

Toward a General Strategy for the Synthesis of Heterobimetallic Coordination Complexes for Use as Precursors to Metal Oxide Materials: Synthesis, Characterization, and Thermal Decomposition of $\text{Bi}_2(\text{Hsal})_6 \cdot \text{M}(\text{Acac})_3$ ($\text{M} = \text{Al}, \text{Co}, \text{V}, \text{Fe}, \text{Cr}$)

John H. Thurston, Daniel Trahan, Teyeb Ould-Ely, and Kenton H. Whitmire*

Department of Chemistry MS60, Rice University, 6100 Main Street, Houston, Texas 77005-1892

Received November 6, 2003

Bismuth(III) salicylate, $[\text{Bi}(\text{Hsal})_3]_n$, reacts readily with the trivalent metal β -diketonate compounds $\text{M}(\text{acac})_3$ (acac = acetylacetonate; $\text{M} = \text{Al}, \text{V}, \text{Cr}, \text{Fe}, \text{Co}$) to produce trinuclear coordination complexes of the general formula $\text{Bi}_2(\text{Hsal})_6 \cdot \text{M}(\text{acac})_3$ ($\text{M} = \text{Al}, \text{V}, \text{Cr}, \text{Fe}, \text{Co}$) in 60–90% yields. Spectroscopic and single crystal X-ray diffraction experiments indicate that these complexes possess an unusual asymmetric nested structure in both solution and solid state. Upon standing in dichloromethane solution, $\text{Bi}_2(\text{Hsal})_6 \cdot \text{Co}(\text{acac})_3$ eliminates $\text{Bi}(\text{Hsal})_3$ to give the 1:1 adduct $\text{Bi}(\text{Hsal})_3 \cdot \text{Co}(\text{acac})_3$. The 2:1 heterobimetallic molecular compounds undergo facile thermal decomposition on heating in air to 475 °C to produce heterometallic oxide materials, which upon annealing for 2 h at 700 °C form crystalline oxide materials. The synthetic approach detailed here represents a unique, general approach to the formation of heterobimetallic bismuth-based coordination complexes via the coordination of $\text{M}(\text{acac})_3$ complexes to bismuth(III) salicylate.

Introduction

Decomposition of discrete, well-defined bi- or multi-metallic compounds as single-source precursors (SSMPs) has been shown to produce crystalline oxide phases under significantly reduced annealing conditions and in higher purity than what is achievable by traditional solid-state approaches.^{1–10} The mild conditions required for the formation of crystalline oxides from molecular complexes results in the ability to produce and isolate metastable phases and allow for the formation of materials with unusual or desirable morphologies.^{2,10,11} The ease of crystallization of oxides produced from SSMPs has been attributed to the direct atomic ordering

of the two or more metal species with respect to one another in the molecular lattice. Furthermore, these molecular precursor complexes frequently display other attractive characteristics including high solubility in common organic solvents, increased hydrolytic stability, ease of purification, and, in some cases, volatility. This combination of physical and chemical properties generally allows SSMPs to be used in conjunction with well-established techniques for the deposition of thin or thick oxide films such as metal-organic decomposition (MOD), metal-organic chemical vapor deposition (MOCVD), and sol–gel techniques.⁴

Bimetallic and multimetallic bismuth oxides have been investigated for a host of applications including solid-state electrolytes,¹² fast-ion conducting ceramics,¹³ oxidation catalysts,¹⁴ high T_c superconductors,^{15,16} and novel magnetic and luminescent materials.^{17–20} Consequently, routes to the

* To whom correspondence should be addressed. E-mail: whitmir@rice.edu. Phone: 713-348-5650. Fax: 713-348-5155.

- (1) Kessler, V. G. *Chem. Commun.* **2003**, *11*, 1213–1222.
- (2) Veith, M. J. *Chem. Soc., Dalton Trans.* **2002**, *12*, 2405–2412.
- (3) Hubert-Pfaltzgraf, L. G. *New J. Chem.* **1995**, *19*, 727–750.
- (4) Hubert-Pfaltzgraf, L. G. *Inorg. Chem. Commun.* **2003**, *6*, 102–120.
- (5) Hubert-Pfaltzgraf, L. G. *Crit. Rev. Opt. Sci. Technol.* **1997**, *CR68*, 3–24.
- (6) Hubert-Pfaltzgraf, L. G. *Korean J. Ceram.* **2000**, *6*, 370–379.
- (7) Hubert-Pfaltzgraf, L. G.; Daniele, S.; Boulmaaz, S.; Papiernik, R. *Mater. Res. Soc. Symp. Proc.* **1994**, *346*, 21–27.
- (8) Hubert-Pfaltzgraf, L. G. *Polyhedron* **1994**, *13*, 1181–1195.
- (9) Thurston, J. H.; Whitmire, K. H. *Inorg. Chem.* **2002**, *41*, 4194–4205.
- (10) Thurston, J. H.; Whitmire, K. H. *Inorg. Chem.* **2003**, *42*, 2014–2023.
- (11) Gopalakrishnan, J. *Chem. Mater.* **1995**, *7*, 1265–75.

- (12) Zha, S.; Cheng, J.; Liu, Y.; Liu, X.; Meng, G. *Solid State Ionics* **2003**, *156*, 197–200.
- (13) Abrahams, I.; Bush, A. J.; Hawkes, G. E.; Nunes, T. *J. Solid State Chem.* **1999**, *147*, 631–636.
- (14) Shido, T.; Okita, G.; Asakura, K.; Iwasawa, Y. *J. Phys. Chem. B* **2000**, *104*, 12263–12268.
- (15) Maeda, H. *Materia* **2001**, *40*, 947–950.
- (16) Maeda, H.; Tanaka, Y.; Fukutomi, M.; Asano, T. *Jpn. J. Appl. Phys.* **1988**, *27*, L209.
- (17) Brixner, L. H. *Mater. Res. Bull.* **1978**, *13*, 563–566.
- (18) Blasse, G.; Ho, O. B. *J. Lumin.* **1980**, *21*, 165–168.

formation of discrete heterobimetallic bismuth-based coordination complexes, including microhydrolysis,²¹ bifunctional ligands,^{9,10} Lewis acid–base adduct formation,²² and ligand-elimination reactions²³ have been reported; however, no single, general synthetic approach route that allows for the systematic introduction of a wide variety of metal species into the bismuth coordination sphere has yet been developed. The development of a synthetic approach to give compounds with a common metal stoichiometry and produce structurally similar compounds independent of the metal species can potentially allow for access to a broad range of bimetallic or multimetallic oxide materials through a single synthetic strategy. We have, therefore, examined the ability of β -diketonate compounds to complex with bismuth salicylate, in part due to their excellent solubility and stability, and because there is very little structural deviation in the series $M(\text{acac})_3$ ($M = \text{Al}, \text{V}, \text{Cr}, \text{Co}, \text{Fe}$). We were particularly interested in targeting bismuth compounds with vanadium and aluminum as these mixed oxides show high oxide-ion conductivity. In particular, the phases BiVO_4 , $\text{Bi}_4\text{V}_2\text{O}_{11}$, and $\text{Bi}_2\text{Al}_4\text{O}_9$ have demonstrated high ionic conductivities.²⁴ Of the two vanadium compounds, $\text{Bi}_4\text{V}_2\text{O}_{11}$ appears to be more stable, and its properties can be tuned by the substitution of vanadium by other transition metals. To this end, we have developed a general method of preparing heterometallic coordination compounds containing bismuth and vanadium or aluminum by treating bismuth(III) salicylate with the appropriate $M(\text{acac})_3$ ($\text{acac} = \text{acetylacetonate}$) complex. In addition to V and Al, we explored several other transition $M(\text{acac})_3$ complexes, which could potentially serve as dopants in the bismuth–vanadium oxide system and establish the generality of the synthetic process. The solid-state structure of the first coordination complex containing both bismuth and aluminum is reported as well as the behavior of these molecular complexes during thermal decomposition in air. These results will be discussed in relation to the thermal decomposition of related complexes and the ability of these new compounds to act as viable molecular precursors for oxide-ion conducting ceramics or novel magnetic materials.

Experimental Section

General. All synthetic reactions were carried out using standard Schlenk or glovebox techniques under an atmosphere of purified nitrogen or argon. Solvents were purified with an appropriate drying reagent under argon and were degassed prior to use.²⁵ The metal complexes $M(\text{acac})_3$ ($M = \text{Al}, \text{V}, \text{Fe}, \text{Co}, \text{and Cr}$) and triphenylbismuth were purchased from Strem Chemical Co. and salicylic

acid from Aldrich Chemical Co. The reagents were used as received. Galbraith Laboratories performed all elemental analyses. Solution-state NMR studies were performed on a Bruker 200 MHz, a Bruker 400 MHz, or a Bruker 500 MHz Avance instrument. The samples were referenced to the protio impurity in the deuterated solvent (^1H), to the solvent signal (^{13}C), or to an external 1 M solution of $\text{Al}(\text{NO}_3)_3$ in D_2O (^{27}Al). Solid-state NMR studies were performed on a Bruker 200 MHz or Bruker 500 MHz Avance instrument and were referenced to glycine (^{13}C) or to a 1 M solution of $\text{Al}(\text{NO}_3)_3$ in D_2O (^{27}Al). Infrared spectra of the complexes were collected on a Thermo-Nicolet 630 FT-IR instrument using ATR methodology with a germanium window. TGA studies were performed on a Sieko DT/TGA 200 instrument in platinum pans under an air atmosphere. Approximately 10 mg of the sample to be studied was heated to 475 °C at a rate of 5 °C min^{-1} . Phase changes that occurred during thermal decomposition of the molecular precursor were monitored by simultaneous differential thermal analysis (DTA). Powder X-ray diffraction studies were performed on a Siemens Diffraktometer using $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). Data were collected on 2θ in the range 20–60° in 0.1° increments at 13 s per frame. Data processing of the powder diffraction spectra and phase identification was accomplished using the program JADE.²⁶ In the case of the solid-state metal oxide products, elemental analyses indicated that no carbon or hydrogen was present under the conditions of the thermolysis within the detection limits of the analysis (<0.5%). These results were in agreement with the mass losses observed during the TGA experiments.

Syntheses. $\text{Bi}_2(\text{Hsal})_6\cdot\text{Al}(\text{acac})_3$. A yellow suspension of bismuth salicylate in toluene was generated from the reaction of triphenylbismuth (0.44 g, 1.0 mmol) with salicylic acid (0.54 g, 4.0 mmol) at 110 °C. The mixture was allowed to cool to room temperature, and then, a clear, colorless solution of $\text{Al}(\text{acac})_3$ in 20 mL of toluene was added by cannula. The resulting clear yellow solution was stirred at room temperature for 15 h. During this time, a white crystalline solid deposited in the flask. After the reaction period, the solid was collected by filtration, washed with toluene (2 × 15 mL) and diethyl ether (1 × 15 mL), and dried in vacuo to give the product as a free flowing powder. The material generated in this fashion invariably cocrystallized with toluene, as reflected by the elemental analyses and by NMR investigations. Allowing the initial yellow bismuth–aluminum solution to stand undisturbed at room temperature for 24 h produced small colorless crystals of the complex appropriate for single crystal X-ray diffraction investigations. Yield: 0.75 g of white microcrystalline solid (94% based on Bi, 0.48 mmol). ^1H NMR (400 MHz, 25 °C, CD_2Cl_2): 7.80 (s, 6H, salH), 7.45 (s, 6H, salH), 6.91 (s, 12H, salH), 5.52 (s, 3H, CH), 2.03 (s, 9H, CH_3), 1.97 (s, 9H, CH_3). ^1H NMR (400 MHz, 25 °C, d_6 -DMSO): 7.72 (s, 6H, salH), 7.38 (s, 6H, salH), 6.83 (s, 12H, salH), 5.51 (s, 3H, CH), 1.87 (s, 18H, CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, 25 °C, CD_2Cl_2): 25.14, 27.10, 90.80, 101.47, 118.12, 119.90, 128.70, 129.51, 131.24, 191.90, 192.03. ^{27}Al NMR (115 MHz, 25 °C, CD_2Cl_2): 0.88. ^{27}Al MQ-MAS NMR (115 MHz, 25 °C, 20 kHz MAS): 1.59, –0.18. FT-IR (ATR, Ge): 1626, 1593, 1582, 1530, 1484, 1434, 1395, 1311, 1292, 1245, 1226, 1161, 1029, 946, 876, 823, 763, 754, 723, 705. Elemental analysis % obsd (% calcd for $\text{AlBi}_2\text{C}_{57}\text{H}_{51}\text{O}_{24}\cdot 0.7\text{C}_7\text{H}_8$): C, 45.59 (45.61); H, 3.64 (3.50).

$\text{Bi}_2(\text{Hsal})_6\cdot\text{Co}(\text{acac})_3$. This compound was prepared in a manner analogous to that for $\text{Bi}_2(\text{Hsal})_6\cdot\text{Al}(\text{acac})_3$, with the substitution of $\text{Co}(\text{acac})_3$ for $\text{Al}(\text{acac})_3$. The resulting green solution was stirred

- (19) Timmermans, C. W. M.; Blasse, G. *J. Solid State Chem.* **1984**, *52*, 222–232.
 (20) Volkov, V. V.; Egorycheva, A. V. *Opt. Mater.* **1996**, *5*, 273–277.
 (21) Parola, S.; Papiernik, R.; Hubert-Pfalzgraf, L. G.; Jagner, S.; Hakanson, M. *J. Chem. Soc., Dalton Trans* **1997**, 4631.
 (22) Thurston, J. H.; Whitmire, K. H. *Chem. Mater.* **2003**, *15*, 4407–16.
 (23) Whitmire, K. H.; Hoppe, S.; Sydora, O.; Jolas, J. L.; Jones, C. M. *Inorg. Chem.* **2000**, *39*, 85–97.
 (24) (a) Watanabe, A.; Das, K. *J. Solid State Chem.* **2002**, *163*, 224–230. (b) Boivin, J.-C. *Int. J. Inorg. Mater.* **2001**, *3*, 1261–1266. (c) Kim, S.-K.; Miyayama, M. *Solid State Ionics* **1997**, *104*, 295–302. (d) Lee, C. K.; West, A. R. *Solid State Ionics* **1996**, *86–88*, 235–239. (e) Thery, O.; Vannier, R. N.; Dion, C.; Abraham, F. *Solid State Ionics* **1996**, *90*, 105–110. (f) Lee, C. K.; Bay, B. H.; West, A. R. *J. Mater. Chem.* **1996**, *6*, 331–5.

- (25) Armarego, W. L. F.; Perry, D. D. *Purification of Laboratory Chemicals*, 4th ed.; Butterworth-Heinemann: Boston, 1996.
 (26) JADE, 2.1 ed.; MDI: Livermore, CA, 1994.

at room temperature for 15 h during which time a pale green powder deposited in the flask. The product was collected by filtration, washed with toluene (2×15 mL) and diethyl ether (1×15 mL), and dried in vacuo to give the product as a free flowing powder. Yield: 0.72 g of green powder (0.94 mmol, 94%). $^{13}\text{C}\{^1\text{H}\}$ NMR (6000 Hz MAS, 50 MHz, 25 °C): 26.3, 28.2, 99.6, 116.4, 118.4, 124.6, 128.9, 130.9, 137.8, 161.0, 179.3, 187.3, 196.4. FT-IR (ATR, Ge): 1627, 1595, 1583, 1570, 1519, 1484, 1434, 1397, 1372, 1311, 1280, 1245, 1227, 1165, 1025, 946, 876, 823, 764, 754, 723, 705. Elemental Analysis % obsd (% calcd for $\text{CoBi}_2\text{C}_{57}\text{H}_{51}\text{O}_{24} \cdot 0.8\text{C}_7\text{H}_8$): C, 45.04 (44.99); H, 3.58 (3.46).

$\text{Bi}_2(\text{Hsal})_6 \cdot \text{Fe}(\text{acac})_3$. This compound was prepared in a manner analogous to that for $\text{Bi}_2(\text{Hsal})_6 \cdot \text{Al}(\text{acac})_3$, with the substitution of $\text{Fe}(\text{acac})_3$ for $\text{Al}(\text{acac})_3$. The resulting deep red solution was stirred at room temperature for 15 h during which time an orange powder deposited in the flask. The product was collected by filtration, washed with toluene (2×15 mL) and diethyl ether (1×15 mL), and dried in vacuo to give the product as a free flowing powder. Yield: 0.82 g of orange powder (0.91 mmol, 91%). FT-IR (ATR, Ge): 1627, 1595, 1583, 1562, 1528, 1484, 1435, 1398, 1364, 1311, 1279, 1246, 1226, 1161, 1027, 936, 876, 823, 764, 754, 729, 705. Elemental analysis % obsd (% calcd for $\text{FeBi}_2\text{C}_{57}\text{H}_{51}\text{O}_{24} \cdot \text{C}_7\text{H}_8$): C, 45.58 (45.56); H, 3.66 (3.53).

$\text{Bi}_2(\text{Hsal})_6 \cdot \text{Cr}(\text{acac})_3$. This compound was prepared in a manner analogous to that for $\text{Bi}_2(\text{Hsal})_6 \cdot \text{Al}(\text{acac})_3$, with the substitution of $\text{Cr}(\text{acac})_3$ for $\text{Al}(\text{acac})_3$. The resulting purple solution was stirred at room temperature for 15 h during which time a pale purple powder deposited in the flask. The product was collected by filtration, washed with toluene (2×15 mL) and diethyl ether (1×15 mL), and dried in vacuo to give the product as a free flowing powder. Yield: 0.62 g of purple microcrystalline solid (0.85 mmol, 85%). FT-IR (ATR, Ge): 1626, 1594, 1573, 1520, 1483, 1435, 1397, 1367, 1311, 1279, 1245, 1226, 1161, 1029, 935, 876, 823, 764, 754, 724, 705. Elemental Analysis % obsd (% calcd for $\text{CrBi}_2\text{C}_{57}\text{H}_{51}\text{O}_{24}$): C, 42.85 (43.07); H, 3.18 (3.23).

$\text{Bi}_2(\text{Hsal})_6 \cdot \text{V}(\text{acac})_3$. This compound was prepared in a manner analogous to that for $\text{Bi}_2(\text{Hsal})_6 \cdot \text{Al}(\text{acac})_3$, with the substitution of $\text{V}(\text{acac})_3$ for $\text{Al}(\text{acac})_3$. The resulting brown solution was stirred at room temperature for 15 h during which time a yellow powder deposited in the flask. The product was collected by filtration, washed with toluene (2×15 mL) and diethyl ether (1×15 mL), and dried in vacuo to give the product as a free flowing powder. Yield: 0.78 g of yellow powder (0.98 mmol, 98%). FT-IR (ATR, Ge): 1627, 1594, 1583, 1570, 1522, 1484, 1434, 1398, 1364, 1311, 1280, 1246, 1226, 1161, 1027, 936, 877, 824, 764, 755, 725, 705. Elemental analysis % obsd (% calcd for $\text{VBi}_2\text{C}_{57}\text{H}_{51}\text{O}_{24} \cdot 0.6\text{C}_7\text{H}_8$): C, 44.62 (44.69); H, 3.54 (3.42).

$\text{Bi}(\text{Hsal})_3 \cdot \text{Co}(\text{acac})_3$. A suspension of $\text{Bi}_2(\text{Hsal})_6 \cdot \text{Co}(\text{acac})_3$ (0.25 g, 0.33 mmol) in 25 mL of dichloromethane was stirred at room temperature for 3 days. During this time, the color of the solid gradually changed from green to gray-white. After the reaction period, the solution was filtered through Celite, and the solvent was removed from the clear green filtrate to give 80 mg of $\text{Bi}(\text{Hsal})_3 \cdot \text{Co}(\text{acac})_3$ as a pale green powder. ^1H NMR (CD_2Cl_2 , 400 MHz, 25 °C): 2.14 (s, CH_3 , 18H), 5.55 (s, CH, 3H), 6.93 (t, ArH, 3H, $J = 6.66$ Hz), 6.98 (d, ArH, 3H, $J = 8.03$ Hz), 7.51 (t, ArH, 3H, $J = 7.78$ Hz), 7.88 (d, ArH, 3H, $J = 7.70$ Hz). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 125 MHz, 25 °C): 26.12 (CH_3), 97.35 (CH), 117.92, 119.72, 125.61, 128.53, 129.34, 131.04, 136.86, 162.49, 189.89. Elemental analysis % obsd (% calcd for $\text{CoBiC}_3\text{H}_3\text{O}_{15}$): C, 44.01 (44.27); H, 3.50 (3.72).

Solid State Structure of $\text{Bi}_2(\text{Hsal})_6 \cdot \text{Al}(\text{acac})_3$. Single crystals of the compound $\text{Bi}_2(\text{Hsal})_6 \cdot \text{Al}(\text{acac})_3$ were studied on a Bruker

Smart 1000 diffractometer equipped with a CCD area detector. The data were corrected for Lorentz and polarization effects. Absorption correction was applied using the program SADABS.²⁷ The structure was solved using direct methods with the SHELXTL software package.²⁸ All atoms were identified by successive Fourier difference maps of the residual electron density, and refined using the full-matrix least-squares technique on F^2 . All non-hydrogen atoms, with the exceptions discussed below, were refined anisotropically. Hydrogen atoms in all of the complexes were placed in calculated positions, using the default distances in the program XL, and allowed to ride on the adjacent atom. Hydrogen atoms associated with phenolic oxygen atoms were placed in calculated positions and refined geometrically using a riding model. The hydrogen atom was oriented so that the most likely hydrogen bond, in this case to a carboxylate oxygen atom of the same molecule, was realized. Due to the small size of the crystals, and resultant weak data, aromatic rings in the complex were refined as rigid bodies. Investigation of the packing structures of the three molecules using the program PLATON did not reveal the presence of intermolecular hydrogen bonds.²⁹ Refinement of the model parameters against the observed data led to convergence.

Results and Discussion

Synthesis and Reactivity of Bismuth(III) Salicylate–Metal Acetylacetonate Complexes. Bismuth(III) salicylate reacts readily with the trivalent metal β -diketonate complexes $\text{M}(\text{acac})_3$ ($\text{M} = \text{Al}, \text{V}, \text{Cr}, \text{Co}, \text{Fe}$) via direct Lewis acid–base adduct formation to produce 2:1 heterobimetallic coordination complexes in excellent yields under mild conditions. The compounds produced in this manner have been probed spectroscopically and by single crystal X-ray diffraction studies, revealing that the initially formed heterobimetallic systems have a general formula of $\text{Bi}_2(\text{Hsal})_6 \cdot \text{M}(\text{acac})_3$ ($\text{M} = \text{Al}, \text{V}, \text{Cr}, \text{Co}, \text{Fe}$) and represent rare examples of heterometallic compounds that are compositionally rich in bismuth. Indeed, only a handful of examples of such compounds precede this manuscript, likely due to the high coordination requirements of the bismuth center.^{21,30}

The solid-state structure of $\text{Bi}_2(\text{Hsal})_6 \cdot \text{Al}(\text{acac})_3$ has been determined by single crystal X-ray diffraction studies and is presented in Figure 1, while pertinent details relating to the data collection and refinement are presented in Tables 1 and 2. Analysis of the X-ray data reveals that, in addition to the remarkable composition of the system, the complex adopts an unusual asymmetric structure in the solid state in which one bismuth(III) salicylate molecule is nested within the salicylate ligand set attached to an adjacent bismuth center. It is interesting that the molecule chooses to form in a Bi–Bi–Al arrangement and does not adopt a more symmetrical structure in which both bismuth atoms are coordinated to three oxygen atoms of acac ligands on a central $\text{Al}(\text{acac})_3$ unit. Such a Bi–Al–Bi arrangement is plausible and would not seem to be excluded upon steric grounds. The

(27) Sheldrick, G. *SHELXTL*, 5.1 ed.; University of Göttingen: Göttingen, Germany, 1997.

(28) Sheldrick, G. *SHELXTL*, 6.1 ed.; University of Göttingen: Göttingen, Germany, 2001.

(29) Spek, A. L. *PLATON, A multipurpose crystallographic tool*; Utrecht, The Netherlands, 1980–2003.

(30) Jolas, J.; Hoppe, S.; Whitmire, K. *Inorg. Chem.* **1997**, *36*, 3335–3340.

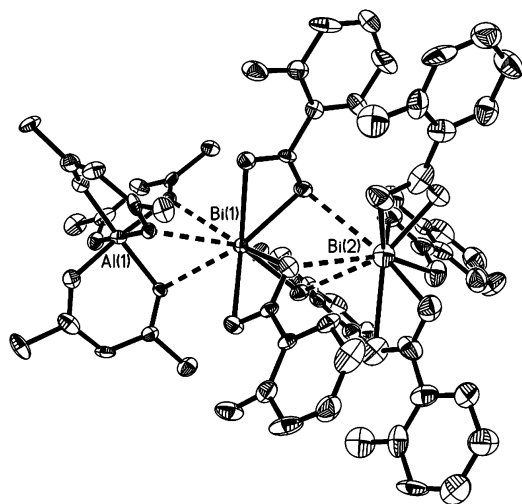


Figure 1. ORTEP representation of the solid-state structure of $\text{Bi}_2(\text{Hsal})_6 \cdot \text{Al}(\text{acac})_3$. Thermal ellipsoids have been drawn at the 30% probability level. Hydrogen atoms have been omitted for clarity.

Table 1. Crystallographic Data for $\text{Bi}_2(\text{Hsal})_6 \cdot \text{Al}(\text{acac})_3$

formula	$\text{C}_{57}\text{H}_{51}\text{AlBi}_2\text{O}_{24}$
fw	1564.92
space group	$R\bar{3}$
Z	6
cryst syst	rhombohedral (hexagonal setting)
a (Å)	12.130(2)
c (Å)	15.073(3)
V (Å ³)	3779.9(13)
D_{calcd} (g·mm ⁻³)	1.793
T (°C)	25
λ , Mo K α (Å)	0.71073
μ (cm ⁻¹)	61.61
R1 ^a	0.1058
wR2 ^b	0.3079

^a Conventional R on F_{hkl} : $\sum |F_o| - |F_c| / \sum |F_o|$. ^b Weighted R on $|F_{\text{hkl}}|^2$: $\{\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)\}^{1/2}$.

metal β -diketonate complex is relatively strongly associated with the central bismuth center as indicated by the Bi–O_{acac} bond distance of 2.702(5) Å as well as the spectroscopic findings discussed below. This bond distance is considerably shorter than the similar bond distance observed in the complex $[\text{Bi}(\text{tmhd})_3]_2$ ($d_{\text{Bi-O}} = 3.073$ Å)³¹ and is comparable to what is observed for the Bi–O_{salen} bond distances in the complexes $\text{Bi}(\text{Hsal})_3 \cdot \text{Cu}(\text{salen})$ and $\text{Bi}(\text{Hsal})_3 \cdot \text{Ni}(\text{salen}) \cdot \text{CH}_2\text{Cl}_2$ ($d_{\text{Bi-O}_{\text{salen}}} = 2.709(4)–2.743(8)$ Å).²² The two bismuth atoms in the complex interact via bridging salicylate ligands. The bridging Bi–O_{salicylate} bond distance is 3.000(10) Å and is similar to what has been reported for the complex $[\text{Bi}(\text{Hsal})_3(2,2'\text{-bipyridine})(\text{C}_7\text{H}_8)]_2$ ($d_{\text{Bi-O}} = 2.906(8)$ Å).³² Additional stabilization of the interaction of the two bismuth atoms may arise from weak π -interactions between adjacent parallel salicylate ligands ($d_{\text{centroid-centroid}} = 4.061(12)$ Å).

The composition and structural information of $\text{Bi}_2(\text{Hsal})_6 \cdot \text{Al}(\text{acac})_3$ derived from the results of the single crystal X-ray diffraction experiments are supported spectroscopically by multinuclear NMR experiments that have been conducted

(31) Fukin, G. K.; Pisarevskii, A. P.; Yanovskii, A. I.; Struchkov, Y. T. *Russ. J. Inorg. Chem.* **1993**, *38*, 1205–1211.

(32) Thurston, J. H.; Marlier, E. E.; Whitmire, K. H. *J. Chem. Soc., Chem. Commun.* **2002**, *23*, 2834–2835.

Table 2. Selected Bond Lengths [Å] and Angles [deg] for $\text{Bi}_2(\text{Hsal})_6 \cdot \text{Al}(\text{acac})_3$ ^a

Distances			
Bi(1)–O(13)	2.339(17)	Bi(2)–O(22)	2.61(3)
Bi(1)–O(12)	2.548(18)	Bi(2)–O(13)	2.963(18)
Bi(1)–O(1)	2.765(15)	Al(1)–O(2)	1.840(19)
Bi(2)–O(23)	2.26(2)	Al(1)–O(1)	1.902(17)
Angles			
O(13)#1–Bi(1)–O(13)	79.4(7)	O(22)–Bi(2)–O(22)#1	119.94(5)
O(13)#1–Bi(1)–O(12)	130.6(6)	O(23)–Bi(2)–O(13)	154.4(8)
O(13)–Bi(1)–O(12)	52.9(6)	O(23)#2–Bi(2)–O(13)	119.4(8)
O(13)#2–Bi(1)–O(12)	79.7(7)	O(23)#1–Bi(2)–O(13)	96.1(8)
O(12)–Bi(1)–O(12)#2	119.58(10)	O(22)–Bi(2)–O(13)	123.7(7)
O(13)#1–Bi(1)–O(1)	127.3(6)	O(22)#1–Bi(2)–O(13)	77.1(7)
O(13)–Bi(1)–O(1)	101.9(6)	O(22)#2–Bi(2)–O(13)	67.0(7)
O(13)#2–Bi(1)–O(1)	153.2(6)	C(27)–Bi(2)–O(13)	144.8(9)
O(12)–Bi(1)–O(1)	80.1(5)	C(27)#1–Bi(2)–O(13)	86.2(8)
O(12)#2–Bi(1)–O(1)	126.2(5)	C(27)#2–Bi(2)–O(13)	94.3(9)
O(12)#1–Bi(1)–O(1)	75.2(5)	O(2)–Al(1)–O(2)	91.5(9)
O(1)–Bi(1)–C(17)#2	146.5(6)	O(2)–Al(1)–O(1)#1	92.9(7)
C(17)#1–Bi(1)–C(17)#2	103.6(6)	O(2)#1–Al(1)–O(1)	175.4(9)
O(23)–Bi(2)–O(23)#2	86.1(10)	O(2)–Al(1)–O(1)	89.9(7)
O(23)–Bi(2)–O(22)	53.0(9)	O(1)#1–Al(1)–O(1)	85.6(8)
O(23)#2–Bi(2)–O(22)	84.2(10)	Al(1)–O(1)–Bi(1)	95.6(7)
O(23)#1–Bi(2)–O(22)	138.4(9)	Bi(1)–O(13)–Bi(2)	96.8(6)

^a Symmetry transformations used to generate equivalent atoms: #1, $-x + y, -x, z$; #2, $-y, x - y, z$.

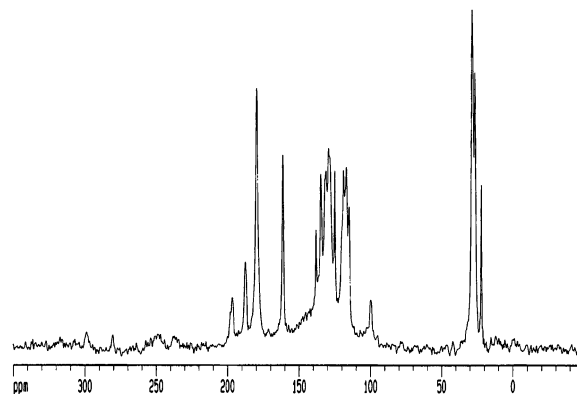


Figure 2. MAS $^{13}\text{C}\{^1\text{H}\}$ spectrum of $\text{Bi}_2(\text{Hsal})_6 \cdot \text{Co}(\text{acac})_3$. The experiment consisted of a 90° ^{13}C pulse, 25.65 ms FID, and 20 s relaxation delay with 3512 scans. 6000 Hz MAS was used during data collection so that spinning sidebands are at multiples of ± 119.2 ppm from the centerband. All signals from 90 to 210 ppm are centerbands.

on $\text{Bi}_2(\text{Hsal})_6 \cdot \text{Al}(\text{acac})_3$ and $\text{Bi}_2(\text{Hsal})_6 \cdot \text{Co}(\text{acac})_3$. Solid-state $^{13}\text{C}\{^1\text{H}\}$ MAS NMR studies of $\text{Bi}_2(\text{Hsal})_6 \cdot \text{Co}(\text{acac})_3$ exhibited a salicylate/acetylacetonate ligand ratio of 1.9:1 which, within the bounds of experimental error, agrees with the 2:1 ratio determined from the single crystal X-ray diffraction studies (Figure 2). Additionally, the solid-state ^{13}C NMR spectrum reveals two distinct methyl resonances at $\delta = 26.3$ and 28.2 ppm, consistent with the asymmetric environment of the β -diketonate ligand seen in the solid state. Direct evidence for the interaction of the β -diketonate with the bismuth center has been obtained via solid-state ^{27}Al NMR studies on $\text{Bi}_2(\text{Hsal})_6 \cdot \text{Al}(\text{acac})_3$, which shows a single resonance with peaks at $\delta = 1.59$ and -0.18 ppm (Figure 3). The splitting of the peak is characteristic of the solid-state spectra obtained from ^{27}Al nuclei which possess a generally symmetric coordination environment.³³ In this case, the bond lengths and angles of the complex, as determined

(33) Alemany, L. *Appl. Magn. Reson.* **1993**, *4*, 179–201.

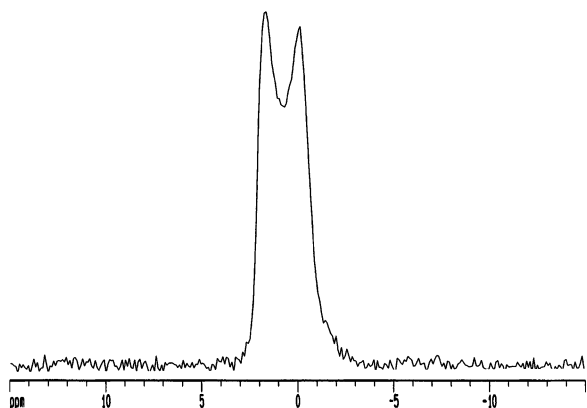


Figure 3. MAS ^{27}Al NMR spectrum of $\text{Bi}_2(\text{Hsal})_6 \cdot \text{Al}(\text{acac})_3$. 20 kHz MAS was employed during data collection. The experiment consisted of a $0.3 \mu\text{s}$ pulse (using 1-kW amplifier; solution 90° pulse = $0.97 \mu\text{s}$), 41 ms FID, and 2 s relaxation delay. 256 scans were collected. No line broadening was employed in data processing.

from the single crystal X-ray diffraction study, reveal that there is only a minor perturbation in the aluminum coordination environment on interaction of the complex with the bismuth center, which is consistent with the results of the solid-state NMR studies. However, the aluminum resonance of the heterobimetallic complex shows both a significant change in peak shape and a downfield shift in peak location versus free aluminum(III) acetylacetonate ($\delta = -1.57$ vs -4.72 ppm), consistent with the electronically deshielding nature of bismuth. Such deshielding effects have been observed in other coordination complexes of bismuth including alkoxides²¹ and diketonates.³⁴ These results suggest that though the interaction of the aluminum complex with the bismuth center has relatively minor effects on the structure of the diketonate complex, it does have a significant electronic effect on the aluminum center.

The behavior of the compounds $\text{Bi}_2(\text{Hsal})_6 \cdot \text{M}(\text{acac})_3$ ($\text{M} = \text{Al}, \text{Co}$) in solution was also probed by multinuclear NMR studies. In the case of $\text{Bi}_2(\text{Hsal})_6 \cdot \text{Al}(\text{acac})_3$, ^1H NMR investigations in noncoordinating solvents such as dichloromethane reveal the presence of two distinct methyl resonances at $\delta = 1.97$ and 2.03 ppm. The position of the methyl resonances are consistent with the presence of the diketonate complex in an asymmetric environment and suggest that the metal β -diketonate remains associated with the bismuth center in solution. These results have been confirmed by the addition of a small portion of DMSO to the sample which results in both a collapse of the methyl peaks to single signal and an upfield shift to $\delta = 1.87$ ppm, consistent with the formation of free $\text{Al}(\text{acac})_3$. The continued interaction of the diketonate complex with the bismuth center in noncoordinating solvents has been confirmed by the ^{27}Al resonance of $\text{Bi}_2(\text{Hsal})_6 \cdot \text{Al}(\text{acac})_3$ in dichloromethane, which occurs at $\delta = 0.88$ ppm, and, like the solid-state spectra of the compound, shows a downfield shift versus free $\text{Al}(\text{acac})_3$ ($\delta = 0.66$ ppm) (Figure 4).

The ^1H NMR spectra of $\text{Bi}_2(\text{Hsal})_6 \cdot \text{Al}(\text{acac})_3$ in solution revealed only a single chemical environment for the salicylate

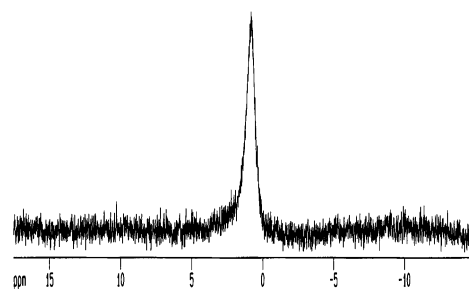


Figure 4. Solution-state ^{27}Al NMR spectrum of $\text{Bi}_2(\text{Hsal})_6 \cdot \text{Al}(\text{acac})_3$.

ligands, characterized by four broad singlets. The features of the aromatic region of these complexes are reminiscent of the spectra that have been observed for other bismuth salicylate complexes including $\text{Bi}_2\text{Nb}_2(\text{sal})_4(\text{Hsal})_4(\text{OEt})_4$ and $[\text{Bi}(\text{Hsal})_3(2,2'\text{-bipyridine})(\text{toluene})]_2$, suggesting that the salicylate ligands are fluxional on the NMR time scale.^{9,32} The exact mechanism by which the salicylate ligands may be exchanged between the two metal centers is not clear at this point. As a result of the scrambling of the salicylate ligands, it is difficult to conclusively determine the nature of the interaction between the two bismuth centers in these compounds in solution. However, it seems very likely that the bismuth atoms remain associated with one another in a manner that may approximate what is observed in the solid-state structure of $\text{Bi}_2(\text{Hsal})_6 \cdot \text{Al}(\text{acac})_3$. Further evidence to support this is discussed below.

The stability of the complexes in solution is dependent on the identity of the metal species in the diketonate complex. For example, the complex $\text{Bi}_2(\text{Hsal})_6 \cdot \text{Al}(\text{acac})_3$ is stable in solution for days, whereas $\text{Bi}_2(\text{Hsal})_6 \cdot \text{Co}(\text{acac})_3$ rapidly eliminates $[\text{Bi}(\text{Hsal})_3]_n$ so that the only species detectable in solution is the dinuclear 1:1 complex $\text{Bi}(\text{Hsal})_3 \cdot \text{Co}(\text{acac})_3$. Comparison of the NMR spectra obtained from the complexes $\text{Bi}_2(\text{Hsal})_6 \cdot \text{Al}(\text{acac})_3$ and $\text{Bi}(\text{Hsal})_3 \cdot \text{Co}(\text{acac})_3$ provides some insight into the behavior of the salicylate ligands in solution. As noted above, the ^1H NMR spectrum of $\text{Bi}_2(\text{Hsal})_6 \cdot \text{Al}(\text{acac})_3$ reveals the presence of only a single salicylate environment, characterized by four broad peaks. There is no evidence of the proton–proton through-bond coupling that would be expected for the salicylate ligands in this complex. This suggests that the salicylate ligands are scrambling between the two bismuth centers at a rate that is rapid on the NMR time scale. Such an exchange process would explain both the observation of only a single salicylate environment in solution and the lack of through-bond coupling. In contrast to $\text{Bi}_2(\text{Hsal})_6 \cdot \text{Al}(\text{acac})_3$, the ^1H NMR spectrum of $\text{Bi}(\text{Hsal})_3 \cdot \text{Co}(\text{acac})_3$ shows the anticipated proton–proton through-bond coupling of the aromatic rings, indicating that there is only a single salicylate environment in solution. The slight broadening of the peaks that is observed at room temperature suggests that there might be some minor fluctuations in the structure in solution that are rapid on the NMR time scale. The resolution of the peaks in the ^1H NMR spectrum of $\text{Bi}(\text{Hsal})_3 \cdot \text{Co}(\text{acac})_3$ suggests that the salicylate ligands in the complex are essentially static and there is no observable intermolecular mechanism for salicylate scrambling.

(34) Parola, S.; Papiernik, R.; Hubert-Pfalzgraf, L. G.; Bois, C. *J. Chem. Soc., Dalton Trans.* **1998**, 737–739.

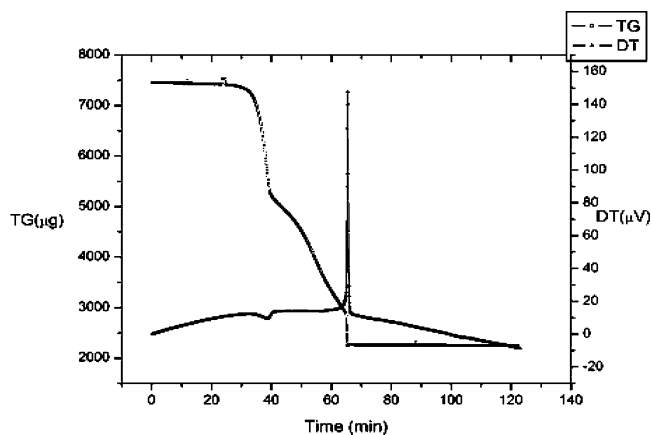


Figure 5. TGA/DTA traces of the thermal decomposition of $\text{Bi}_2(\text{Hsal})_6 \cdot \text{Al}(\text{acac})_3$ in air.

It is important to note that the dissociation of the bismuth(III) salicylate from $\text{Bi}_2(\text{Hsal})_6 \cdot \text{Co}(\text{acac})_3$ is quantitative (by NMR spectroscopy), and that the free bismuth(III) salicylate rapidly forms as a white solid. In the case of $\text{Bi}_2(\text{Hsal})_6 \cdot \text{Al}(\text{acac})_3$, the two bismuth atoms appear to remain associated with one another in solution, as not only is there no elimination of solid $\text{Bi}(\text{Hsal})_3$, but also the integration of the peaks of the salicylate to the diketonate are observed in the anticipated 2:1 ratio.

The solution-state structure of $[\text{Bi}(\text{Hsal})_3]_n$ is not known, but the observed solution chemistry is consistent with the existence of a hypothetical dimeric complex $[\text{Bi}(\text{Hsal})_3]_2 \cdot (\text{solvent})_x$. The reaction of such a dimer with the $\text{M}(\text{acac})_3$ in toluene may thus be kinetically driven to produce insoluble $\text{Bi}_2(\text{Hsal})_6 \cdot \text{M}(\text{acac})_3$. Dissolution of the complexes in dichloromethane may allow for conversion of the complexes to the thermodynamically stable dinuclear species via loss of bismuth salicylate, as is observed in the case of $\text{Bi}_2(\text{Hsal})_6 \cdot \text{Co}(\text{acac})_3$ to give $\text{Bi}(\text{Hsal})_3 \cdot \text{Co}(\text{acac})_3$. Surprisingly, elimination of $\text{Bi}(\text{Hsal})_3$ from the Al derivative was not observed even upon letting the solutions stand for several days. More work will be required to completely elucidate whether a dimeric bismuth salicylate complex is involved as a reaction intermediate.

Thermal Decomposition Studies. The thermal decomposition of all of the complexes produced in this manner has been probed by TGA/DTA and, in the case of $\text{Bi}_2(\text{Hsal})_6 \cdot \text{M}(\text{acac})_3$ ($\text{M} = \text{Al}, \text{V}$), by powder X-ray diffraction studies. In all cases, it was found that the compounds smoothly underwent thermal decomposition on heating in air. The thermal decomposition of $\text{Bi}_2(\text{Hsal})_6 \cdot \text{Al}(\text{acac})_3$ begins at 179 °C and is complete at 380 °C (Figure 5). The decomposition of the molecular complex proceeds in three steps and is punctuated by an abrupt mass loss (approximately 7%) at 353 °C. A small endotherm is observed in the DTA of the sample and corresponds to the onset of decomposition as opposed to a melting of the complex. The release of lattice solvent is observed in all cases, and the mass loss attributed to release of included toluene agrees within experimental error with the results from elemental analysis.

The thermal decomposition of the compounds $\text{Bi}_2(\text{Hsal})_6 \cdot \text{M}(\text{acac})_3$ ($\text{M} = \text{Fe}, \text{Cr}, \text{Co}$) mirrors what was observed for

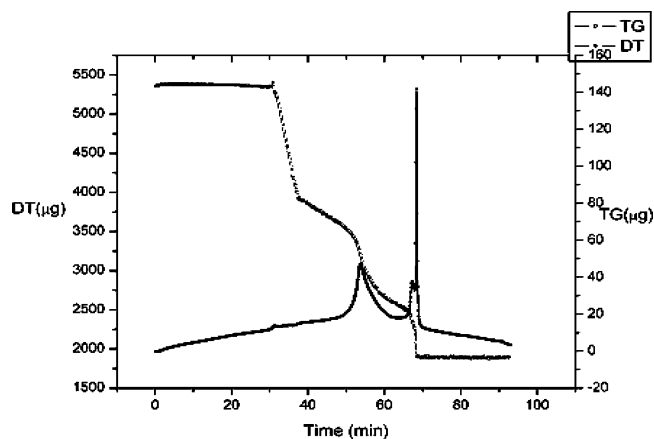


Figure 6. TGA/DTA traces of the thermal decomposition of $\text{Bi}_2(\text{Hsal})_6 \cdot \text{V}(\text{acac})_3$ in air.

the pyrolysis of $\text{Bi}_2(\text{Hsal})_6 \cdot \text{Al}(\text{acac})_3$. In each case, the thermal decomposition of the complex proceeds in several steps ending with an abrupt loss of mass to produce the heterobimetallic oxide material. As with $\text{Bi}_2(\text{Hsal})_6 \cdot \text{Al}(\text{acac})_3$, the DTA reveals a small endothermic event which directly corresponds to the onset of decomposition of the molecular complex. The final oxides are achieved at temperatures of 340, 347, and 360 °C for the series $\text{M} = \text{Fe}, \text{Cr}, \text{Co}$, respectively. In all cases, the formation of the final material is accompanied by a strong exotherm in the DTA, which we have assigned as corresponding to reorganization in the oxide lattice as essentially no mass is lost in the process. This exothermic event on complete decomposition of a heterobimetallic bismuth coordination complex is consistent with other complexes that we have investigated for bismuth-containing complexes.^{9,10,22}

The pyrolysis of $\text{Bi}_2(\text{Hsal})_6 \cdot \text{V}(\text{acac})_3$ differs slightly from the other heterobimetallic complexes in this respect, as three distinct exotherms are observed in DTA (Figure 6). We have assigned the first two exothermic events as corresponding to the $\text{V}^{3+} \rightarrow \text{V}^{4+}$ and to the $\text{V}^{4+} \rightarrow \text{V}^{5+}$ oxidation steps that would be required for the conversion of the molecular complex to $\text{Bi}_4\text{V}_2\text{O}_{11}$. Support for these assignments is found in the thermal decomposition of the complex $\text{Bi}(\text{Hsal})(\text{sal}) \cdot \text{V}(\text{O})(\text{salen})^*$ in which the $\text{V}^{4+} \rightarrow \text{V}^{5+}$ transition is observed to occur at almost the same temperature as for this system.²² The final exothermic event in the thermal decomposition of $\text{Bi}_2(\text{Hsal})_6 \cdot \text{V}(\text{acac})_3$ has been treated analogously to the other compounds presented here and assigned to a reorganization event in the oxide lattice. It is important to note that the formation of the final materials occurs at temperatures that are significantly lower than what have been reported for traditional solid-state syntheses, and, in some cases, lower even than what has been required for other similar molecular complexes such as $\text{Bi}_2\text{Ti}_4(\text{sal})_{10}(\text{Hsal})(\text{O}^i\text{Pr})$ and $\text{Bi}_2\text{Ti}_3(\text{sal})_8(\text{Hsal})_2$ ($T_{\text{decomposition}} = 500$ and 430 °C, respectively).⁹

One of the principle advantages of the use of discrete molecular complexes for the formation of oxide materials is that the presence of bridging organic ligands helps to prevent unwanted metal segregation during oxide formation.³⁵ The compounds developed in this study present an interesting intermediate state between the use of rigidly constructed

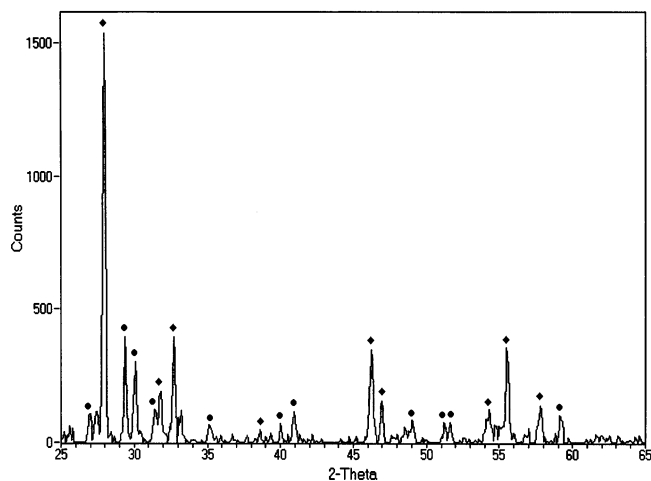


Figure 7. Powder X-ray diffraction pattern of the material produced from the thermal decomposition of $\text{Bi}_2(\text{Hsal})_6\cdot\text{Al}(\text{acac})_3$. The sample was annealed at $750\text{ }^\circ\text{C}$ in air for 2 h. Peaks marked with a \blacklozenge represent the tetragonal phase of Bi_2O_3 , while peaks marked with a \bullet represent $\text{Bi}_2\text{Al}_4\text{O}_9$.

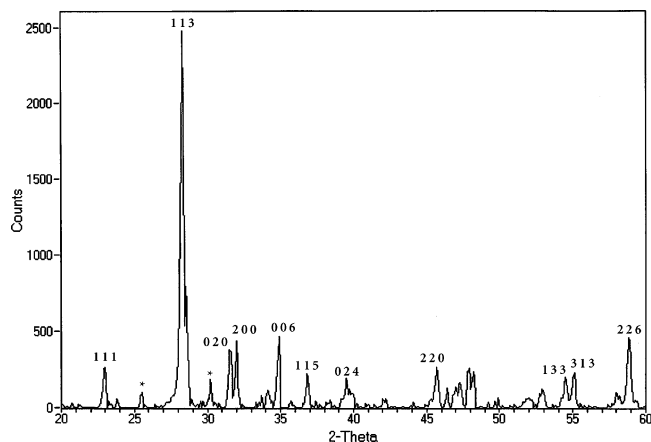


Figure 8. Powder X-ray diffraction spectrum of $\text{Bi}_4\text{V}_2\text{O}_{11}$ produced from the thermal decomposition of $\text{Bi}_2(\text{Hsal})_6\cdot\text{V}(\text{acac})_3$. The sample was annealed at $750\text{ }^\circ\text{C}$ in air for 2 h. Peaks marked with a * represent an unidentified trace impurity.

heterobimetallic systems employing bifunctional ligands and the amorphous precursor materials that are obtained from coprecipitation or sol–gel methods. In the case of $\text{Bi}_2(\text{Hsal})_6\cdot\text{V}(\text{acac})_3$, the metal species are present in the desired stoichiometry, but this is not true of the aluminum species where a 1:2 ratio would be required instead. The behavior of the molecular complexes on thermal decomposition has been further probed by detailed powder X-ray diffraction studies. Pyrolysis of $\text{Bi}_2(\text{Hsal})_6\cdot\text{Al}(\text{acac})_3$ for 2 h at $700\text{ }^\circ\text{C}$ produces a mixture of the phases $\text{Bi}_2\text{Al}_4\text{O}_9$ and tetragonal Bi_2O_3 , whereas thermal decomposition of $\text{Bi}_2(\text{Hsal})_6\cdot\text{V}(\text{acac})_3$ under identical conditions produced monoclinic $\text{Bi}_4\text{V}_2\text{O}_{11}$ as the major crystalline phase (Figures 7 and 8). In the latter case, only a very minor amount of an impurity could be detected in the powder X-ray diffraction spectrum, while in the former case the formation of bismuth oxide in addition

to the heterometallic oxide phase was expected given the mismatch in stoichiometry between the precursor and desired product. In both cases, the oxide phases that are produced in the course of thermal decomposition of the molecular precursors agree with those predicted by the corresponding binary phase diagrams. It is important to observe that there is no evidence of unwanted metal segregation in the decomposition product of $\text{Bi}_2(\text{Hsal})_6\cdot\text{V}(\text{acac})_3$. This indicates that, despite the lack of a bridging organic ligand between the two metal species, thermal decomposition of the molecular precursors as in the case of vanadium is able to afford crystalline oxide phases in good purity at very mild conditions.

Conclusions

In summary, the Lewis acidity of the bismuth center allows for a convenient handle for the facile formation of heterobimetallic coordination complexes via direct adduct formation with metal complexes bearing Lewis base donor atoms and the bismuth center of bismuth salicylate. Surprisingly stable 2:1 Bi/M complexes are obtained. The reaction is general and allows for the facile generation of compounds incorporating a wide range of main group elements and transition metals. This approach offers significantly more control over the stoichiometry of the complexes at the molecular level compared to other methods such as microhydrolysis and may offer the possibility of developing a rational, directed approach to the formation of single-source molecular precursors for advanced oxide materials. We have shown that these complexes will readily produce bimetallic oxides on thermal decomposition with no apparent loss of the β -diketonate species to sublimation. Additionally, the ability to directly synthesize isomorphous complexes that incorporate a wide variety of transition metals opens the possibility of producing single source precursors for termetallic or multimetallic species via simple doping/isomorphous replacement techniques. In the case of cobalt, the 2:1 Bi/Co compound was shown to eliminate bismuth salicylate to produce a 1:1 species that may prove useful in the formation of 1:1 heterometallic oxides. These species, which have not yet yielded to the formation of single crystals, are undergoing further study.

Acknowledgment. This work was supported by grants from the Robert A. Welch Foundation and from the United States National Science Foundation (Grant CHE-9983352). J.H.T. would like to thank Dr. Andrew R. Barron for use of the TGA/DTA and Drs. Larry Alemany and Yunxuan Xiao for assistance with the multinuclear NMR experiments.

Supporting Information Available: X-ray crystal data of $\text{Bi}_2(\text{Hsal})_6\cdot\text{Al}(\text{acac})_3$ in CIF format. Detailed TGA/DTA traces of the thermal decomposition of $\text{Bi}_2(\text{Hsal})_6\cdot\text{M}(\text{acac})_3$ ($\text{M} = \text{Cr}, \text{Co}, \text{Fe}$) and additional spectra from the solid-state $^{13}\text{C}\{^1\text{H}\}$ NMR studies of $\text{Bi}_2(\text{Hsal})_6\cdot\text{Co}(\text{acac})_3$. This material is available free of charge via the Internet at <http://pubs.acs.org>.

(35) Kessler, V. G.; Hubert-Pfalzgraf, L. G.; Daniele, S.; Gleizes, A. *Chem. Mater.* **1994**, *6*, 2336–2342.