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Hydrothermal Synthesis of Two Cationic Bismuthate Clusters: An Alkylenedisulfonate Bridged Hexamer, $[Bi_6O_4(OH)_4(H_2O)_2][(CH_2)_2(SO_3)_2]_3$ and a Rare Nonamer Templated by Triflate, $[Bi_9O_8(OH)_6][CF_3SO_3]_5$

David L. Rogow,[†] Honghan Fei,[†] Daniel P. Brennan,[†] Mariko Ikehata,[†] Peter Y. Zavalij,[‡] Allen G. Oliver,[†] and Scott R. J. Oliver*[,†]

[†]*Department of Chemistry and Biochemistry, University of California, Santa Cruz, 1156 High Street, Santa Cruz, California 95064, and* [‡]*Department of Chemistry and Biochemistry, University of Maryland, College Park, Maryland 20742*

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This paper reports the synthesis, characterization, and application of two cationic bismuthate clusters by anion templating. The compounds were synthesized under mild hydrothermal treatment and characterized by powder and single-crystal X-ray diffraction, infrared spectroscopy, and thermogravimetric analysis. The first material consists of a cationic hexanuclear bismuthate cluster octahedral in geometry and linked by 1,2-ethanedisulfonate molecules. This structure is thermally stable to about 235 °C. In the second compound, discrete cationic nonanuclear bismuthate clusters interact electrostatically with trifluoromethanesulfonate anions to pack into a nearly layered assembly. The material undergoes a transformation to Bi_2O_3 upon loss of the triflate groups at about 385 °C. Both materials demonstrate the use of sulfonate groups for the anion-directed assembly of these rare cationic inorganic structures. The application of the 3D octahedral bismuth cluster material toward acidic heterogeneous catalysis is also reported.

Introduction

A major goal of our research has been the synthesis of cationic three-dimensional (3D) inorganic materials for anion-based applications such as anion exchange and heterogeneous catalysis.[1] The two-dimensional (2D) cationic materials $Pb_3F_5\cdot NO_3$, $[Sb_4O_4(OH)_2][C_2H_4(SO_3)_2]\cdot H_2O$, and $Pb_{4.5}F_8\cdot ClO_4$ reported previously by this group represent our first major steps toward achieving this goal.[2-4] Because of the success with antimony and lead-based materials, a logical extension for creating cationic inorganic materials was to utilize other metal centers with the inert pair effect. The naturally occurring francisite[5] is a 2D mixed metal (Cu/Bi and SeO_3) cationic oxychalcogenide with the inert pair of the selenium pointing to the chloride ions that are locked inside the channels. We therefore extended our studies to bismuth for the formation of higher dimensionality cationic frameworks.

The extensively studied hydrolysis behavior of Bi^{3+} makes it a particularly desirable system for hydrothermal studies.[6] The existence of polyoxo Bi_n clusters with $n = 2$ to 9 has been supported by solution NMR evidence,[7-9] but only octahedral Bi_6 oxocations and a single case of a polyoxo Bi_9 cluster have been characterized crystallographically.[10] In the case of the only nonanuclear report, the cluster is synthesized by base hydrolysis of $BiO(ClO_4)$, with ClO_4^- anions directing cluster formation and providing charge balance.[10] By understanding the conditions favorable for the formation of larger clusters, it is possible that infinitely extended cationic bismuthate materials can be synthesized. While not nearly as well explored as the cluster cations, the presence of higher dimensionality cationic bismuthate features such as a one-dimensional (1D) ribbon[11] and a 2D layer[12-14] support the

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*To whom correspondence should be addressed. E-mail: soliver@chemistry.ucsc.edu. Fax: (831) 459-2935. Phone: (831) 459-5448.

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Table 1. Crystallographic Data Collection and Refinement Statistics for SLUG-9 and SLUG-16

	SLUG-9	SLUG-16
empirical formula	$C_6H_{12}Bi_6O_{28}S_6$	$C_5Bi_9F_{15}O_{29}S_5$
formula weight ($g \cdot mol^{-1}$)	1978.40	2850.17
crystal size (mm^3)	0.340 × 0.230 × 0.170	0.310 × 0.145 × 0.015
crystal system	monoclinic	monoclinic
space group	$P2_1$	$C2/c$
crystal color, habit	colorless, block	colorless, plate
a (Å)	12.561(1)	17.463(6)
b (Å)	9.462(1)	10.114(4)
c (Å)	13.727(2)	23.924(9)
β (deg)	114.062(1)	99.665(7)
volume (Å^3)	1489.6(3)	4166(3)
Z	2	4
D_c ($Mg \cdot m^3$)	4.411	4.545
μ (mm^{-1})	35.847	38.279
$F(000)$ (e^-)	1732	4896
θ range (deg)	1.78 to 28.64	2.37 to 28.28
index ranges	$-16 \leq h \leq 6$ $-12 \leq k \leq 12$ $-18 \leq l \leq 18$	$-23 \leq h \leq 23$ $-13 \leq k \leq 13$ $-31 \leq l \leq 31$
reflections collected	16758	23984
independent reflections	7425	5161
completeness to $\theta = 28.64$ (%)	98.3	99.3
absorption correction type	empirical	empirical
min. and max. transmission	0.51 and 1.00	0.067 and 0.563
data/restraints/parameters	7425/205/416	5161/105/325
goodness of fit on F^2	1.074	1.028
R_1 [$I > 2\sigma(I)$]	0.0286	0.0382
wR_2 (all data)	0.0716	0.0596
largest diff. peak and hole ($e^-/Å^3$)	2.348 and −2.420	2.335 and −1.248

potential of Bi^{3+} as the metal center for 3D cationic inorganic materials.

The major drawback in applying our nitrate templating strategy that was successful for $Pb_3F_5(NO_3)$ to Bi-based systems concerns their tendency to form oxynitrates in the presence of the nitrate ion. Other non-coordinating anions such as BF_4^- and PF_6^- do not survive under hydrothermal conditions. For these reasons, it was necessary to explore other possible anion templating species for the growth of a cationic material. The weakly coordinating sulfonate anions provided a logical choice for a non-coordinating species that would direct the structure without ligating the metal centers, as observed for Sb.[3] Sulfonate groups can, however, coordinate directly to certain metals such as silver, barium, and lead.[15,16] The use of trifluoromethanesulfonate as a counteranion for inorganic complexes is well-known in the literature.[17,18]

We describe here the synthesis and solid state characterization of the first organosulfonate-bridged hexabismuth cluster $[Bi_6O_4(OH)_4(H_2O)_2][(CH_2)_2(SO_3)_2]_3$ and a sulfonate-templated nonabismuth polyoxocation cluster, $[Bi_9O_8(OH)_6][CF_3SO_3]_5$, only the second crystal structure of a Bi cluster of this nuclearity reported (Table 1). In our preparation, hydrothermal treatment of Bi_2O_3 in the presence of trifluoromethanesulfonic (triflic) acid produces the nonabismuth cluster arranged in layers with interlamellar triflate groups. While this structure decomposes under reflux, the octahedral bismuth cluster material is stable and displays activity toward acid catalyzed ketone protection. Cationic organotin clusters have been used to increase the catalytic activity of neutral organotin clusters toward Lewis acidic alcohol acetylation reactions.[19] The tin-oxo clusters were discrete clusters and used as homogeneous catalysts, in contrast to the organosulfonate bismuth-oxo cluster described here which behaves as a reusable, easily recoverable heterogeneous catalyst.

Experimental Section

Synthesis. $[Bi_6O_4(OH)_4(H_2O)_2][(CH_2)_2(SO_3)_2]_3$. $[Bi_6O_4(OH)_4(H_2O)_2][(CH_2)_2(SO_3)_2]_3$ (which we denote SLUG-9, for University of California, Santa Cruz, Structure No. 9) was synthesized hydrothermally. Bismuth(III) oxide (Acros, 99.9%), 1,2-ethanedisulfonic acid (TCI America, 95%), and deionized water in a molar ratio of 1:4:400, respectively, were scaled to 15.3 mL and added to a 23 mL Teflon lined stainless steel autoclave (Parr Instrument Company). The autoclave was heated at 175 °C for 2 days, then allowed to cool to room temperature before filtering and rinsing the crystals with deionized water. The pH increased slightly from 1.54 before the reaction to 1.71 after opening the autoclave. The average yield was 1.33 g (90% based on Bi_2O_3).

$[Bi_9O_8(OH)_6][CF_3SO_3]_5$. $[Bi_9O_8(OH)_6][CF_3SO_3]_5$ (denoted SLUG-16) was synthesized as above. Bismuth(III) oxide, trifluoromethanesulfonic acid (Acros, 99%), and deionized water in a molar ratio of 1:2:400 were scaled to 15.3 mL. The yellow suspension was allowed to stir for ~10 min, after which time the mixture appeared slightly more opaque, with a milky consistency. The pH of the reaction mixture was 0.9. The pH was adjusted to ~3.1 by the dropwise addition of concentrated aqueous ammonia (NH_4OH, Fisher, 29.7%, ACS reagent grade) before it was transferred to a 23 mL Parr autoclave. The autoclave was sealed and heated at 175 °C for 2 days, after which time it was removed from the oven and allowed to cool to room temperature. When the autoclave was opened, a crop of crystals was visible at the bottom of the Teflon liner. The pH of the mother liquor was 2.8. The crystals were recovered by vacuum filtration, rinsed with deionized water, and allowed to air-dry overnight (average yield: 1.17 g, 89% based on Bi_2O_3).

Characterization Methods. Instrumental Details. Powder X-ray diffraction (PXRD) data were recorded using a Rigaku MiniFlex II Plus powder diffractometer with Cu−Kα radiation ($\lambda = 1.5418$ Å). The irradiated area of the sample was a constant 4 mm^2 by a variable slit mechanism. Thermogravimetric Analysis (TGA) was performed using a TGA 2050 (TA Instruments). The samples were heated on a platinum pan from 25 to 1000 °C at a rate of 15 °C per minute under a nitrogen gas purge. Fourier Transform Infrared Spectroscopy (FTIR) was carried out with a Perkin-Elmer Spectrum One spectrophotometer. Samples were prepared as KBr pellets. ^1H NMR spectra were measured on a Varian Unity Inova spectrometer equipped with a 600 MHz HCN 5 mm cold probe system. Spectra were taken in deuterated chloroform.

X-ray Crystal Structure Determination. Single-crystal data for SLUG-9 were recorded at 150(2) K using a Bruker SMART APEX II CCD area detector X-ray diffractometer using graphite monochromated Mo−Kα radiation ($\lambda = 0.71073$ Å) from a fine-focus sealed tube operated at 50 kV and 30 mA. Single-crystal data for SLUG-16 were measured at 299(2) K on a three-circle diffractometer system equipped with a Bruker SMART APEX CCD area detector using a graphite monochromator and a Mo−Kα fine-focus sealed tube ($\lambda = 0.71073$ Å) operated at

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50 kV and 30 mA. The structures were solved by direct methods and expanded routinely. The models were refined by full-matrix least-squares analysis of F^2 against all reflections. All non-hydrogen atoms were refined with anisotropic thermal displacement parameters. Thermal parameters for the hydrogen atoms were tied to the isotropic thermal parameter of the atom to which they are bonded. Programs used were APEX-II v2.1.4,[20] SHELXTL v6.14,[21] and Diamond v3.1e.[22] Crystallographic data collection and refinement parameters are listed in Table 1.

Catalytic Studies. In a typical reaction, 0.05 g (25 μmol) of SLUG-9 was placed in a 100 mL round-bottom flask along with 15.0 mL (168 mmol) of 2-butanone (methylethyl ketone, MEK, Acros 99+ %, extra pure) and 9.35 mL (168 mmol) of ethylene glycol (Acros, 99+ %). Other carbonyl substrates used were acetone (Fisher, ACS reagent grade, 99.7%), benzaldehyde (Aldrich, ≥ 99%), 2-pentanone (TCI America, min. 97%), and acetaldehyde (Acros, 99%). This mixture was refluxed under Dean−Stark conditions to remove water product. After a specified amount of reflux time, the reaction mixture was allowed to cool to room temperature, and the catalyst was removed by suction filtration. PXRD patterns of the solid were collected as well as NMR spectra of the filtrate to determine the robustness of the catalyst and percent yield of the reaction, respectively. ^{1}H NMR peaks used to calculate the percent yields were those of ethylene glycol (δ 3.726, d or t, 4H) and the corresponding peaks in the product: 2-ethyl-2-methyl-1,3-dioxolane (δ 3.88−3.97, m, 4H), 2,2-dimethyl-1,3-dioxolane (δ 3.912, s, 4H), 2-methyl-1,3-dioxolane (δ 3.83−3.92, m, 4H), 2-phenyl-1,3-dioxolane (δ 4.00−4.20, m, 4H) and 2-methyl-2-propyl-1,3-dioxolane (δ 3.89−3.98, m, 4H).

Results and Discussion

SLUG-9. The synthesis of $[Bi_6O_4(OH)_4(H_2O)_2][(CH_2)_2(SO_3)_2]_3$ is straightforward and results in a pure phase of the structure with high yield (90%). The Bi_2O_3 reagent does not dissolve in the water before the autoclave is heated, but the reaction conditions are sufficient to dissolve the reagent. The resulting colorless crystals are large in size (average ca. 400 × 400 × 200 μm^3) and block shaped. The complex consists of an octahedral core of Bi atoms. Each face of the octahedron is bridged by one oxygen atom (μ_3-oxo). These bridging oxygens have shorter than usual bond distances to the Bi atoms [ranging from 2.119(6) to 2.505(6) Å, (Supporting Information, Table S1); mean Bi−O distance = 2.424 ± 0.245 Å: CSD].[23] Two of the bismuth atoms have a terminal oxygen [O(9) and O(10)], which are most likely water molecules. Hydrogen atoms could not be observed, however, in the Fourier difference electron density maps because of the high electron density of the six bismuth atoms. The bond distances are 2.618(7) and 2.671(7) Å for Bi(2)−O(9) and Bi(5)−O(10), respectively (Supporting Information, Table S1). These distances are longer than the average Bi−O bond (~ 2.5 Å: CSD), indicating that they may be coordinated water molecules. Further evidence for water molecules is corroborated by the FTIR spectrum (3300 to 3500 cm^{-1}, Supporting Information, Figure S1). Bound hydroxyl is also evident in the infrared spectrum.

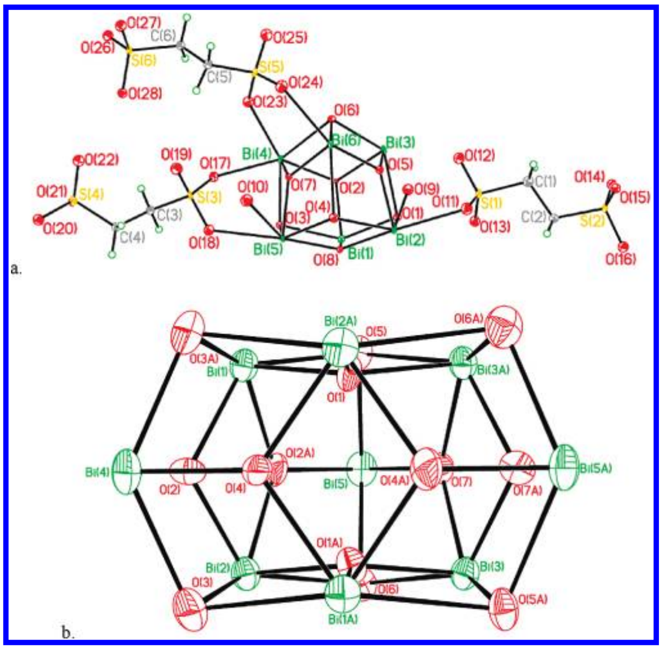

Figure 1. ORTEP diagrams of SLUG-9 (a) and SLUG-16 (b; triflate anions omitted for clarity). Thermal ellipsoids are calculated at 50% probability.

Four of the cluster capping oxygen atoms are likely protonated. The distances of these oxygen atoms from the plane of the three Bi atoms which they bridge are as follows: O(1) = 1.101(7) Å, O(3) = 1.106(7) Å, O(4) = 1.108(7) Å, and O(6) = 1.127(6) Å. The rest of the cluster oxygens are likely unprotonated as their distances from the planes of the metals that they bridge are much smaller than the four hydroxyl groups: O(2) = 0.319(6) Å, O(5) = 0.386(7) Å, O(7) = 0.356(7) Å, and O(8) = 0.465(6) Å. For charge balance, four cluster hydroxyls would give the entire cluster a net charge of +6. The three disulfonate groups balance this charge and link the clusters with Bi−O−S covalent bonds as well as two long electrostatic contacts [Bi(3)−O(12) = 2.712(7) and Bi(1)−O(26)A = 2.751(7) Å] (Figure 1a). The bismuth cluster is coordinated by two oxygen atoms on each end of the ethanedisulfonate molecules. The third ethanedisulfonate coordinates by only one oxygen atom, Bi(2) to O(11). The organosulfonate groups cross-link to adjacent Bi octahedra resulting in a 3D metal−organic network. The clusters are discrete from each other and arranged in an alternating manner, nearly resembling cubic close packed (Figure 2a,b). The experimental powder pattern of SLUG-9 matches closely to the theoretical pattern generated by the structure solution (Figure 3).

SLUG-16. The entire product after recovery was a crop of colorless plates (average size ca. 450 × 400 × 20 μm^3). The product was synthesized in nearly 90% yield, a significant improvement over the 70% yield reported for the first nonabismuth cluster compound.[10] After the product had dried, a small amount of sample was used for PXRD analysis. The resultant PXRD pattern (Figure 3) could not be matched to any known phase. A suitable single crystal was selected for SCXRD, and the structure solution confirmed that the product is a new crystal structure. The close agreement between the experimental PXRD pattern and the pattern projected from single

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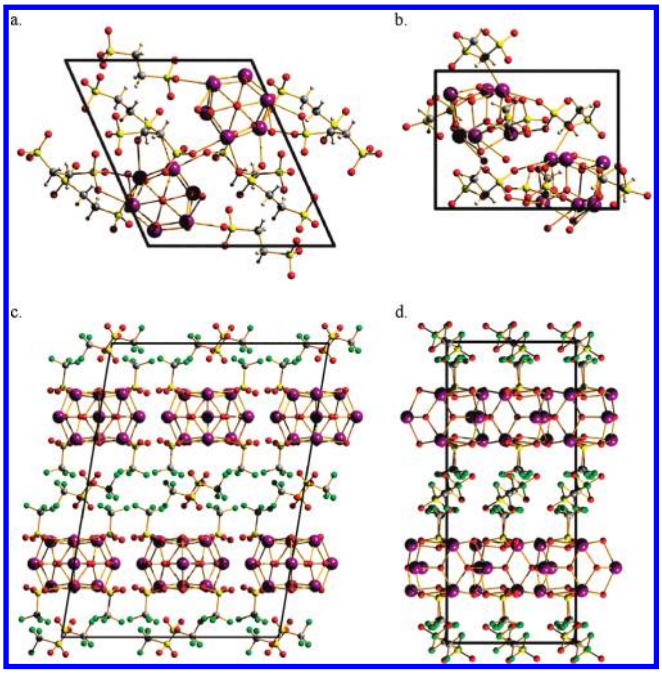

Figure 2. Crystallographic images of SLUG-9 in the *a-c* (a) and *b-c* (b) planes, and SLUG-16 in the *a-c* (c) and *b-c* (d) planes (bismuth, violet; oxygen, red; sulfur, yellow; fluorine, green; carbon, dark gray; and hydrogen, light gray).

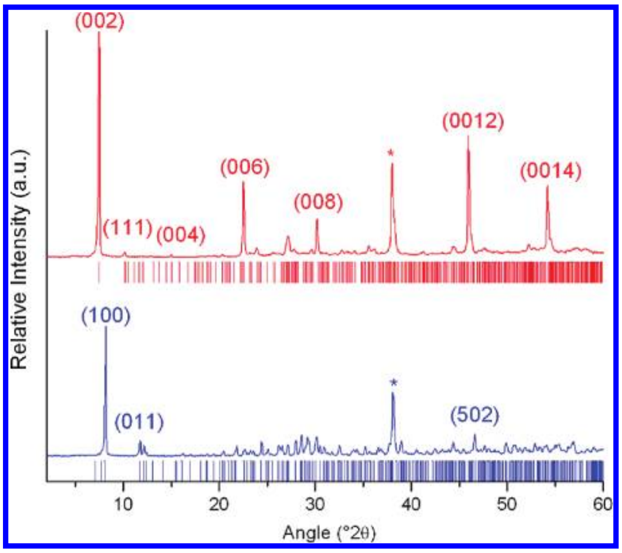

Figure 3. PXRD patterns of SLUG-9 (bottom, blue) and SLUG-16 (top, red). Theoretical patterns are shown below as bars (asterisk: peak from the aluminum sample holder).

crystal data indicates that the as-synthesized product is a pure phase (Figure 3). The SLUG-16 structure is not stable under reflux conditions and was therefore not pursued as a possible heterogeneous catalyst.

The structure is made up of discrete nonabismuth cluster cations charge-balanced by trifluoromethanesulfonate anions. Figure 1b shows the Oak Ridge Thermal Ellipsoid Plot (ORTEP) diagram and atom labeling scheme for the nonabismuth structure (SLUG-16). The cluster is composed of nine Bi atoms. Bi(4), Bi(4)A, Bi(5), and Bi(5)A are four coordinate in a slightly distorted square pyramidal geometry where the Bi atom is at the vertice (Figure 1b, Supporting Information, Table S2). The rest of the Bi atoms are each coordinated to 5 O atoms within the cluster to define a D_{3h} trigonal bipyrimidal geometry around each metal center. The overall formula of the cationic cluster is $[Bi_9O_8(OH)_6]^{5+}$. The clusters are arranged into sheets with long electrostatic contacts between three cluster bismuth atoms on the corners of the cluster and all three oxygen atoms of the trifluoromethanesulfonate anions. The through space distances range from 2.987(7) Å between Bi(1) and O(13), to 4.317(7) Å between Bi(1) and O(11). These distances are beyond the accepted range of covalent Bi−O bonds. There are also triflate anions between the clusters that are not close enough to interact with the clusters and remain in the periphery (Figure 2c,d).

All O atoms are triply bridging (μ_3-oxo), with each Bi center linking to the eight other Bi atoms through Bi−O−Bi bonding. The H atoms could not be located from SCXRD data, but their presence, necessary for the charge balance of the compound, is confirmed by the occurrence of two sharp peaks in the IR spectrum (3600 and 3669 cm^{-1}, Supporting Information, Figure S1), indicating the presence of bound hydroxyl groups. Furthermore, the nonabismuth cluster characterized previously by Thurston et al. contained 6 μ_3 cluster hydroxyls. These were assigned by necessity of charge balance as well as the distance of the oxygen atoms above the plane of the three Bi atoms to which they are bonded.[10] The average above-plane distance of the μ_3 cluster hydroxyls [O(3), O(5), O(6), O(3)A, O(5)A and O(6)A], is 1.207(7) Å. The unprotonated μ_3-oxos [O(2), O(4), O(7), O(2)A, O(4)A, and O(7)A] lie an average of 0.368(6) Å above the plane of the three Bi atoms to which they bridge. The other two unprotonated μ_3 oxygens [O(1) and O(1)A] actually lie 0.234(7) Å concave with respect to the cluster.

FTIR spectra for both structures are shown in Supporting Information, Figure S1. Strong peaks for sulfonate stretching between about 1100 and 1300 cm^{-1} are observed for SLUG-9. Peaks corresponding to the trifluoromethane (CF_3) group in SLUG-16 are observed between 1100 and 1350 cm^{-1}, in the stretching region known for perfluorinated sulfonate.[24] The sharp absorbance peaks in both spectra between 1000 and 1050 cm^{-1} are also assigned to the sulfonate groups. A broad adsorbed water peak is observed centered at 3436 cm^{-1} for SLUG-16. Sharp bound hydroxyl stretching peaks appear at 3600 and 3669 cm^{-1} for SLUG-16, and at 3445 and 3499 cm^{-1} for SLUG-9. A somewhat broad and weak bound water stretch appears at 3233 cm^{-1} in the SLUG-9 spectrum. Sharp peaks are observed as a doublet in SLUG-9 at 1603 and 1659 cm^{-1} and are due to lattice H_2O scissoring.[25,26] The presence of hydroxyl and water in SLUG-9 confirms the structural assignment based on charge balance and oxygen distances above the plane of the three Bi atoms they bridge. The sharp peak at

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1630 cm^{-1} in SLUG-16 is most likely due to physisorbed water on the surface of the sample, as observed in the TGA trace below 50 °C (Supporting Information, Figure S2). This peak appears as a similarly shaped singlet in the spectrum of liquid H_2O.[26] The CF_3 stretching peak is very strong and overshadows the alkylene peaks of the sulfonate. In SLUG-9, sharp peaks at 741, 761 are from the $-CH_2-$ group, and the absorbance at 1416 cm^{-1} is assigned to $-CH_2-S$.

Thermal Characterization. Thermogravimetric analysis was performed to observe the thermal behavior of the clusters, including possible linkage into higher dimensionality. The TGA trace of SLUG-9 indicates that the structure is thermally stable until about 235 °C, where a small loss of weight is followed by a plateau until about 350 °C (blue, Supporting Information, Figure S2). After this first weight loss step, about 96.5 wt % of the structure remains intact. This corresponds closely to 2 hydroxyl groups and two water molecules (3.5 wt % theoretical). Ex-situ heating to 250 °C and subsequent PXRD revealed that the structure remains intact but undergoes a slight contraction in the spaces between the clusters. The water molecules are lost, and hydroxides are most likely being evolved by intermolecular condensation. The second, major weight loss step with onset at about 350 °C leaves 68 wt % of the original structure by 450 °C. This likely corresponds to loss of the three ethanedisulfonate molecules in the structure (28.4 wt % theoretical). A slight weight gain is observed in the temperature region of 400 to 1000 °C, possibly a result of nitrogen uptake by the unsaturated bismuth atoms. Ex-situ heating to 800 °C under a nitrogen atmosphere gave bismuth metal (ICDD PDF # 44−1246). The final product obtained after ex-situ heating to 1000 °C under ambient atmosphere was also bismuth metal (ICDD PDF # 44−1246).

The TGA trace of SLUG-16 (red, Supporting Information, Figure S2) displays a small weight loss of ~0.5 wt % below 50 °C because of removal of adsorbed water on the surface of the solid. The sample plateaus in the region from 50 to 350 °C. There is a small weight loss of 1.8% between 325 and 375 °C likely because of the loss of 3 hydroxyls to intermolecular condensation (1.8 wt % theoretical). The major weight loss step occurs over the range of about 385 to 425 °C and then slows considerably until the end of the measurement range. The rate of weight loss decreases and almost plateaus at about 600 °C where about 77% of the original weight remains. The loss is likely due to the removal of 79% of the trifluoromethanesulfonate anions (theoretical 26.1% for all triflates). The product obtained after heating to 600 °C is Bi_2O_3 (ICDD PDF # 41−1449). After ex-situ heating to 1000 °C in ambient atmosphere, the final product is bismuth metal (ICDD PDF # 44−1246).

Catalytic Reaction of SLUG-9. The SLUG-9 structure showed significant activity as an acidic catalyst toward formation of a cyclic ketal protecting group in the reaction between ketones or aldehydes and ethylene glycol (Scheme 1). This reaction is useful in organic synthesis for protecting carbonyl groups, especially the cyclic ketal formation reaction demonstrated here.[27,28] In our case, no harmful solvents are needed, only the reactants themselves, and thus the reaction can be considered "green". Also, the catalyst can be used as prepared with no activation or pretreatment required. The reaction using benzaldehyde as the carbonyl substrate goes to 96% completion in 3 h, as confirmed by ^1H NMR (Table 2 and Supporting Information, Figure S3).

Scheme 1. Ketal Formation Reaction between Carbonyl Substrate and Ethylene Glycol

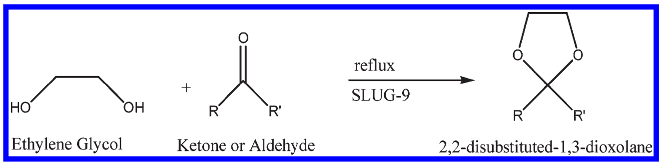

Table 2. Percent Yields for the Different Ketal Formation Substrates

catalyst	carbonyl substrate	reaction time (hours)	yield (%)
SLUG-9	acetone	6	30
SLUG-9	2-butanone	6	54
SLUG-9	2-pentanone	3	86
SLUG-9	benzaldehyde	3	96
SLUG-9	acetaldehyde	4	10
Bi_2O_3	acetone	6	< 0.1
Bi_2O_3	2-butanone	6	< 0.1
Bi_2O_3	2-pentanone	3	< 0.1
Bi_2O_3	benzaldehyde	3	81

A typical homogeneous iodine catalyst reported by Banik et al. shows ketal formation reactions going to 90% in 16 h.[28] In addition, the catalyst reported here is a heterogeneous catalyst. Solid metal phosphonates of Sn, Ti, and Zr show reaction yields as high as 90% in 3 h.[27] Although SLUG-9 remains intact after the reaction, the crystallinity is reduced slightly after the catalytic reaction as observed by decreased intensity of the majority peaks in the PXRD pattern (Supporting Information, Figure S8). Control reactions were conducted using only Bi_2O_3 added to the reactants. Very little products were formed (< 0.1% with MEK substrate, Table 2) using the starting material Bi_2O_3. A reaction was also run for 3 h, after which the solid catalyst was filtered off and then the reaction was run for 3 more hours. No further product formation occurred after the catalyst was removed, proving that (i) turnover requires the presence of the solid catalyst and (ii) no species were being leached from the solid that could be active homogenously. Furthermore, no evidence of ethanedisulfonate was found in the ^1H NMR spectra of any of the products. The catalyst is reusable for at least two more cycles with little diminished yield (average ~5%).

It is possible that the hydroxyl groups are responsible for the catalytic acivity. Bi(III) is Lewis acidic; however, it is bonded to the sulfonate oxygen atoms and may be coordinatively inaccessible. Organosulfonate ligands, however, are known to be "flexible" in that they may adjust their coordination mode to accommodate structural changes.[29] In either case, the reaction is occurring at

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[27] Patel, S. M.; Chudasama, U. V.; Ganeshpure, P. A. *J. Mol. Catal. A: Chem.* **2003**, *194*(1−2), 267–271.

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the surface of the material, inferred from the observation that the bulkier substrates such as 2-pentanone and benzaldehyde showed the greatest percent conversion. Indeed, there is no real void space inside the structure (no solvent accessible void space, calculated by PLATON[30]) so reactant diffusion into the material can be ruled out. The substrates that have the most electron delocalization ability gave the highest percent yields, possibly because of the stabilization of the oxocation intermediate. Ketal formation in general requires protic acids; therefore, we would conclude that the cluster hydroxyl groups are responsible for the catalytic activity.

Conclusions

In summary, two cationic bismuthate clusters have been synthesized by anion templating. Infrared spectroscopy and thermogravimetric analysis confirms the presence of hydroxyl groups on both clusters and coordinated water on the octahedral cluster. The trifluoromethansulfonate-templated nonabismuth structure displays greater thermal stability, but does not survive under reflux conditions. The hexabismuth octahedral cluster bridged by alkylenedisulfonate shows significant activity as an acidic heterogeneous catalyst toward cyclic ketal formation without the need for activation. We believe that higher dimensionality cationic bismuthate materials are possible using suitably shaped anionic sulfonate templates under favorable conditions of reaction time, temperature, and pH.

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Supporting Information Available: Crystallographic information files (.cif) containing fractional atomic coordinates, bond lengths and angles and refinement parameters, Infrared spectra, TGA traces, proton NMR spectra of the catalytic reaction products and PXRD of the catalyst after reaction and tables of bond lengths and angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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