

Synthesis and Structural Characterization of a New Heterobimetallic Coordination Complex of Barium and Cobalt for Use as a Precursor for Chemical Vapor Deposition

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Ba(dmae)₂ (dmaeH = *N,N*-dimethylaminoethanol, C₄H₁₁NO) reacts with Co(acac)₂ (acac = 2,4-pentanedionate) to produce the trinuclear coordination complex [Ba₂Co(acac)₄(dmae)₃(dmaeH)] in an 85% yield. Spectroscopic and single-crystal X-ray diffraction experiments indicate that the complex possesses a structure in which two barium atoms and a cobalt atom are bridged by acac and dmae groups. The barium centers are eight and nine coordinate with BaO₇N and BaO₇N₂ coordination spheres while the cobalt is a more regular CoO₅N octahedron. This 2:1 heterobimetallic molecular complex was investigated as precursor for the deposition of thin film by AACVD. The film was characterized by SEM and XRD. TGA shows that the complex starts thermal decomposition upon heating in nitrogen atmosphere at 105 °C to produce barium cobalt oxide material of a Ba₂CoO₃ composition with an orthorhombic structure. The synthetic approach detailed here represents a unique route to the formation of a heterobimetallic barium cobalt coordination complex.

Introduction

There has been considerable interest in recent years in the development of new precursors for chemical vapor deposition (CVD) of ceramic materials. In general, such precursors must be volatile, have sufficient stability for the transportation to the deposition site, and decompose cleanly to give the desired materials. Various acetylacetonate and alkoxide complexes¹ of both main group and transition metals have been used to deposit thin films of metals and metal oxides.^{2,3} Much of the more recent focus in this area has been the synthesis of heterobimetallic, metallorganic precursors,⁴ which have become a cornerstone of advances in new materials. Single-source bimetallic compounds, which deliver both elements of a final material simultaneously, can generate complex

ceramic materials in a single step, removing the need to match the reaction rates required of a multicomponent precursor mixture.⁵ Typical examples, among many possibilities, are the deposition of SrTa₂O₆ and SrNb₂O₆ directly from [SrTa₂(OEt)₁₀(dmae)₂]⁶ and [SrNb₂(OEt)₈(μ-OEt)₂(μ₂-dmae)₂],⁷ respectively ([dmaeH = *N,N*-dimethylaminoethanol HOCH₂CH₂N(CH₃)₂]).

The wide interest in cobalt oxide with main group metal oxides is a result of their applications in solid-state fuel cells⁸ and cobalt-based superconductors⁹ and the potential applications of La_{1-x}Sr_xCoO₃ and Ba_{1-x}Sr_xCoO₃ as gas and ion sensors^{10,11} in electrodes and ferroelectric capacitors.¹² Ba-

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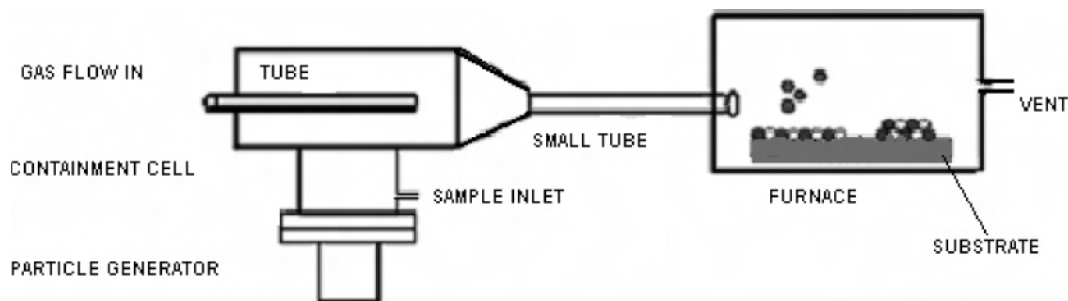


Figure 1. Schematic diagram of the aerosol-assisted chemical vapor deposition process.

CoO_3 is a material which has been studied because of its interesting magnetic and transport,¹³ sensor, catalyst, and semiconducting¹⁴ properties.

To our knowledge, the “single-source” precursor approach using a bimetallic barium/cobalt complex has not previously been reported. In this paper, we report the facile synthesis and structural characterization of the crystalline heterobimetallic precursor $[\text{Ba}_2\text{Co}(\text{acac})_4(\text{dmae})_3(\text{dmaeH})]$ which undergoes thermal decomposition to a barium cobalt oxide of composition Ba_2CoO_3 .

Experimental Section

All manipulations were carried out under an atmosphere of dry argon using a standard Schlenk tube apparatus and glovebox techniques. Solvents were rigorously predried, distilled over calcium oxide, and redistilled over sodium metal/benzophenone. Barium metal and $\text{Co}(\text{acac})_2$ were purchased from Aldrich chemicals and were stored in a glovebox under argon. All other reagents were from Fluka chemicals. Elemental analysis was performed using a Perkin-Elmer elemental analyzer (2004).

NMR spectra were recorded at 300 MHz on a Varian Mercury 300 spectrometer, using the proton impurities of deuterated solvents as a reference for ^1H spectra and the ^{13}C resonance of the solvent as a reference for ^{13}C spectra. Chemical shifts (ppm) were also independently referenced to tetramethylsilane (ca. 1% added by volume).

Controlled thermal analysis of the complex was investigated using Perkin-Elmer Thermogravimetric Analyzer TGA7 with computer interface. The measurements were carried out in an alumina crucible under an atmosphere of flowing (25 mL/min) nitrogen gas, using a heating rate of 10 °C/min. The descriptions that follow in this section detail the observed and calculated percent weight losses. IR spectra were recorded on Bio-Rad Excalibur FT-IR Model FTS 3000 MX using KBr disks.

SEM was carried out using a Hitachi-5570 filament scan electron microscope with a beryllium window. XRD peak patterns of the film were collected using a JEOL JDX-3532 diffractometer with $\text{Cu K}\alpha$ radiations.

Synthesis of $[\text{Ba}_2\text{Co}(\text{acac})_4(\text{dmae})_3(\text{dmaeH})]$. Ba metal (0.50 g, 3.64 mmol) was added to a stirred solution of dmaeH (0.65 g, 7.3 mmol) in dry THF (10 mL). The mixture was stirred for 2 h until all of the Ba was consumed. The volatiles were removed in vacuo to give $\text{Ba}(\text{dmae})_2$ as a pale yellow solid, which was redissolved in dry THF (10 mL). $\text{Co}(\text{acac})_2$ (0.94 g, 3.64 mmol) was then added with stirring to the above solution of $\text{Ba}(\text{dmae})_2$,

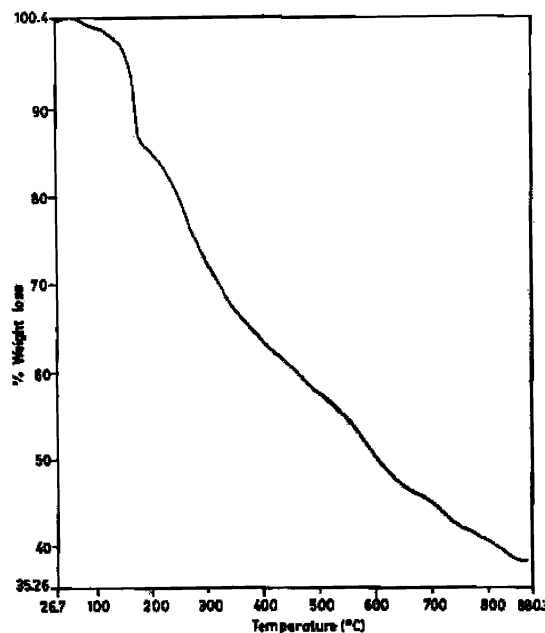


Figure 2. TGA plot of $[\text{Ba}_2\text{Co}(\text{acac})_4(\text{dmae})_3(\text{dmaeH})]$.

Table 1. Growth Conditions for the Aerosol-Assisted Chemical Vapor Deposition of Barium Cobalt Oxide Film from $\text{Ba}_2\text{Co}(\text{acac})_4(\text{dmae})_3(\text{dmaeH})$

precursor concentration	0.2 g/25 mL (toluene)
carrier gas (N_2) flow rate	20 cm^3/min
sample injection	0.27 ml/min
furnace temp	500 °C
substrate	soda glass
deposition time	1.5 h

and the mixture was stirred for 12 h to obtain a deep green solution, which was cannula filtered to remove any traces of solid residue and placed in refrigerator at -15 °C for crystallization. Crystals obtained after two weeks were recrystallized from toluene (yield 85% based on Ba). mp: 215 °C dec. Anal. Calcd for $\text{C}_{36}\text{H}_{69}\text{N}_4\text{O}_{12}\text{Ba}_2\text{Co}$: C, 39.88; H, 6.37; N, 5.17. Found: C, 39.72; H, 6.37; N, 5.18. TGA: 105–168 °C, 8.28% loss of dmaeH (calcd 8.21%); 168–182 °C, 4.8% loss of 0.5 acac (calcd 4.57%); 182–429 °C, 24.3% loss of 3 dmae (calcd 24.4%); 429–856 °C, a gradual defragmentation of acac groups leaving residue 35.1% (calcd for Ba_2CoO_3 35.1%). ^1H NMR(300.17 MHz, 20 °C, CDCl_3): δ 1.92 (s, $\text{CH}_3\text{C}=\text{O}$, 12H), 2.00 (s, $\text{CH}_3\text{C}=\text{O}$, 12H), 2.15–2.35 (b, NMe_2 , 24H), 2.50–2.61 (m, CH_2-NMe_2 , 8H), 2.75–2.89 (m, OCH_2 , 8H), 3.55 (b, OH, 1H) 6.87 (s, CH, 4H). ^{13}C NMR(75.47 MHz, 20 °C, CDCl_3): δ 28.43, (CH_3C), 47.94 (NMe), 59.71 (CH), 64.05 (CH_2-NMe), 68.92 (OCH_2-CH_2) 187.71 (CO).

AACVD Experiments. The aerosol-assisted chemical vapor deposition (AACVD) technique was used for the deposition of barium cobalt oxide thin films on the soda glass substrate. An ultrasonic

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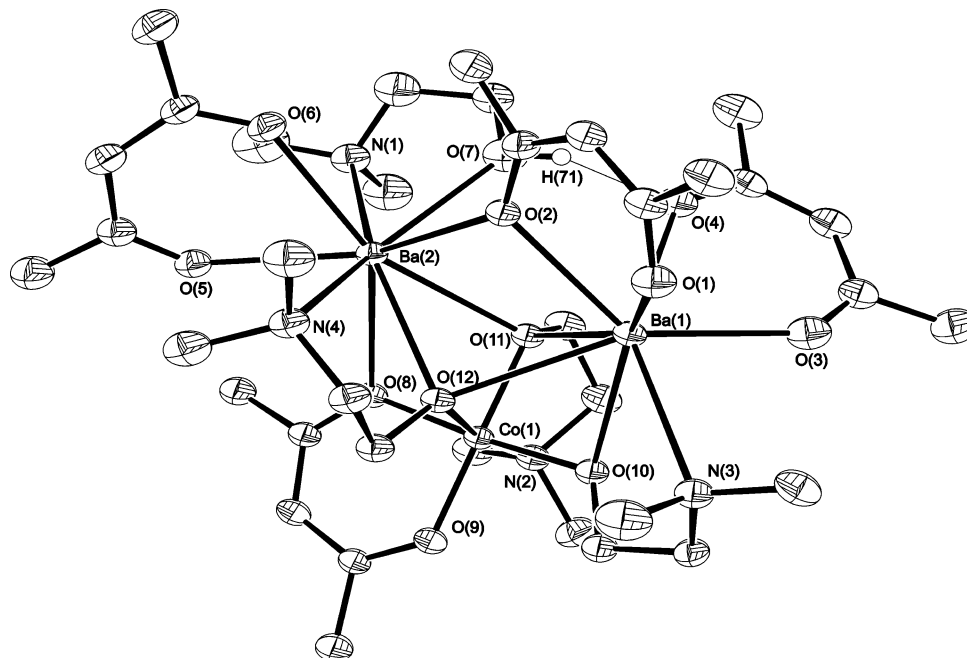


Figure 3. Asymmetric unit of $[\text{Ba}_2\text{Co}(\text{acac})_4(\text{dmae})_3(\text{dmaeH})]$. Only key atoms have been labeled for clarity. Ellipsoids are at the 30% probability level.

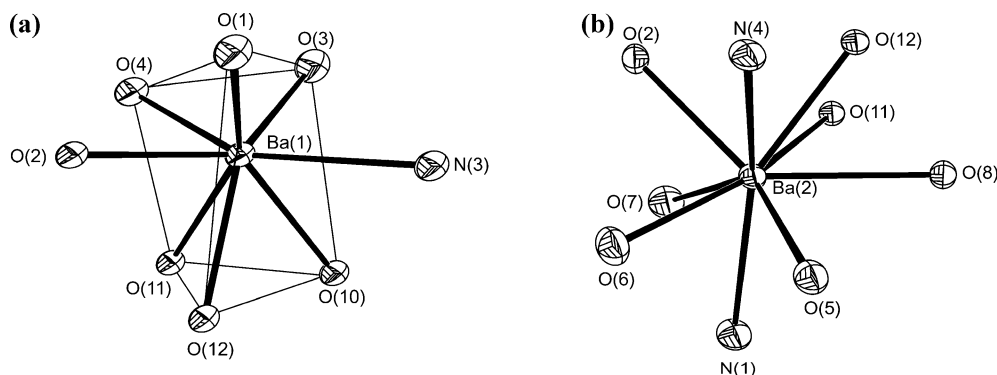


Figure 4. Coordination spheres of Ba(1) (a) and Ba(2) (b) in $[\text{Ba}_2\text{Co}(\text{acac})_4(\text{dmae})_3(\text{dmaeH})]$.

nebulizer (Sonaer) (Figure 1) was used for the generation of the aerosol. The substrate was 1.5×4 cm slides placed horizontally in a glass tube in a furnace fitted with an aerosol generator. The flow of nitrogen gas and the sample was manually controlled. Parameters for the growth of the thin film are listed in Table 1.

X-ray Crystallography. Crystal data: $\text{C}_{36}\text{H}_{69}\text{Ba}_2\text{CoN}_4\text{O}_{12}$, fw = 1083.56, monoclinic, $P2_1/c$, $a = 11.14100(10)$ Å, $b = 19.3710(2)$ Å, $c = 22.3220(3)$ Å, $\beta = 99.8710(10)^\circ$, $V = 4746.05(9)$ Å³, $Z = 4$, $\mu(\text{Mo K}\alpha) = 2.043$ mm⁻¹. Data were collected on a Kappa CCD diffractometer at 173(2) K using Mo K α radiation (0.71073 Å) in the θ range of 3.53–27.72°. Data were corrected for Lorentz, polarization, and absorption; 79460 reflections were collected, of which 10874 were unique [$R(\text{int}) = 0.1317$]. Refinement was by full-matrix least-squares on F^2 ; goodness-of-fit on F^2 was 1.032. Final R indices where $I > 2\sigma(I)$ are $R1 = 0.0380$ and $wR2 = 0.0766$. The final R indices with all data are $R1 = 0.0631$ and $wR2 = 0.0862$. The largest difference peak and hole are 1.095 and -1.129 e Å³, respectively

Results and Discussion

$\text{Ba}(\text{dmae})_2$ reacts readily with $\text{Co}(\text{acac})_2$ via direct Lewis acid–base adduct formation to produce a 2:1 heterobimetallic coordination complex in good yield under mild conditions.

This type of synthetic strategy has some notable features. First, this approach aims to coordinatively saturate each metal center using chelating ligands (e.g., diketonate, functionalized alcohols, etc). This point is of importance and presumably results in their exceptional stability in the atmosphere, since the chelating ligands are less easily hydrolyzed than would be monodentate alkoxides.^{15,16} Second, the application of multidentate ligands has previously been shown to force oligomeric complexes into a more strictly molecular regime, generally reducing the possibility of interactions between monomeric units. Last, this technique of using a preformed metal β -diketonate leads to water-free products. Thus, hard Lewis bases (either O- or N-based) can utilize the entropic advantage of the chelate effect and facilitate the preparation of anhydrous heterobimetallic β -diketonates via a low cost route. This later point is of possible importance if such materials are going to have real applications as either sol–

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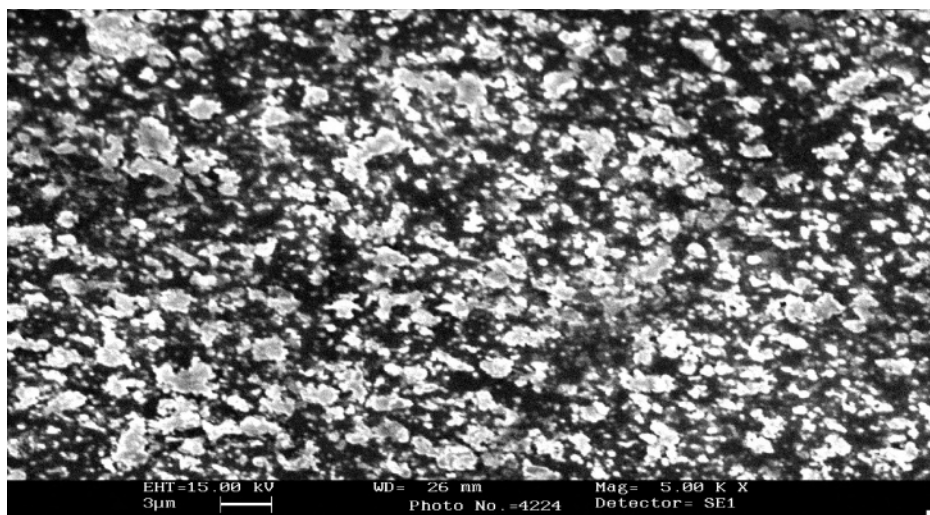


Figure 5. SEM micrograph of a Ba_2CoO_3 thin film.

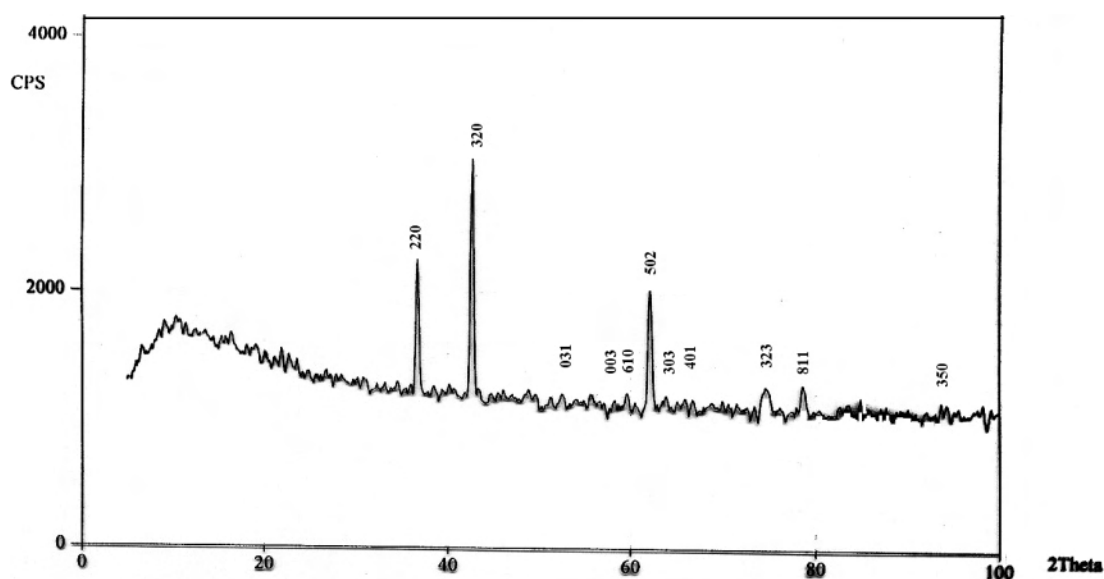


Figure 6. X-ray diffraction plot of a Ba_2CoO_3 thin film.

Table 2. Selected XRD Data of Ba_2CoO_3

peak no.	2θ	d	hkl	INT	I/I_0
1	36.70	2.447	220	674	74
2	42.700	2.116	320	913	100
3	52.600	1.739	031	363	40
4	58.200	1.584	003	346	38
5	59.600	1.550	610	366	40
6	62.200	1.502	502	607	66
7	65.100	1.432	303	349	38
8	66.800	1.399	401	352	39
9	74.800	1.268	323	377	41
10	78.700	1.144	811	377	41
11	93.600	1.057	350	350	38

gel or CVD precursors, where low-cost chemicals that can be manipulated on the open laboratory bench are an important objective.^{17,18}

The thermal behavior of this complex was studied by TGA/DTA analysis over a range of 25–880 °C under a

nitrogen environment. The TGA plot (Figure 2) shows that the complex smoothly underwent thermal decomposition. The decomposition begins at 105 °C and is completed at 856 °C. The decomposition of the molecular complex proceeds in four steps, and the maximum weight loss (approximately 24%) takes place at 429 °C. The TGA study shows the decomposition of a complex with poor sublimation properties.

The molecular structure of the complex $\text{Ba}_2\text{Co}(\text{acac})_4(\text{dmae})_3(\text{dmaeH})$ is shown in (Figure 3). The hydrogen on one dmae ligand was located in the difference map because of its rigid position by virtue of the hydrogen bond it forms to an adjacent acac ligand. No further hydrogen atoms appear to be present on the oxygen centers of either the remaining acac or dmae ligands (although locating them can be expected to be difficult in view of the proximity of the three heavy metals), but the resulting formula, containing Ba(II) and Co(III), is consistent with the diamagnetic nature of the species; any further protonation would require the presence of paramagnetic Co(II)

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Table 3. Selected Metrical Data for [Ba₂Co(acac)₄(dmae)₃(dmaeH)]

bond distances (Å)			bond angles (deg)				
Ba(1)–O(1)	2.702(2)	O(1)–Ba(1)–O(2)	66.45(7)	O(11)–Ba(1)–N(3)	121.68(8)	O(5)–Ba(2)–O(7)	132.60(8)
Ba(1)–O(2)	2.698(2)	O(1)–Ba(1)–O(3)	99.82(9)	O(12)–Ba(1)–N(3)	90.01(8)	O(5)–Ba(2)–O(8)	80.93(7)
Ba(1)–O(3)	2.648(3)	O(1)–Ba(1)–O(4)	104.06(8)	O(8)–Co(1)–O(9)	93.96(10)	O(5)–Ba(2)–O(11)	134.72(7)
Ba(1)–O(4)	2.748(2)	O(1)–Ba(1)–O(10)	136.47(7)	O(8)–Co(1)–O(10)	174.84(10)	O(5)–Ba(2)–O(12)	10.11(7)
Ba(1)–O(10)	2.693(2)	O(1)–Ba(1)–O(11)	148.80(7)	O(8)–Co(1)–O(11)	86.63(10)	O(5)–Ba(2)–N(1)	76.74(8)
Ba(1)–O(11)	2.691(2)	O(1)–Ba(1)–O(12)	108.26(7)	O(8)–Co(1)–O(12)	88.80(10)	O(5)–Ba(2)–N(4)	77.72(8)
Ba(1)–O(12)	2.926(2)	O(1)–Ba(1)–N(3)	77.64(8)	O(8)–Co(1)–N(2)	92.85(11)	O(6)–Ba(2)–O(7)	91.01(9)
Ba(1)–N(3)	2.943(3)	O(2)–Ba(1)–O(3)	133.67(8)	O(9)–Co(1)–O(10)	90.99(10)	O(6)–Ba(2)–O(8)	144.72(8)
Ba(2)–O(2)	2.770(2)	O(2)–Ba(1)–O(4)	74.67(7)	O(9)–Co(1)–O(11)	179.35(11)	O(6)–Ba(2)–O(11)	158.08(8)
Ba(2)–O(5)	2.668(3)	O(2)–Ba(1)–O(10)	128.02(7)	O(9)–Co(1)–O(12)	97.22(10)	O(6)–Ba(2)–O(12)	139.49(8)
Ba(2)–O(6)	2.681(3)	O(2)–Ba(1)–O(11)	83.21(7)	O(9)–Co(1)–N(2)	92.82(11)	O(6)–Ba(2)–N(1)	75.95(9)
Ba(2)–O(7)	2.758(3)	O(2)–Ba(1)–O(12)	72.75(7)	O(10)–Co(1)–O(11)	88.41(10)	O(6)–Ba(2)–N(4)	79.45(8)
Ba(2)–O(8)	2.917(2)	O(2)–Ba(1)–N(3)	131.64(8)	O(10)–Co(1)–O(12)	89.14(10)	O(7)–Ba(2)–O(8)	110.40(8)
Ba(2)–O(11)	2.842(2)	O(3)–Ba(1)–O(4)	66.00(8)	O(10)–Co(1)–N(2)	88.35(11)	O(7)–Ba(2)–O(11)	67.86(8)
Ba(2)–O(12)	2.752(2)	O(3)–Ba(1)–O(10)	93.20(8)	O(11)–Co(1)–O(12)	82.52(9)	O(7)–Ba(2)–O(12)	114.23(7)
Ba(2)–N(1)	3.079(3)	O(3)–Ba(1)–O(11)	106.65(8)	O(11)–Co(1)–N(2)	87.43(11)	O(7)–Ba(2)–N(1)	57.61(8)
Ba(2)–N(4)	3.056(3)	O(3)–Ba(1)–O(12)	148.45(8)	O(12)–Co(1)–O(2)	169.70(11)	O(7)–Ba(2)–N(4)	139.71(9)
Co(1)–O(8)	1.936(2)	O(3)–Ba(1)–N(3)	82.08(8)	O(2)–Ba(2)–O(5)	142.19(7)	O(8)–Ba(2)–O(11)	54.33(7)
Co(1)–O(9)	1.896(2)	O(4)–Ba(1)–O(10)	119.14(7)	O(2)–Ba(2)–O(6)	87.73(8)	O(8)–Ba(2)–O(12)	56.40(6)
Co(1)–O(10)	1.897(2)	O(4)–Ba(1)–O(11)	73.03(7)	O(2)–Ba(2)–O(7)	68.18(8)	O(8)–Ba(2)–N(1)	91.84(8)
Co(1)–O(11)	1.897(2)	O(4)–Ba(1)–O(12)	118.60(7)	O(2)–Ba(2)–O(8)	125.73(7)	O(8)–Ba(2)–N(4)	98.87(7)
Co(1)–O(12)	1.898(2)	O(4)–Ba(1)–N(3)	147.96(8)	O(2)–Ba(2)–O(11)	79.22(7)	O(11)–Ba(2)–O(12)	53.13(6)
Co(1)–N(2)	2.033(3)	O(10)–Ba(1)–O(11)	58.86(7)	O(2)–Ba(2)–O(12)	74.43(7)	O(11)–Ba(2)–N(1)	96.22(7)
		O(10)–Ba(1)–O(12)	56.41(7)	O(2)–Ba(2)–N(1)	122.45(8)	O(11)–Ba(2)–N(4)	112.55(7)
		O(10)–Ba(1)–N(3)	63.21(8)	O(2)–Ba(2)–N(4)	72.36(8)	O(12)–Ba(2)–N(1)	144.11(8)
		O(11)–Ba(1)–O(12)	52.73(6)	O(5)–Ba(2)–O(6)	64.17(8)	O(12)–Ba(2)–N(4)	60.66(7)
						N(1)–Ba(2)–N(4)	150.30(8)

Ba(1) has a coordination number (CN) of eight with a BaO₇N ligation set composed of two acac groups, one of which has a bridging role between the barium centers [O(1), O(2)] and the other is purely chelating [O(3), O(4)], a similar chelating/bridging dmae ligand [O(10), N(3)], and the oxygen atoms of two triply bridging dmae ligands [(O(11), O(12))]. Ba(2) has CN = 9 with a BaO₇N₂ set of ligating atoms. These are made up of a chelating acac [O(5), O(6)], two chelating dmae ligands [O(7), N(1); O(12), N(4)], one of which is protonated [O(7)], the oxygen atoms of two bridging acac groups [O(2), O(8)], and a further oxygen from a bridging dmae [O(12)]. The most regular coordination sphere occurs at cobalt, which is octahedral with an O₅N coordination set. This is composed of one chelating acac [O(8), O(9)], one chelating dmae [O(11), N(2)], and the oxygen atoms of two bridging dmae groups [O(10), O(12)].

Both types of ligand span a range of coordination modes. The acac ligands are either chelating [O(5), O(6)], chelating and hydrogen bonding [O(3), O(4)], or both chelating and bridging [O(1), O(2); O(8), O(9)]. For the dmae groups, chelating and hydrogen bonding [O(7), N(1)], chelating/bridging two metals [O(10), N(3)], and chelating/bridging three metals [O(11), N(2); O(12), N(3)] are all observed.

The differing bite angles of the two ligand types renders the coordination sphere of each barium irregular. That of Ba(1) can be described as a bicapped trigonal prism with O(2) and N(3) as the capping atoms (Figure 4a), even though the Ba(1)–O(2) bond is not one of the longer interactions involving this metal center. No simple polygon describes the coordination sphere of Ba(2) (Figure 4b). For comparison, H₂Ba₄(tmhd)₆(OCH₂CH₂OPr)₄ contains both eight- and nine-coordinate barium with bicapped trigonal prismatic and monocapped square prismatic geometries.¹⁹

There are no apparent trends in the Ba–O bond lengths, either with the coordination number at barium or the number of metal centers to which the ligand is bonded. This may be a result of an extremely congested molecule where bond lengths are dictated more by steric than electronic effects. It is noteworthy, however, that, for both barium centers, the coordination by nitrogen is weaker than any of the Ba–O interactions and that the Ba–N bonds are significantly longer for nine-coordinate Ba(2) than eight-coordinate Ba(1).

For cobalt, the coordination approaches that of a regular octahedron, and the three Co–O bonds involving dmae ligands are identical [1.896(2) Å] even though O(10) links only two metals, while O(11) and O(12) bridge three such centers. The longest Co–O bond involves the oxygen of the bridging acac ligand [Co(1)–O(8) 1.936(2) Å], while, as with barium, the Co–N bond is the longest [Co(1)–N(2) 2.033(3) Å] of the set of Co–X interactions (X = O, N).

The thin film deposited on the glass substrate by AACVD was studied by SEM and XRD. The thin film is generally reflecting and has good adhesion. The SEM photograph shown in Figure 5 indicates the deposition of dense microstructure with grain size ranging from 0.64 to 2.2 μm. The SEM image shows the crystallites with loss of perfect orientation.

The thin films of oxides show well-defined XRD patterns (Figure 6 and Table 2) of crystalline material. The 2θ peak pattern shows the decomposition of the complex yielding Ba₂CoO₃ as the orthorhombic crystalline phase with lattice parameters of $a = 9.6958 \pm 0.0210$ Å, $b = 5.5954 \pm 0.0028$ Å, $c = 4.7527 \pm 0.0036$ Å, and cell volume 257.846 ± 0.042 Å³. The FTIR of the residue obtained from TG studies show

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two peaks at 570 and 460 cm^{-1} indicating the presence of an O–Ba–O mode of vibration in Ba_2CoO_3 .²⁰

Conclusion

The $[\text{Ba}_2\text{Co}(\text{acac})_4(\text{dmae})_3(\text{dmaeH})]$ heterobimetallic complex of barium and cobalt was synthesized by simple chemical reaction between $\text{Ba}(\text{dmae})_2$ and $\text{Co}(\text{acac})_2$ with a molar ratio of 2:1 under mild conditions. The complex possesses a structure in which two barium atoms and a cobalt atom are bridged by dmae and acac groups. The barium centers are eight and nine coordinate with BaO_7N and BaO_7N_2 coordination spheres, while the cobalt atoms have a regular CoO_5N octahedral environment. This heterobime-

tallic complex has been used for metalloorganic chemical vapor deposition at 500 °C with a short sintering time. The XRD and SEM of the thin films show formation of Ba_2CoO_3 with an orthorhombic structure and grain size ranging from 0.64 to 2.2 μm .

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Supporting Information Available: Crystallographic data in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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