

Bismuth Alkoxides. The First Structurally-Characterized Bismuth–Transition Metal Heterobimetallic Alkoxide: $[\text{BiCl}_3\text{OV}(\text{OC}_2\text{H}_4\text{OCH}_3)_3]_2$

J. W. Pell, W. C. Davis, and H. C. zur Loye*

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

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There has been much recent interest in bismuth alkoxides as potential precursors for sol–gel and chemical vapor deposition preparations of bismuth-containing superconductors^{1,2} and ferroelectrics, notably $\text{Bi}_3\text{Ti}_4\text{O}_{12}$.^{3–5} We have sought to synthesize films^{6,7} of $\text{Bi}_2\text{V}_x\text{Me}_{1-x}\text{O}_{5.5-\delta}$ (Me = Cu, Fe, Mn, Ti, Nb, Ta, ..., $0.1 < x < 0.5$),^{8–11} which exhibit high oxide ion conductivity, for use in air separation and partial oxidation membrane reactor applications.^{12–14} Heterometallic alkoxides with the correct metal ratios for the final product are especially sought after. There is, however, a dearth of information about even the homometallic alkoxides of bismuth. Insoluble bismuth alkoxides have been known since 1966,¹⁵ and recently a number of soluble bismuth alkoxide complexes have been isolated.^{1,2,16–21} While several groups have claimed the existence of a bismuth–transition metal precursor in their sol–gel processes,^{4,5,22,23} no such species have been isolated.²⁴ In this communication, we report the synthesis and structure of $[\text{BiCl}_3(\mu\text{-O})(\mu\text{-OC}_2\text{H}_4\text{-}$

$\text{OCH}_3)_2(\text{OC}_2\text{H}_4\text{OCH}_3\text{V})_2]$ (**1**), which to our knowledge represents the first structural description of a heterobimetallic bismuth-containing alkoxide complex.

The bismuth–vanadium complex was prepared under argon. Vanadium triisopropoxide oxide (6.8 mmol, 10% w/v in 2-propanol) was mixed with bismuth chloride (2.1 g, 6.5 mmol), and 10 mL of 2-methoxyethanol (2MOE) was added. On stirring of the mixture at room temperature, a clear yellow solution was obtained. Solvent was removed under vacuum with mild warming to yield an oily orange precipitate. This was redissolved in 5 mL of 2MOE. Orange crystals were obtained in 35% yield (first crop, based on bismuth) after 2 weeks at 2 °C. Single-crystal XRD indicated a dimeric complex (Figure 1).^{25–28} The crystals were stable under argon but darkened after 1 h in air.

There are relatively few compounds available with which to compare $[\text{BiCl}_3(\mu\text{-O})(\mu\text{-OC}_2\text{H}_4\text{OCH}_3)_2(\text{OC}_2\text{H}_4\text{OCH}_3\text{V})_2]$. The asymmetric unit contains one bismuth and one vanadium atom (Figure 1). The vanadium atom is located in a distorted octahedral environment that is unusual among vanadium(V) alkoxides, which prefer a square pyramidal geometry. The shortest V–O distance of 160 pm, belonging to the bridging oxide atom O(4), compares well with the usual vanadyl distance of 158 pm.^{29–31} A band at 945 cm^{-1} confirms a weakening of the vanadyl bond (usually 950–990 cm^{-1}).³⁰ Taking O(4) as the “top” vertex of the octahedron, the equatorial plane (defined relative to O(4)) is deflected slightly downward. The trans oxygen, O(2), and V form an angle of 170° with O(4), the deviation from 180° presumably caused by the short reach of the 2MOE group. Two of the 2MOE groups are bidentate on vanadium, in contrast with the cases found in lead(II) 2-methoxyethoxide³² and bismuth 2-methoxyethoxide,¹⁷ where the ligand is monodentate; bidentate 2MOE has been observed in a barium–titanium complex.³³

* To whom all correspondence should be addressed.

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(25) Crystal data for $\text{C}_9\text{H}_{21}\text{BiCl}_3\text{O}_7\text{V}$: $M = 607.53$, monoclinic, $P2_1/n$, $a = 10.7405(8)$ Å, $b = 14.9328(11)$ Å, $c = 11.2839(8)$ Å, $\beta = 97.2330(10)^\circ$, $V = 1795.4(2)$ Å³, $T = 188(2)$ K, $Z = 4$, $D_c = 2.248$ g/cm³, $\lambda = 0.71073$ Å (Mo K α). Of the 7070 reflections collected, 2567 were independent with $I > 2\sigma(I)$, yielding $R_1 = 0.0258$, $wR_2 = 0.0508$.

(26) NMR data: ⁵¹V (δ , ppm; 300 MHz; DMSO-*d*₆; $\text{VOCl}_3 = 0$ ppm) –553.07 (s); ¹H (δ , ppm; 300 MHz; DMSO-*d*₆) 3.24 (s, 3H), 3.30 (s, 6H), 3.33 (t, ³J = 5.2 Hz, 2H), 3.49 (q, ⁴J = 5.2 Hz, 2H), 3.57 (t, ³J = 4.8 Hz, 6H), 4.58 (t, ³J = 5.2 Hz, 1H), 4.92–4.95 (broad, 4H); ¹³C (δ , ppm; 300 MHz; DMSO-*d*₆) 57.95, 73.25, 80.36, 86.18, 92.09, 102.21, high background noise. It should be noted that the DMSO-*d*₆ used was contaminated with a small quantity of water, which we believe to have protonated O(3). This gives rise to the extra splitting in the 3.49 ppm peak (to a quartet) and in the 4.58 ppm peak in the proton spectrum.

(27) Anal. Found: C, 17.38; H, 3.36; Cl, 15.67; Bi, 35.03; V, 8.11. Calcd: C, 17.8; H, 3.5; Cl, 17.5; Bi, 34.4; V, 8.4.

(28) FTIR data (cm^{-1}): 2930 s, 1447 m, 1341 m, 1250, 1224, 1192 broad, m, 1050 m, 944, 911, 830, 647, 600, 576, 507 m/w.

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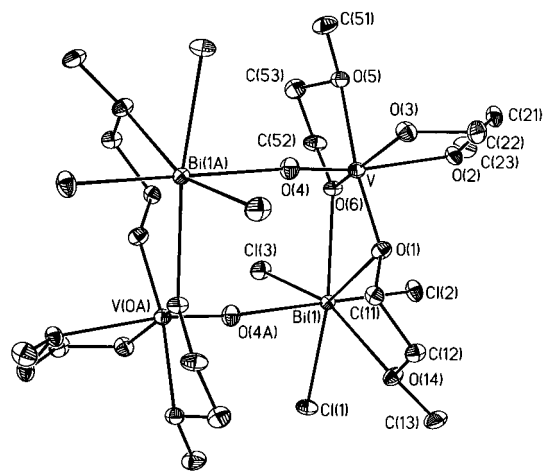


Figure 1. ORTEP representation of the Bi–V alkoxide. Protons have been omitted for clarity. Selected bond distances (pm): Bi–Cl(1) 257.1, Bi–Cl(2) 251.7, Bi–Cl(3) 250.8, Bi–O(6) 259.7, Bi–O(1) 284.9, Bi–O(4) 270.3, Bi–O(14) 279.8, V–O(1) 178.9, V–O(2) 236.0, V–O(3) 180.0, V–O(4) 160.3, V–O(5) 216.8, V–O(6) 190.7, Bi(1A)–V(OA) 368.8. Selected bond angles (deg): Cl(3)–Bi–Cl(2) 93.81, Cl(3)–Bi–Cl(1) 87.44, Cl(2)–Bi–Cl(1) 94.35, Cl(3)–Bi–O(6) 82.28, Cl(2)–Bi–O(6) 88.46, Cl(1)–Bi–O(6) 169.51, Cl(3)–Bi–O(4) 89.31, Cl(2)–Bi–O(4) 176.74, Cl(1)–Bi–O(4) 86.73, O(6)–Bi–O(4) 91.02, O(14)–Bi–O(4) 89.37, O(14)–Bi–O(6) 114.19, O(14)–Bi–Cl(1) 75.8, O(14)–Bi–Cl(2) 91.94, O(14)–Bi–Cl(3) 162.69.

The coordination environment around the bismuth atom is a distorted capped octahedron with the chlorine atoms and O(4), O(6), and O(14) as octahedral vertices. The alkoxy oxygen O(1) caps the O(4)–O(6)–O(14) face at 284.9 pm. This atom connects nearly at the equator (taking the bridging oxygen O(4) as the top vertex), distorting O(6)–Bi–O(14) to 114° and pinching O(6)–Bi–Cl(3) and O(14)–Bi–Cl(1) to 82 and 75°, respectively. The Bi–O(1) bond may be designated as a secondary bond.³⁴

The examples of other bismuth alkoxides suggest that a stereochemically active lone pair should be sought.^{17,19,20} The distortion around the bismuth center implies that such a lone pair would be directed toward the O(6)–O(14)–O(4) face. In this case, it is expected that the Bi–O(1) bond would be weak; however, this bond is only slightly longer than the complex's

other Bi–O bond distances. The distortion in the octahedron is small, indicating no real gap in the coordination geometry; and the Bi–Cl(3) and Bi–Cl(2) bonds, which are trans to the expected location of a lone pair, are not significantly shorter than Bi–Cl(1). Thus we conclude that a stereochemically active lone pair is absent.

Combined TGA/DTA of the compound in oxygen shows an endotherm at 144 °C with no attendant weight change, which is assigned to a separation of the complex into the original BiCl₃ and VO(OC₂H₄OCH₃)₃ parts. If this is indeed the case, the complex is surprisingly stable. Stepped exothermic weight losses up to 328 °C correspond to the removal of the –OC₂H₄OCH₃ groups, while the weight loss from 375–450 °C is assigned to the dissociation of the six chlorine atoms. The final product was identified by powder XRD to be primarily BiVO₄ (JCPDS No. 14-688), with some V₂O₅ (JCPDS No. 9-387) and Bi₄V₂O₁₁ (JCPDS No. 42-135).

The complex is soluble only in donor solvents. ⁵¹V NMR of the complex and parent V alkoxide both gave a single peak.^{26,29} In the ¹³C and ¹H NMR spectra,²⁶ peaks corresponding to the bidentate ligands are shifted only slightly from the corresponding peaks of the parent vanadium alkoxide, while additional peaks arise from the bridging 2MOE group. This suggests that the heterometallic complex maintains its structure in DMSO solution. In alcohols (methanol, diglyme), the complex appears to break apart.

To our knowledge, [BiCl₃(μ-O)(μ-OC₂H₄OCH₃)₂(OC₂H₄OCH₃)₃V]₂ is the first example of a heterobimetallic alkoxide involving bismuth. The presence of chlorine in the structure allows for further substitution by alkali metal-containing alkoxides, with the potential for increasing the number of metals present. Chemistry similar to that described in this communication could lead to the synthesis of other single-source alkoxide precursors for bismuth-containing ceramics.

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Supporting Information Available: Tables of crystallographic data, positional and thermal parameters, and interatomic distances and angles for **1** (6 pages). Ordering information is given on any current masthead page.

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