Oligomerization and Oxide Formation in Bismuth Aryloxides: Synthesis, Characterization, and Structures of $[NaBi(OC_6F_5)_4(THF)]_\infty$ and $Na_4Bi_2(\mu_6\text{-}O)(OC_6F_5)_8(THF)_4$

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The reaction of $[Bi(OR_f)_3{\cdot}C_7H_8]_2$ ($R_f = C_6F_5$) with sodium pentafluorophenolate leads to two new mixed-metal aryloxide complexes depending upon stoichiometry. Using 1 equiv of $NaOR_f$ per bismuth atom, a polymeric chain with the formula $[NaBi(OC_6F_5)_4(THF)]_\infty$, **1**, was isolated. If 2 equiv of $NaOR_f$ is used, the heterometallic oxo/aryloxide $Na_4Bi_2(\mu_6\text{-}O)(OC_6F_5)_8(THF)_4$, **2**, is formed. The mass spectroscopic data confirms the elimination of the bis(pentafluorophenyl) ether, R_fOR_f, concomitant with oxo-ligand formation. The compounds have been characterized spectroscopically and by single-crystal X-ray diffraction: Compound **1** crystallizes in the chiral monoclinic space group $P2_1$, with $a = 12.324(2)$ Å, $b = 10.934(2)$ Å, $c = 13.334(3)$ Å, $\beta = 91.19(3)°$, $V = 1796.4(6)$ Å^3, and $Z = 2$. The polymeric chain in **1** sits about the 2-fold screw axis and is the source of chirality for the compound. Compound **2** crystallizes in the triclinic space group $P\bar{1}$, with $a = 14.059(3)$ Å, $b = 14.060(3)$ Å, $c = 11.531(2)$ Å, $\alpha = 108.47(3)°$, $\beta = 102.78(3)°$, $\gamma = 108.61(3)°$, $V = 1912.6(7)$ Å^3, and $Z = 1$ and shows occupational disorder of the sodium and bismuth atom positions. Variable-temperature ^{19}F-NMR studies show dynamic behavior of these bismuth aryloxide complexes in solution.

Introduction

Metal alkoxides have been studied intensely over the past decade as a means of preparing precursors for MOCVD or sol−gel syntheses of high-purity metal oxides.[1] Bismuth oxide species are found in high-T_c superconductors[2] and in catalysts for olefin oxidation and ammoxidation.[3] Other applications range from ceramic insulators and piezoelectric materials to bioactive materials.[4] The first homometallic bismuth alkoxides were synthesized by Mehrotra in 1966[5] *via* reaction of $BiCl_3$ with alkali metal alkoxides. Several other bismuth alkoxides have been prepared in the last 30 years, and a few have also been structurally characterized.[6−12]

Many bismuth oxide materials contain other metals. To synthesize useful heterometallic precursors from known homometallic aryloxides, ideal aryloxide ligands must be found which stabilize the complexes and still allow controlled addition or oligomerization reactions to occur. As reported earlier, the $-OR_f$ ($R_f = C_6F_5$) group leads to the formation of easily crystallizable multinuclear homometallic complexes, like $[Bi(OR_f)_3{\cdot}x(\text{solvent})]_2$ and $Bi_6(\mu_3\text{-}O)_4(\mu_3\text{-}OR_f)\{\mu_3\text{-}OBi(OR_f)_4\}_3$[13] as well as several heterometallic aryloxides including $NaBi_3(\mu_4\text{-}O)(OR_f)_8(THF)$, $NaBi_4(\mu_3\text{-}O)_2(OR_f)_9{\cdot}2THF$, and $Na_2Bi_4(\mu_3\text{-}O)_2(OR_f)_{10}$.[14]

All the sodium bismuth aryloxides mentioned above, which contain oxide ligands, were synthesized *via* reaction of $BiCl_3$ with $NaOR_f$, where slight changes in reaction conditions dramatically altered the products formed.[14] Adventitious water could result in oxide ligand formation *via* hydrolysis reactions, but oxide ligand formation occurred even under rigorously dry conditions. This paper represents efforts to understand and control the oxo-ligand formation in this system.

Experimental Section

General Considerations. All reactions were carried out under an inert atmosphere of either argon or nitrogen using Schlenk line, drybox, or high-vacuum techniques.[15] Solvents were freshly distilled from the appropriate drying agents prior to use: THF ($LiAlH_4$ followed by Na/Ph_2CO), toluene (CaH_2), and acetone-d_6 (molecular sieves). $BiPh_3$ (Strem) was used as received. C_6F_5OH (PCR, Inc.) was sublimed from molecular sieves under reduced pressure. Sodium hydride (Aldrich), received as a mineral suspension, was washed with hexane and dried under vacuum. $[Bi(OR_f)_3{\cdot}C_7H_8]_2$ was prepared by the literature method.[8] NMR spectra were recorded on a Bruker AC250 (235.34 MHz ^{19}F) spectrometer; chemical shifts are reported in ppm on a scale relative to $CFCl_3$ (^{19}F NMR) as $\delta = 0$ ppm. Infrared spectra in the region 400−4000 cm^{-1} were taken on a Perkin-Elmer 1600 series spectrometer as KBr pellets which were prepared in a drybox. Mass spectra were obtained on a Finnigan MAT95 spectrometer. Elemental analyses were performed on a Perkin-Elmer Plasma 400 ICP-AES.

Synthesis of $[NaBi(OR_f)_4{\cdot}THF]_\infty$, 1. The compound $[Bi(OR_f)_3{\cdot}C_7H_8]_2$ (0.820 g, 0.482 mmol) was dissolved in 50 mL of THF, which will form the THF adduct $[Bi(OR_f)_3{\cdot}2THF]_2$.[8] The $NaOR_f$ solution was prepared by adding HOR_f (0.184 g, 1.0 mmol) in 20 mL of THF to a slurry of NaH (0.269 g, 11.2 mmol) in 20 mL of THF *via* cannula. The NaH excess ensures the dryness of solvent and phenol as well as a complete formation of sodium aryloxide. This solution was allowed to stir for 1 h and was then filtered through diatomaceous earth. The

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Table 1. Crystallographic Data Collection and Structure Refinement Parameters for Compounds **1** and **2**

	compound	
	1	**2**
empirical formula	$C_{28}H_8BiF_{20}NaO_5$	$C_{64}H_{32}Bi_2F_{40}Na_4O_{13}$
fw	1036.31	2278.82
space group	$P2_1$ (No. 4)	$P\bar{1}$ (No. 2)
a, Å	12.324(2)	14.059(3)
b, Å	10.934(2)	14.060(3)
c, Å	13.334(3)	11.531(2)
α, deg	90	108.47(3)
β, deg	91.19(3)	102.78(3)
γ, deg	90	108.61(3)
V, $Å^3$	1796.4(6)	1912.6(7)
Z	2	1
D (calcd), Mg/m^3	1.916	1.978
abs coeff, mm^{-1}	5.059	4.774
transm factor	0.5519−1.0	0.8055−1.0
$R1$ (on F) $[I > 2\sigma(I)]$[a]	0.0580	0.0833
$wR2$ (on F^2) $[I > 2\sigma(I)]$[b]	0.1558	0.200

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{1/2}$.

filtrate was added to the $[Bi(OR_f)_3{\cdot}2THF]_2$ solution. After being stirred overnight, the solvent was removed in vacuo and toluene was added. After being filtered through diatomaceous earth again, the toluene solution was concentrated and yellow diamond-shaped crystals formed in the freezer within 2 days. Yield: 72% based on Bi. Anal. Calc: Bi, 20.17; Na, 2.22. Found: Bi, 18.98; Na, 2.61. Infrared spectrum (cm^{-1}): 411 (s), 459 (m), 515 (m), 566 (m), 609 (s), 622 (s), 639 (sh), 668 (b), 699 (m) 804 (w), 986 (m), 1157 (m), 1247 (m), 1304 (m), 1377 (w), 1464 (s), 1504 (s), 1630 (m), 1652 (m).

Synthesis of $Na_4Bi_2(O)(OR_f)_8{\cdot}4THF$, 2. $[Bi(OR_f)_3{\cdot}C_7H_8]_2$ (0.874 g, 0.51 mmol) was dissolved in 50 mL of THF. The $NaOR_f$ solution was prepared like above, using 0.374 g of HOR_f (2.03 mmol) and 0.510 g of NaH (21.2 mmol) and added to the $[Bi(OR_f)_3{\cdot}2THF]_2$ solution. The reaction mixture was stirred overnight and the solvent removed in vacuo, leaving a yellow oil, which was extracted with toluene, filtered through diatomaceous earth, and concentrated to ∼20 mL. Opaque crystals formed overnight. They were recrystallized from toluene to yield pale yellow, diamond-shaped crystals suitable for X-ray diffraction. Yield: 79% based on Bi. Anal. Calc: Bi, 18.34; Na, 4.04. Found: Bi, 18.22; Na, 4.16. Infrared spectrum (cm^{-1}): 454 (s), 518 (m), 569 (sh), 611 (s), 621 (m), 724 (m), 805 (w), 860 (m), 990 (s), 1157 (m), 1304 (m), 1382 (w), 1463 (s), 1503 (s), 1627 (m), 1653 (m). The second product of this reaction, R_fOR_f , was identified in the reaction mixture by mass spectrometric analysis ($M^+ = 350$) of the hexane wash of the initial reaction mixture.[16]

Single-Crystal Structure Determination. These compounds are extremely sensitive to air and moisture. The crystals were examined under the microscope in mineral oil with a stream of argon flowing over the crystals in order to prevent decomposition. They were mounted with epoxy cement on the tip of a glass fiber and placed immediately on the diffractometer in a cold stream of $N_2(g)$. Data collection parameters for compounds **1** and **2** are found in Table 1. The data were collected using the TEXSAN automatic data collection series[17] on a Rigaku AFC5S diffractometer using Mo Kα radiation (λ = 0.710 73 Å). The data were corrected for Lorentz and polarization factors and for absorption using ψ-scans. The structures were solved by direct methods using the SHELXTL-PC package,[18] and the structure refinements were performed on F^2 with SHELXL-93.[19] The analytical form of the scattering factors for the appropriate neutral atoms was corrected for both the real ($\Delta f'$) and imaginary ($\Delta f''$) components of anomalous dispersion.[20] Weighted *R*-factors w*R* and all goodnesses of fit (*S*) are based on F^2; conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. *R*-factors based on F^2 are statistically about twice as large as those based on *F*. The OR_f ligands were refined as rigid groups. All R_f rings were restrained to fit local C_{2v} symmetry (C_2 axis along the O−C(1)−C(4) vector) rather than a regular hexagon. The fluorine and aryloxide oxygen atoms were refined with a common distance to each of the ring carbons *ortho* to their position. Selected bond angles and distances for compounds **1** and **2** are given in Tables 2 and 3.

Single-Crystal Structure Determination of 1. Compound **1** was found to crystallize in the acentric space group $P2_1$. The Flack parameter for the absolute structure indicated that the correct enantiomer had been chosen. The origin of the asymmetry is the helical chain structure along the 2_1 screw axis. The sodium, bismuth, and oxygen atoms as well as the fluorine atoms on two of the phenyl rings were refined anisotropically. Due to the disorder in the other two phenyl rings, anisotropic refinement of these two rings was not possible. One of those two phenyl rings showed disorder with a common oxygen atom location. It was modeled with two ring orientations. The THF ligand was also disordered and was modeled with a single oxygen but two positions for each carbon atom. The population ratio was found to be ca. 1:1 upon refinement.

Single-Crystal Structure Determination of 2. This molecule is located with the μ_6-oxygen on the crystallographic inversion center. There is disorder of the metal atoms, similar to that reported for the related compounds $Na_4Bi_2(O)(O^tBu)_8$, **3**, and $K_4Sb_2(O)(O^tBu)_8{\cdot}4THF$, **4**, by Veith *et al.*[21] and $Na_4[Sb_2O(OSiMe_3)_8]$, **5**, by Schmidbaur *et al.*[22] The metal atoms were refined so that the occupancy of each was part bismuth and part sodium. The three independent metal atoms were constrained to have a total occupancy equal to two for sodium and to one for bismuth. These will be referred to as M1, M2 and M3 in figures and text. The overall occupancy of M1 was found to be predominantly bismuth with a 0.71:0.29 (Bi:Na) ratio. The other two metal positions were mostly sodium (Bi:Na): M2, 0.17:0.83; M3, 0.12:0.88. The oxygen atoms as well as the carbon and fluorine atoms of three phenyl rings were refined anisotropically, while the fourth phenyl ring showed disorder and was refined isotropically. The THF rings were found to be disordered over two sites and were refined with a single oxygen atom and two positions for each carbon atom. The largest difference peak was a shadow peak located 0.427 Å from Na(2).

Results and Discussion

Synthesis, Structure, and Dynamics of Compound 1. Bismuth atoms in coordination compounds are well-known to function as Lewis acids giving rise to the formation of hypervalent bonding environments. Bismuth(III) centers with single lone pairs and four or five other ligands are common. This is well-documented for complex ions such as $[Bi_2Cl_8]^{2-}$.[23] It was anticipated that addition of $NaOR_f$ to “$Bi(OR_f)_3$” would lead to a similar adduct of the formulation $Na[Bi(OR_f)_4]$. This hypothesis was found to be essentially accurate when the stoichiometry of the reactants is exactly 1:1. An excess of $NaOR_f$ resulted in the formation of oxide-containing products, such as **2** or others, reported earlier.[14] Using exact stoichiometric amounts, compound **1** was obtained in form of a polymeric chain (Figure 1) with THF coordinated to bismuth (eq 1). As expected, the mass spectrometric analysis of the volatiles of the initial reaction did not show any peaks indicative of side products containing R_f.

$$^{1}/_{2}[Bi(OR_f)_3(C_7H_8)]_2 + NaOR_f \xrightarrow{THF} \underset{\mathbf{1}}{Na[Bi(OR_f)_4(THF)]_\infty} \tag{1}$$

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Table 2. Selected Bond Lengths (Å) and Angles (deg) for **1**[a]

Distances			
Bi(1)−O(10)	2.16(2)	Na(1)−F(42)	2.55(2)
Bi(1)−O(20)	2.18(2)	Na(1)−F(22BY)	2.88(4)
Bi(1)−O(40)	2.22(2)	Na(1)−F(36X)	2.99(2)
Bi(1)−O(30)	2.313(13)	O(20)−Na(1Y)	2.42(2)
Na(1)−O(30X)	2.24(2)	F(22A)−Na(1Y)	2.47(3)
Na(1)−O(40)	2.35(2)	F(22B)−Na(1Y)	2.88(4)
Na(1)−O(10)	2.41(2)	O(30)−Na(1Y)	2.24(2)
Na(1)−O(20X)	2.42(2)	F(36)−Na(1Y)	2.99(2)
Na(1)−F(22AX)	2.47(3)		
Angles			
O(10)−Bi(1)−O(20)	90.9(6)	O(30X)−Na(1)−F(36X)	61.1(5)
O(10)−Bi(1)−O(40)	73.4(6)	O(40)−Na(1)−F(36X)	81.9(6)
O(20)−Bi(1)−O(40)	88.1(5)	O(10)−Na(1)−F(36X)	142.4(7)
O(10)−Bi(1)−O(30)	88.0(6)	O(20X)−Na(1)−F(36X)	126.0(7)
O(20)−Bi(1)−O(30)	73.5(6)	F(22AX)−Na(1)−F(36X)	110.2(7)
O(40)−Bi(1)−O(30)	153.8(5)	F(42)−Na(1)−F(36X)	58.6(6)
O(30X)−Na(1)−O(40)	133.7(7)	F(22BX)−Na(1)−F(36X)	121.7(10)
O(30X)−Na(1)−O(10)	129.3(8)	C(11)−O(10)−Bi(1)	123.8(13)
O(40)−Na(1)−O(10)	66.8(6)	C(11)−O(10)−Na(1)	122.4(12)
O(30X)−Na(1)−O(20X)	70.4(6)	Bi(1)−O(10)−Na(1)	109.2(7)
O(40)−Na(1)−O(20X)	152.0(7)	C(21A)−O(20)−Bi(1)	136(3)
O(10)−Na(1)−O(20X)	87.0(7)	C(21B)−O(20)−Bi(1)	129(2)
O(30X)−Na(1)−F(22AX)	112.7(8)	C(21A)−O(20)−Na(1Y)	109(2)
O(40)−Na(1)−F(22AX)	105.5(8)	C(21B)−O(20)−Na(1Y)	121(2)
O(10)−Na(1)−F(22AX)	98.2(8)	Bi(1)−O(20)−Na(1Y)	107.2(6)
O(20X)−Na(1)−F(22AX)	67.6(6)	C(22A)−F(22A)−Na(1Y)	109(2)
O(30X)−Na(1)−F(42)	109.0(7)	C(22B)−F(22B)−Na(1Y)	108(3)
O(40)−Na(1)−F(42)	67.3(5)	C(31)−O(30)−Na(1Y)	125.6(12)
O(10)−Na(1)−F(42)	121.1(7)	C(31)−O(30)−Bi(1)	125.7(12)
O(20X)−Na(1)−F(42)	124.2(7)	Na(1Y)−O(30)−Bi(1)	108.7(6)
F(22AX)−Na(1)−F(42)	61.7(7)	C(36)−F(36)−Na(1Y)	103.8(12)
O(30X)−Na(1)−F(22BX)	115.1(12)	C(41)−O(40)−Bi(1)	124.8(11)
O(40)−Na(1)−F(22BX)	107.7(11)	C(41)−O(40)−Na(1)	119.5(11)
O(10)−Na(1)−F(22BX)	88.6(12)	Bi(1)−O(40)−Na(1)	109.6(6)
O(20X)−Na(1)−F(22BX)	60.2(8)	C(42)−F(42)−Na(1)	114.3(11)
F(42)−Na(1)−F(22BX)	72.4(8)		

[a] Symmetry transformations used to generate equivalent atoms: (X) $-x + 1, y - {}^1/_2, -z + 1$; (Y) $-x + 1, y + {}^1/_2, -z + 1$.

Since the direct reaction of $\mathrm{NaOR_f}$ with $\mathrm{BiCl_3}$ always produces oxo-based species, we conclude that the elimination of $\mathrm{R_fOR_f}$ from the intermediate species $\mathrm{Bi(OR_f)_xCl_{3-x}}$ ($x = 1$, 2) upon reaction with $\mathrm{NaOR_f}$ must be competitive with formation of $\mathrm{Bi(OR_f)_3}$ and the subsequent adduct $\mathrm{NaBi(OR_f)_4}$.

The solid-state structure of **1** (Figure 1) has all four $\mathrm{OR_f}$ groups bridging between one sodium and one bismuth atom in an infinite chain similar to $\mathrm{KBi(OtBu)_4}$, **6**.[21] Compound **1** is unique, however, in that it possesses an additional solvent THF molecule coordinated to Bi. The aryloxide ligands are all crystallographically independent, although the coordination environments are very similar. The polymer is situated about a crystallographic 2-fold screw axis. There are two bridging aryloxides between each sodium and bismuth atom. One of the phenyl rings exists in a minor disordered orientation (41%), and the following discussion deals with only the major component. The compound formulation is conventional, containing one $\mathrm{Bi^{3+}}$ ion and one $\mathrm{Na^+}$ ion whose charges are compensated for by four $\mathrm{^-OR_f}$ ligands per monomeric unit.

The sodium ion environment of **1** is highly irregular (Table 2). As shown in Figure 2, the sodium ion is effectively seven-coordinate, owing to the four bonds to oxygen and three weak interactions to fluorine (F(22A) = 2.47(2), F(42) = 2.55(2), F(36A) = 2.99(2) Å). One could think of the coordination environment as being a monocapped octahedron, but the bond angles are considerably distorted from that interpretation. Perhaps a more appropriate view is to consider the oxygen and fluorine atoms to produce a roughly spherical, negatively-charged cavity encapsulating the $\mathrm{Na^+}$ ion. This feature has been observed for other complexes containing the $\mathrm{OC_6F_5}$ ligand as well.[14]

The bismuth ion of **1** (Figure 3) can be viewed as a square pyramidal arrangement of oxygen donors in which the THF ligand occupies one of the basal sites. The lone pair on the bismuth atom is obviously stereochemically active, and this bonding arrangement is common in bismuth coordination compounds.[24] The THF ligand is more weakly coordinated than the aryloxide ligands as noted by the Bi−O distances which range from 2.16(2) to 2.313(13) Å for the $\mathrm{OR_f}$ groups compared to a value of 2.59(2) Å for the THF oxygen atom. This is consistent with simple electrostatic considerations and bond distance trends found in the bismuth dimer $\mathrm{[Bi(OR_f)_3{\cdot}2THF]_2}$.

The environments about the oxygen atoms of the aryloxide ligands are essentially planar as can be seen by the sum of the angles about them: O(10), 355.4°; O(20), 352.2°; O(30), 359.0°; O(40), 355.9°. The individual angles fall into two classes. The M−O−C angles are large (123°, average) compared to the M-O-M′ values (109°, average). The planarity about the O atoms suggests that there may be significant donation of the remaining oxygen lone pair of electrons to either one or both of the metal atoms. This would also tend to strengthen the bismuth−aryloxide linkages versus the $\mathrm{Bi{-}O_{THF}}$ bonds.

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Table 3. Selected Bond Lengths (Å) and Angles (deg) for **2**[a]

Distances			
Bi(1)−O(1)	2.0937(9)	Na(3)−O(30)	2.461(11)
Bi(1)−O(40)	2.292(10)	Na(3)−O(10)	2.481(12)
Bi(1)−O(30)	2.324(10)	Na(3)−O(1)	2.496(5)
Bi(1)−O(20)	2.331(11)	Na(3)−F(42A)	2.808(13)
Bi(1)−O(10)	2.372(10)	O(1)−Bi(1A)	2.0937(9)
Na(2)−O(40)	2.326(11)	O(1)−Na(2A)	2.380(4)
Na(2)−O(1)	2.380(4)	O(1)−Na(3A)	2.496(5)
Na(2)−O(30)	2.392(12)	O(10)−Na(2A)	2.438(11)
Na(2)−O(10A)	2.438(11)	O(20)−Na(2A)	2.448(11)
Na(2)−O(20A)	2.448(11)	O(20)−Na(3A)	2.455(13)
Na(2)−F(22A)	2.863(14)	F(22)−Na(2A)	2.863(14)
Na(3)−O(40A)	2.354(12)	O(40)−Na(3A)	2.354(12)
Na(3)−O(20A)	2.455(13)	F(42)−Na(3A)	2.808(13)

Angles			
O(1)−Bi(1)−O(40)	78.1(3)	O(20A)−Na(3)−O(30)	79.6(4)
O(1)−Bi(1)−O(30)	76.8(3)	O(40A)−Na(3)−O(10)	84.9(4)
O(40)−Bi(1)−O(30)	88.5(4)	O(20A)−Na(3)−O(10)	137.8(4)
O(1)−Bi(1)−O(20)	77.4(3)	O(30)−Na(3)−O(10)	81.6(4)
O(40)−Bi(1)−O(20)	87.9(4)	O(40A)−Na(3)−O(1)	69.5(3)
O(30)−Bi(1)−O(20)	154.1(4)	O(20A)−Na(3)−O(1)	68.1(3)
O(1)−Bi(1)−O(10)	79.0(3)	O(30)−Na(3)−O(1)	67.4(3)
O(40)−Bi(1)−O(10)	157.1(4)	O(10)−Na(3)−O(1)	69.9(3)
O(30)−Bi(1)−O(10)	86.9(4)	O(40A)−Na(3)−F(42A)	63.2(4)
O(20)−Bi(1)−O(10)	86.6(4)	O(20A)−Na(3)−F(42A)	109.7(4)
O(40)−Na(2)−O(1)	72.0(3)	O(30)−Na(3)−F(42A)	159.8(4)
O(40)−Na(2)−O(30)	86.1(4)	O(10)−Na(3)−F(42A)	100.7(4)
O(1)−Na(2)−O(30)	70.3(3)	O(1)−Na(3)−F(42A)	132.4(3)
O(40)−Na(2)−O(10A)	86.5(4)	Bi(1A)−O(1)−Na(2A)	88.38(9)
O(1)−Na(2)−O(10A)	72.5(3)	Bi(1)−O(1)−Na(2A)	91.62(9)
O(30)−Na(2)−O(10A)	142.6(4)	Bi(1A)−O(1)−Na(2)	91.62(9)
O(40)−Na(2)−O(20A)	142.1(4)	Bi(1)−O(1)−Na(2)	88.38(9)
O(1)−Na(2)−O(20A)	70.1(3)	Na(1A)−O(1)−Na(3A)	91.34(11)
O(30)−Na(2)−O(20A)	81.1(4)	Bi(1A)−O(1)−Na(3A)	91.34(11)
O(10A)−Na(2)−O(20A)	82.6(4)	Bi(1)−O(1)−Na(3A)	88.66(11)
O(40)−Na(2)−F(22A)	151.2(4)	Na(2A)−O(1)−Na(3A)	92.91(14)
O(1)−Na(2)−F(22A)	124.8(3)	Na(2)−O(1)−Na(3A)	87.09(14)
O(30)−Na(2)−F(22A)	120.4(4)	Bi(1A)−O(1)−Na(3)	88.66(11)
O(10A)−Na(2)−F(22A)	78.5(4)	Bi(1)−O(1)−Na(3)	91.34(11)
O(20A)−Na(2)−F(22A)	60.2(4)	Na(2A)−O(1)−Na(3)	87.09(14)
O(40A)−Na(3)−O(20A)	83.7(4)	Na(2)−O(1)−Na(3)	92.91(14)
O(40A)−Na(3)−O(30)	136.8(4)		

[a] Symmetry transformations used to generate equivalent atoms: (A) $-x + 1, -y, -z$.

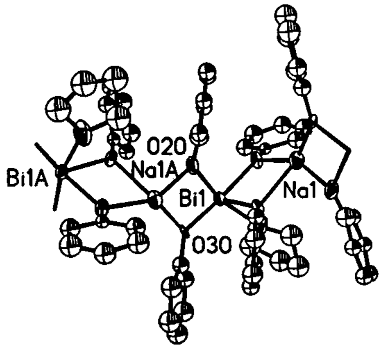


Figure 1. Plot of a part of the polymeric chain of compound **1** showing 50% probability thermal ellipsoids. The fluorine and hydrogen atoms have been omitted for clarity.

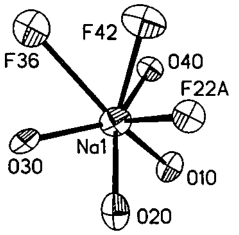


Figure 2. Plot of the coordination environment of sodium in **1** showing 50% probability thermal ellipsoids.

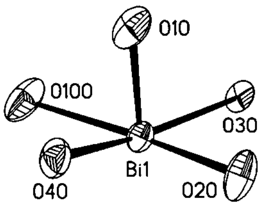


Figure 3. Plot of the coordination environment of bismuth in **1** showing 50% probability thermal ellipsoids.

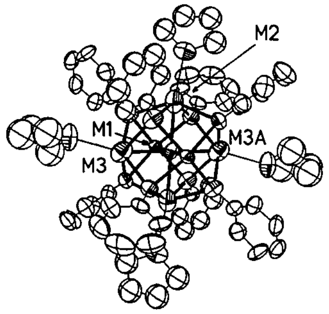
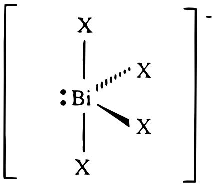
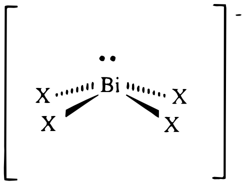


Figure 4. Plot of compound **2** showing 50% probability thermal ellipsoids. The fluorine and hydrogen atoms have been omitted for clarity.

^{19}F NMR was used to probe the structure of compound **1** in solution. At room temperature the ^{19}F NMR spectrum in acetone shows clearly only one environment of the pentafluorophenyl rings with three peaks in ratio 2:2:1 as expected for *ortho*, *meta*, and *para* flourines. This could arise from the accidental equivalence of all four OR_f groups or from fast dynamic exchange. It is likely that the polymer does not exist in solution and that the formulation may be better written as $Na[Bi(OR_f)_4(solvent)_x]$. As the temperature is decreased, the three ^{19}F peaks of the average phenyl ring begin to broaden, indicating the existence of a dynamic structure. According to the VSEPR, model the seesaw structure **A** is predicted but a square pyramidal structure **B** should be close in energy and the two forms would be expected to interconvert rapidly. Solvent coordination or ion pairing to the Na$^+$ counterions could distort these structures, but no convenient spectroscopic handle is available to resolve this question.



A



B

Unfortunately even at 188 K the dynamic process is not resolved and the exchange mechanism could not be elucidated. The sample froze at this temperature, which was also near the limit of the low-temperature capabilities of the spectrometer. Slowing of intramolecular exchange processes or the onset of oligomerization are both possible explanations for these results. (The variable-temperature NMR spectra for compound **1** are available as part of the Supporting Information.)

Synthesis, Structure, and Dynamics of Compound 2. Compound **2** (Figure 4) arises in 80% yield from the reaction of 4 equiv of $NaOR_f$ per $[Bi(OR_f)_3(C_7H_8)]_2$ as given in eq 2.

$$[Bi(OR_f)_3(C_7H_8)]_2 + 4NaOR_f \xrightarrow{THF} \underset{\mathbf{2}}{Na_4Bi_2O(OR_f)_8(THF)_4} + R_fOR_f \quad (2)$$

The production of R_fOR_f was confirmed by electron impact mass spectrometry on the hexane wash of the crude product (parent ion peak at 350 mass units). For comparison, the ether was synthesized using the procedure described in the literature[16] and mass spectroscopically analyzed. Ether formation has been reported to be driving force in the synthesis of other metal oxide compounds.[25] Because of its volatility, the R_fOR_f was not separated from the solvent for a quantitative determination. It is not likely that the ether is formed in the mass spectrometer because similar analyses of HOR_f, $NaOR_f$, and $[Bi(OR_f)_3(solvent)]_2$ showed no signals attributable to R_fOR_f. The R_fOR_f elimination is also interesting in that regard as the synthesis of certain diaryl ethers can be difficult.

Compound **2** is isostructural with compounds $Na_4Bi_2(O)(O^tBu)_8$, **3**, and $K_4Sb_2(O)(O^tBu)_8{\cdot}4THF$, **4**, by Veith, *et al.*[21] and $Na_4[Sb_2O(OSiMe_3)_8]$, **5**, by Schmidbaur *et al.*[22] A central μ_6-O ligand is surrounded by six metal atoms. These six atoms are disordered over the six locations of a regular octahedron, but there is some site preference for the heavier atoms. In compounds **3**−**5**, two positions in a *cis* configuration showed substantially higher populations of the heavy atom component. This *cis*-arrangement was confirmed by solid-state NMR studies. In contrast to this previous work, the two sites which refined to give substantially larger populations of Bi were located *trans* to each other as required by the crystallographic inversion symmetry present at O(1). The crystallographic analysis does not, however, preclude the possibility that the arrangment of Bi atoms in an individual molecule is actually *cis* given the disorder problem. No solid-state NMR capability was available to allow resolution of this question, however, so a variable-temperature solution ^{19}F NMR study was undertaken and consistent with a *cis*-configuration of the two bismuth atoms (vide infra) in solution. Besides being similar to the Schmidbaur and Veith compounds, the formulation is reasonable based upon charge balance with the two Bi^{3+} and four Na^+ ions being compensated by one O^{2-} ion and the eight ^-OR_f ligands.

The local coordination environment of the composite metal atom M1 which is primarily Bi is that of a square pyramid, similar to that of the Bi atom found in **1**. For **2**, the oxide ligand occupies the apical position. THF ligands attached to M2 and M3 which are predominantly sodium ion in character give these metal positions pseudo octahedral coordination. Because of the metal atom positional disorder, very little can be said about the details of the M−aryloxide bonding, although it is clear that the aryloxides are symmetrically located in triply bridging environments about the M6 octahedron (Figure 4).

In the *trans* arrangement all the OR_f groups are equivalent and should show only one set of signals with the ratio 2:2:1 in the ^{19}F NMR spectrum. In fact we observe only three signals (1 = *ortho*, 2 = *meta*, and 3 = *para*) at ambient temperature, indicating either that the molecule adopts a *trans* arrangement of the two Bi atoms or that dynamic exchange is taking place (Figure 5). The assignment of the *meta* and *ortho* peaks was made by comparison to three related bismuth pentafluoroaryloxides for which the F−F coupling constants could be determined.[26] Upon cooling, the peaks broaden and split. At 210 K three different OR_f environments (labeled a−c) may be identified from the resolution of the *ortho* and *para* peaks. The *meta*-fluorine peak shows some splitting, but it is not clearly resolved. The signals for the *meta*- and *ortho*-fluorine were each assigned an overall area of 16, corresponding to eight phenyl rings with two *ortho*- and two *meta*-fluorine atoms per ring. The area of the *para* peak equals 8 for eight phenyl rings with one *para*-fluorine atom per ring. Even though integration was difficult because of peak overlap, reasonable area ratios were determined for the *ortho*-fluorine peaks with a:b:c = 4:8:4 and the *para* fluorine peaks with a:b:c = 2:4:2. This is consistent with the *cis* geometry as three environments in a 2:4:2 ratio are expected, two OR_f groups bridging Na_3 faces, four OR_f groups bridging Na_2Bi faces, and two OR_f groups bridging $NaBi_2$ faces:

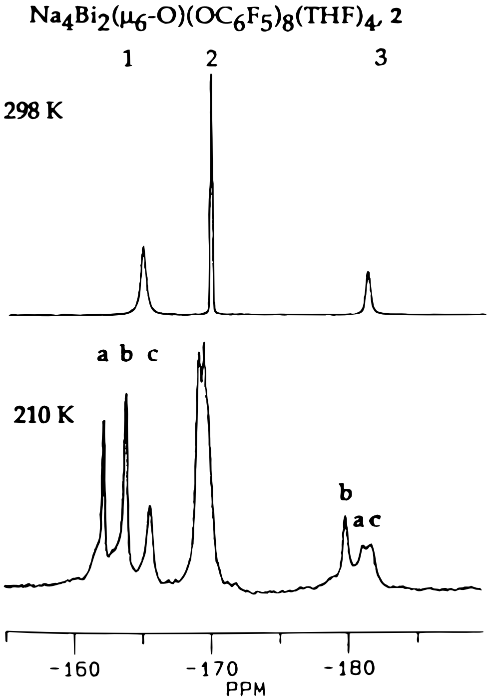
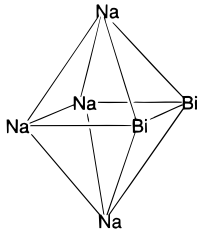


Figure 5. Variable-temperature ^{19}F NMR spectrum of compound **2**.



For a *trans* arrangement of the bismuth atoms, all aryloxide ligands would be expected to be equivalent.

Upon cooling of the sample to 190 K (see Supporting Information), further splitting occurs. This is probably due to slowing of the rotation of the OR_f rings such that F atoms on opposite sides of the rings become inequivalent. The spectrum, however, could not be fully assigned, and freezing of the sample precluded further measurements.

Conclusions

Reactions of sodium pentafluorophenoxide with bismuth chloride and aryloxide complexes lead to oxide-containing bismuth aryloxide complexes, some of which also retain sodium ions tightly bound by interaction with the O and F atoms of the pentafluorophenoxide groups. Careful stoichiometric control can lead to simple Lewis acid/base interactions as evidenced by the formation of compound **1**. The oxide ligand formation in **2** is now understood to arise *via* R_fOR_f elimination rather than hydrolysis.

The bismuth atoms in these compounds are highly Lewis acidic and, given the bridging capabilities of the pentafluorophenoxide group, readily form clusters and oligomeric

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(25) Mehrotra, R. C.; Singh, A.; Sogani, S. *Chem. Rev.* **1994**, *94*, 1643.
(26) Hoppe, S.; Whitmire, K. H. Unpublished results.

structures in the solid state. Solvent molecules are very often found attached to the bismuth atoms, especially when electron-withdrawing ligands like pentafluorophenoxide increase the Lewis acidity at the bismuth or sterically less demanding ligands are attached to the bismuth. The most common bismuth atom coordination geometries observed are the distorted square pyramid and pentagonal bipyramid. The lone pairs of electrons on bismuth atoms in these molecules are apparently stereochemically active, although this is not always the case for bismuth coordination compounds.[27] The bismuth aryloxide complexes are highly fluxional in solution, due in large part to the ability of the aryloxides to adopt μ_2- and μ_3-bridging environments.

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Supporting Information Available: Variable-temperature ^{19}F NMR spectra and computer-generated thermal ellipsoid plots (50% probability level) of **1** and **2** with complete atom labeling schemes (6 pages). X-ray crystallographic files, in CIF format, for complexes **1** and **2** are available on the Internet only. Ordering and access information is given on any current masthead page.

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(27) Whitmire, K. H. Bismuth: Inorganic Chemistry. In *Encyclopedia of Inorganic Chemistry*; King, R. B., Ed.; John Wiley Publishers: New York, 1994; Vol. 1, pp 280−291.