn at 50% probability level. The average O–C distance is 1.37(1) Å.

Bi($OC_6H_3Me_2$-2,6)$_3$, (**2**), was similarly prepared as a yellow powder in 80% yield from $BiCl_3$ and three equivalents of $NaOC_6H_3Me_2$-2,6. The n.m.r. spectra of (**2**) in C_6D_6 were similar to those of (**1**) in that a single type of alkoxide environment was indicated at room temperature.† Single crystals of (**2**) were obtained from toluene at −34 °C which provided crystal structure data which refined properly.‡ Two views of this molecule are given in Figures 1 and 2.

Complex (**2**) crystallizes as a monomer with the three ligands directed away from a fourth co-ordination site presumably occupied by a lone pair. The O–Bi–O angles, which average 92(2)°, are contracted compared to the idealized 109° tetrahedral angle. This is expected for an AB_3E compound where E is a lone pair. The Bi–O–C angles average 123(4)°, which is within the wide range of angles observed for other 2,6-dimethylphenoxide structures.[14] The 2.091(5) Å average Bi–O distance in (**2**) is comparable to the shortest Bi–O distances found in Bi_2O_3 and $CeBi_{12}O_{20}$ complexes, which have Bi–O lengths from 2.08—2.80 Å.[15] The three $OC_6H_3Me_2$-2,6 ligands are not oriented in any regular pattern. The least squares plane of the C(1)–C(6) ring exhibits dihedral angles of 91° with respect to the other ring planes which have a 63° dihedral angle between them. Interestingly, this pattern is similar to that observed in Sc(OC_6H_2Me-4-Bu^t_2-2,6)$_3$[16] and Y($OC_6H_3Bu^t_2$-2,6)$_3$.[17] The Bi–O–C angles involving O(1) and O(3) are bent toward the open fourth position. The other Bi–O–C angle is oriented away from the fourth position.

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† *Selected spectroscopic data* for (**1**); ^1H n.m.r. (C_6D_6): δ 1.42 (s); $^{13}C\{^1H\}$ n.m.r. ([$^2H_8$]THF): δ 36.9 (s, CMe_3), 32.9 (s, CMe_3); i.r. (KBr, cm^{-1}): 2960 vs, 2900 sh, 2870 sh, 1465 s, 1380 sh, 1360 s, 1230 s, 1180 vs, 1030 w, 920 vs, 760 s. For (**2**); ^1H n.m.r. (C_6D_6): δ 2.42 (s, 6H), 6.66 (t, 1H), 7.04 (d, J_{HH} 7.5 Hz, 2H); $^{13}C\{^1H\}$ n.m.r. ([$^2H_8$]THF): δ 159.2 (s), 132.1 (s), 129.0 (s), 121.9 (s), 19.2 (s, Me); i.r. (KBr, cm^{-1}): 2950 br., 1910 br., 1750 w, 1730 w, 1580 w, 1460 s, 1420 s, 1260 s, 1210 vs, 1195 vs, 1080 s, 1030 w, 840 s, 760 s.

‡ *Crystal data* for (**2**); $C_{24}H_{27}O_3Bi$, monoclinic space group $P2_1/n$: $a = 11.871(2)$ Å, $b = 11.0992(14)$ Å, $c = 17.612(3)$ Å, $\beta = 108.999(12)°$, $U = 2194.0(6)$ Å^3, $Z = 4$, $D_c = 1.73$ g cm^{-3}, $\mu = 8.03$ mm^{-1}, 3026 measured reflections, 2232 observed reflections, $2\theta_{max} = 45.0°$, $R = 0.055$, $R_w = 0.055$ [Mo-K_α radiation, $\lambda = 0.710730$ Å, $T = 183$ K]. The data were collected on the Nicolet R3m/V diffractometer system using monochromatized Mo-K_α radiation *via* the omega scan technique using techniques similar to those described in ref. 12. The structure was solved by direct methods and refined by full-matrix least-squares techniques[13] using 2232 reflections with $|F_o| > 3.0\sigma(|F_o|)$. A final difference-Fourier map yielded ρ(max.) = 1.49 eÅ^{-3} at a distance of 1.17 Å from Bi(1). Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

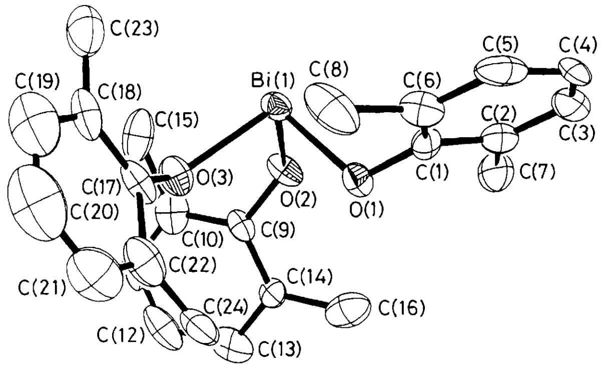

Figure 2. Side view of $Bi(OC_6H_3Me_2\text{-}2,6)_3$.

These structural data establish the monomeric nature of (**2**) and indicate that it has a stereochemically active lone pair.

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