

Editor-in-Chief

ALAN H. COWLEY

The University of Texas at Austin



INORGANIC SYNTHESES

Volume 31



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INORGANIC SYNTHESSES

Volume 31



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PREFACE

The field of inorganic chemistry continues to thrive, as evidenced by the substantial volume of published literature as well as the large number of meetings and symposia that are devoted to the diverse aspects of this subject. *Inorganic Syntheses*, now in its thirty-first volume, plays an extremely important role in the burgeoning literature of inorganic chemistry. Indeed, in a time span exceeding half a century, *Inorganic Syntheses* has become recognized worldwide as *the* primary source for the preparation of a host of useful inorganic compounds. In large measure, this enviable reputation has come about because each preparation is checked completely independently in a laboratory other than that of the submitter(s).

The present volume features over 150 different preparations and the subject matter is divided into four chapters. By a slender margin, the largest number of preparations relate to main-group compounds, and these procedures have been grouped together in Chapter 1. Until relatively recently, main-group chemistry had been a somewhat neglected area of endeavor—particularly in the United States. Happily, this situation is now changing rapidly. One of the driving forces in the renaissance of main-group chemistry is the demand posed by the field of materials science. This trend is represented in Chapter 1 of this volume. The majority of the compounds for which preparations are described represent candidates for molecules-to-materials conversions. *A distinctive feature of this volume, therefore, is the presence of synthetic procedures for a number of important precursors.*

Chapter 2 is devoted both to the synthesis of important ligands and also to the preparation of useful reagents. The syntheses described range from a porphine and catalytically relevant phosphine ligands to relatively complex heteropolytungstate synthons. Organometallic chemistry remains a quintessentially strong area of chemistry and this interesting field is represented in Chapter 3. Finally, and in keeping with previous volumes of *Inorganic Syntheses*, the preparation of several complexes of the d- and f-block elements have been included in Volume 31 (Chapter 4).

Mindful of the many distinguished inorganic chemists who have served as Editor-in-Chief for *Inorganic Syntheses*, it has been an honor to function in this capacity. My sincere thanks are due to many individuals who have rendered invaluable assistance in the preparation of this volume. The list includes the authors and checkers of each article, the Editorial Board for their many helpful comments, and Tom Sloan of *Chemical Abstracts* for fastidious

work on nomenclature. Last, but certainly not least, I am indebted to Ms. Melissa Cabal and Ms. Jennifer Fernandez for their outstanding organizational and secretarial assistance.

ALAN H. COWLEY

Austin, Texas

NOTICE TO CONTRIBUTORS AND CHECKERS

The *Inorganic Syntheses* series is published to provide all users of inorganic substances with detailed and foolproof procedures for the preparation of important and timely compounds. Thus the series is the concern of the entire scientific community. The Editorial Board hopes that all chemists will share in the responsibility of producing *Inorganic Syntheses* by offering their advice and assistance in both the formulation of and the laboratory evaluation of outstanding syntheses. Help of this kind will be invaluable in achieving excellence and pertinence to current scientific interests.

There is no rigid definition of what constitutes a suitable synthesis. The major criterion by which syntheses are judged is the potential value to the scientific community. An ideal synthesis is one that presents a new or revised experimental procedure applicable to a variety of related compounds, at least one of which is critically important in current research. However, syntheses of individual compounds that are of interest or importance are also acceptable. Syntheses of compounds that are readily available commercially at reasonable prices are not acceptable. Corrections and improvements of syntheses already appearing in *Inorganic Syntheses* are suitable for inclusion.

The Editorial Board lists the following criteria of content for submitted manuscripts. Style should conform with that of previous volumes of *Inorganic Syntheses*. The introductory section should include a concise and critical summary of the available procedures for synthesis of the product in question. It should also include an estimate of the time required for the synthesis, an indication of the importance and utility of the product, and an admonition if any potential hazards are associated with the procedure. The Procedure should present detailed and unambiguous laboratory directions and be written so that it anticipates possible mistakes and misunderstandings on the part of the person who attempts to duplicate the procedure. Any unusual equipment or procedure should be clearly described. Line drawings should be included when they can be helpful. All safety measures should be stated clearly. Sources of unusual starting materials must be given, and, if possible, minimal standards of purity of reagents and solvents should be stated. The scale should be reasonable for normal laboratory operation, and any problems involved in scaling the procedure either up or down should be discussed. The criteria for judging the purity of the final product should be delineated clearly. The Properties section should supply and discuss those

physical and chemical characteristics that are relevant to judging the purity of the product and to permitting its handling and use in an intelligent manner. Under References, all pertinent literature citations should be listed in order. A style sheet is available from the Secretary of the Editorial Board.

The Editorial Board determines whether submitted syntheses meet the general specifications outlined above. Every procedure will be checked in an independent laboratory, and publication is contingent upon satisfactory duplication of the syntheses.

Each manuscript should be submitted in duplicate to the Secretary of the Editorial Board, Professor Jay H. Worrell, Department of Chemistry, University of South Florida, Tampa, FL 33620. The manuscript should be typewritten in English. Nomenclature should be consistent and should follow the recommendations presented in *Nomenclature of Inorganic Chemistry*, 2nd ed., Butterworths & Co, London, 1970 and in *Pure and Applied Chemistry*, Volume 28, No. 1 (1971). Abbreviations should conform to those used in publications of the American Chemical Society, particularly *Inorganic Chemistry*.

Chemists willing to check syntheses should contact the editor of a future volume or make this information known to Professor Worrell.

TOXIC SUBSTANCES AND LABORATORY HAZARDS

Chemicals and chemistry are by their very nature hazardous. Chemical reactivity implies that reagents have the ability to combine. This process can be sufficiently vigorous as to cause flame, an explosion, or, often less immediately obvious, a toxic reaction.

The obvious hazards in the syntheses reported in this volume are delineated, where appropriate, in the experimental procedure. It is impossible, however, to foresee every eventuality, such as a new biological effect of a common laboratory reagent. As a consequence, *all* chemicals used and *all* reactions described in this volume should be viewed as potentially hazardous. Care should be taken to avoid inhalation or other physical contact with all reagents and solvents used in this volume. In addition, particular attention should be paid to avoiding sparks, open flames, or other potential sources which could set fire to combustible vapors or gases.

A list of 400 toxic substances may be found in the *Federal Register*, Volume 40, No. 23072, May 28, 1975. An abbreviated list may be obtained from *Inorganic Syntheses*, Vol. 18, p. xv, 1978. A current assessment of the hazards associated with a particular chemical is available in the most recent edition of *Threshold Limit Values for Chemical Substances and Physical Agents in the Workroom Environment* published by the American Conference of Governmental Industrial Hygienists.

The drying of impure ethers can produce a violent explosion. Further information about this hazard may be found in *Inorganic Syntheses*, Volume 12, p. 317.

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Chapter One

MAIN GROUP COMPOUNDS

1. VOLATILE β -DIKETONATE COMPLEXES OF CALCIUM(II), STRONTIUM(II), AND BARIUM(II)

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Efficient, reproducible metal–organic chemical vapor deposition (MOCVD) processes¹ depend crucially upon the availability of high-purity metal–organic precursors with high and stable vapor pressure as well as predictable gas phase reactivity. For MOCVD routes to thin films of high- T_c superconducting (HTS) cuprate materials, the development of effective metal–organic alkaline earth (Ca^{2+} , Sr^{2+} , Ba^{2+}) precursors has presented a major challenge. The small charge-to-radius ratios and kinetic labilities of these ions has rendered encapsulation in sterically encumbered, nonpolar ligation environments, a prerequisite for favorable volatility, particularly difficult.² Initial MOCVD studies employed β -diketonates (acetylacetonates, dipivaloyl-methanates, heptafluorodimethyloctanedionates) which, in most cases, have oligomeric structures and less than satisfactory, unstable vapor pressure characteristics.^{2, 3}

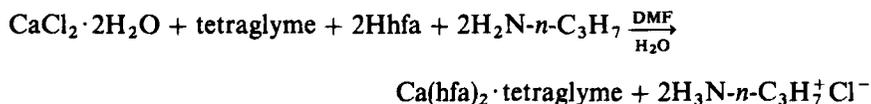
Complexes of the type $\text{M}(\text{hfa})_2 \cdot \text{L}$ [hfa = 1,1,1,5,5,5-hexafluoro-2,4-pentanedionato; M = Ca, Sr, and Ba; L = 2,5,8,11,14-pentaoxapentadecane (tetraglyme), 2,5,8,11-tetraoxadodecane(triglyme), and 2,5,8,11,14,17,20-heptaohaxheneicosane(hexaglyme)] were reported by Meinema et al.⁴

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These complexes exhibit high, stable vapor pressures compared to the aforementioned alkaline earth β -diketonates.⁵ The superior vapor pressure characteristics and thermal stability of the $M(\text{hfa})_2 \cdot \text{tetraglyme}$ complexes have been exploited in the MOCVD growth of high-quality thin films of the Y–Ba–Cu–O,⁶ Bi–Sr–Ca–Cu–O,⁷ and Tl–Ba–Ca–Cu–O⁸ HTS phases as well as of the ferroelectric perovskite BaTiO_3 .⁹ The reported syntheses of these complexes require the use of Schlenk techniques, dried hydrocarbon solvents, and expensive commercial alkaline earth reagents [$M(\text{hfa})_2 \cdot \text{H}_2\text{O}$ or $M\text{H}_2$] of limited purity.^{4, 5} High metal purity is of paramount importance in the formation of defect-free materials in the solid state.¹⁰ The MOCVD-derived films of BaTiO_3 , grown using a low-metal-purity (99%) $\text{Ba}(\text{hfa})_2 \cdot \text{tetraglyme}$ precursor, displayed semiinsulating electrical behavior ($\rho = 200\text{--}1000 \Omega \text{ cm}$). In contrast, a film grown with the high-metal-purity (99.999%) $\text{Ba}(\text{hfa})_2 \cdot \text{tetraglyme}$ precursor displayed insulating electrical behavior ($\rho = 10^6\text{--}10^7 \Omega \text{ cm}$) comparable to reported resistivity values of $10^7\text{--}10^8 \Omega \text{ cm}$.¹¹ Meinema et al.⁴ reported 75–88% yields for the synthesis of $M(\text{hfa})_2 \cdot L$ complexes ($M = \text{Sr}$ and Ba , $L = \text{tetraglyme}$; $M = \text{Ba}$, $L = \text{hexaglyme}$; $M = \text{Ca}$, $L = \text{triglyme}$) by reaction of commercial $M(\text{hfa})_2 \cdot \text{H}_2\text{O}$ complexes with the appropriate L in toluene solution, followed by recrystallization of the product from pentane. Kirilin et al.⁵ reported a 40% yield of $\text{Ba}(\text{hfa})_2 \cdot \text{tetraglyme}$ by treating uncomplexed Hhfa with a suspension of commercial BaH_2 in tetraglyme and rinsing the product with pentane for purification. We present here an efficient (total synthesis time < 48 h), aqueous synthesis of $M(\text{hfa})_2 \cdot \text{tetraglyme}$ complexes ($M = \text{Ca}$, Sr , and Ba) from Hhfa and the metal chlorides or nitrates. This economical procedure affords high yields and offers the possibility of incorporating high-purity (99.999% or greater) metal salts as starting reagents.

A. BIS(1,1,1,5,5,5-HEXAFLUORO-2,4-PENTANEDIONATO-*O,O'*)-CALCIUM(II) (2,5,8,11,14-PENTAOXAPENTADECANE-*O,O',O'',O''',O''''*)



Procedure

■ **Caution.** 1,1,1,5,5,5-Hexafluoro-2,4-pentanedione (*Hhfa*) and $\text{Ba}(\text{NO}_3)_2$ are considered hazardous. Avoid skin contact and inhalation. *Hhfa* is a volatile, noxious liquid and must be handled in a fume hood. $\text{Ba}(\text{NO}_3)_2$ is toxic; $\text{LD}_{50} = 355 \text{ mg/kg}$, $\text{OSHA (PEL)} = 0.5 \text{ mg Ba/m}^3$; $\text{ACVGIH (TLV)} = 0.5 \text{ mg Ba/m}^3$.

To a 1-L, round-bottomed flask containing 150 mL dimethylformamide (DMF)* and a magnetic stirring bar is added 6.15 g (0.042 mol) of 99.997% $\text{CaCl}_2 \cdot x\text{H}_2\text{O}^\dagger$, 9.30 g (0.042 mol) of 99% 2,5,8,11,14-pentaoxapentadecane (tetraglyme),* and 100 mL deionized, distilled water. This mixture is stirred until the calcium salt has dissolved. In a separate 500-mL Erlenmeyer flask containing 100 mL DMF and a magnetic stirring bar is added 17.40 g (0.084 mol) freshly distilled 1,1,1,5,5,5-hexafluoro-2,4-pentanedione (Hhfa) [$\text{bp}_{760} = 60\text{--}70^\circ\text{C}$][‡] and 4.94 g (0.084 mol) 98% *n*-propylamine* with stirring. The Hhfa plus amine solution is added to the stirring Ca^{2+} solution over a period of 30 s. The solvent is then removed using a rotary evaporator until a yellow slurry remains (~ 30 mL volume). Approximately 350 mL deionized, distilled water is then added to the slurry, and the resulting mixture is stirred vigorously for 5 min, at which time the precipitate is collected via suction filtration. This rinse/stir/filtration step is repeated twice. The collected solid is set aside and allowed to dry in air overnight.

Purification

A standard Dailey Pyrex sublimator[§] equipped with a water-cooled cold finger is charged with 19.57 g (0.029 mol) crude pale-yellow solid. The sublimator is evacuated to 4×10^{-3} torr and then heated to 90°C with an oil bath. After 8 h, the white solid on the cold finger is scraped off and subjected to a second sublimation cycle. After the second sublimation cycle, the white solid on the cold finger is collected (scraped off) under ambient conditions, yielding 18.17 g (0.027 mol), 64% $\text{Ca}(\text{hfa})_2 \cdot \text{tetraglyme}$, based on 6.15 g (0.042 mol) of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$.

Anal. Calcd. for $\text{C}_{20}\text{H}_{24}\text{O}_9\text{F}_{12}\text{Ca}$: C, 35.51; H, 3.58. Found: C, 35.49; H, 3.48.

Properties

The colorless crystals (mp $94\text{--}95^\circ\text{C}$) of $\text{Ca}(\text{hfa})_2 \cdot \text{tetraglyme}$ are air-stable and nonhygroscopic. The ^1H NMR spectrum (CDCl_3 solution) exhibits a singlet at δ 3.25 ppm corresponding to the terminal methyl groups of tetraglyme, multiplets at δ 3.41, 3.60, and 3.76 ppm corresponding to the internal methylene groups of tetraglyme, and a singlet at δ 5.92 ppm corresponding to the methine proton of hexafluoroacetylacetonate. A TGA scan (50-mg sample, N_2 atmosphere; temperature ramp, $10^\circ\text{C}/\text{min}$) gives $T_{50} = 248^\circ\text{C}$ with 3%

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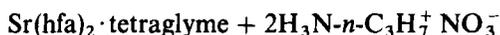
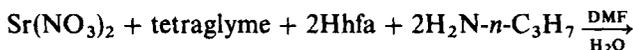
[†] AESAR, Johnson Matthey, P.O. Box 8247, Ward Hill, MA 01835-0747.

[‡] Genzyme, Hollands Road, Haverhill Suffolk, CB9 8PU, England.

[§] Catalog number CG-2100, Chemglass, 3861 North Mill Road, Vineland, NJ 08360.

residue to 350°C.† (Note: T_{50} is defined as the temperature at which 50% of the initial weight of the sample is lost.)

B. BIS(1,1,1,5,5,5-HEXAFLUORO-2,4-PENTANEDIONATO-*O,O'*)-STRONTIUM(II) (2,5,8,11,14-PENTA OXAPENTADECANE-*O,O',O'',O''',O''''*)



Procedure

To a 1-L round-bottomed flask containing 200 mL DMF* and a magnetic stirring bar is added 9.56 g (0.045 mol) of 99.9965% $\text{Sr}(\text{NO}_3)_2$,† 10.04 g (0.045 mol) of 99% 2,5,8,11,14-pentaoxapentadecane (tetraglyme),* and 100 mL distilled, deionized water. This mixture is stirred until the strontium salt has dissolved. In a separate 500-mL Erlenmeyer flask containing 100 mL DMF and a magnetic stirring bar is added 18.79 g (0.090 mol) distilled 1,1,1,5,5,5-hexafluoro-2,4-pentanedione (Hhfa) [bp₇₆₀ = 69–70°C]‡ and 5.34 g (0.090 mol) 98% *n*-propylamine* with stirring. The Hhfa plus amine solution is added to the stirring Sr^{2+} solution over a period of 30 s. The solvent is then removed using a rotary evaporator until a yellow slurry remains (~30 mL volume). Approximately 350 mL deionized, distilled water is then added to the slurry, and the resulting mixture is stirred vigorously for 5 min, at which time the precipitate is collected via suction filtration. This rinse/stir/filtration step is repeated twice. The collected solid is set aside and allowed to dry in air overnight.

Purification

A standard Dailey Pyrex sublimers[§] equipped with a water-cooled cold finger is charged with 24.88 g (0.034 mol) crude pale-yellow solid. The sublimers is evacuated to 4×10^{-3} torr and then heated to 110°C with an oil bath. After 8 h, the white solid on the cold finger is scraped off and subjected to a second sublimation cycle. After the second sublimation cycle, the white solid on

† For a 5-mg sample, the checkers found that $T_{50} = 181^\circ\text{C}$ with 1% residue to 350°C.

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‡ Genzyme, Holland Road, Haverhill Suffolk, CB9 8PU, England.

§ Catalog number CG-2100, Chemglass, 3861 North Mill Road, Vineland, NJ 08360.

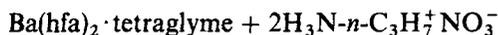
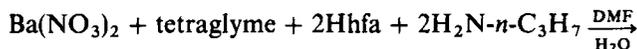
the cold finger is collected (scraped off) under ambient conditions, yielding 23.62 g (0.033 mol), 72% $\text{Sr}(\text{hfa})_2 \cdot \text{tetraglyme}$, based on 9.56 g (0.045 mol) $\text{Sr}(\text{NO}_3)_2$.

Anal. Calc. for $\text{C}_{20}\text{H}_{24}\text{O}_9\text{F}_{12}\text{Sr}$: C, 33.18; H, 3.34. Found: C, 33.21; H, 3.24.

Properties

The colorless crystals (mp 134–135°C) of $\text{Sr}(\text{hfa})_2 \cdot \text{tetraglyme}$ are air-stable and nonhygroscopic. The ^1H NMR spectrum (CDCl_3 solution) exhibits a singlet at δ 3.32 ppm corresponding to the terminal methyl groups of tetraglyme, multiplets at δ 3.42, 3.56, and 3.75 ppm corresponding to the internal methylene groups of tetraglyme, and a singlet at δ 5.86 ppm corresponding to the methine proton of hexafluoroacetylacetonate. A TGA scan (50 mg, N_2 atmosphere; temperature ramp, 10°C/min) gives $T_{50} = 260^\circ\text{C}$ with 4% residue to 350°C.*

C. BIS(1,1,1,5,5,5-HEXAFLUORO-2,4-PENTANEDIONATO-*O,O'*)-BARIUM(II) (2,5,8,11,14-PENTAOXAPENTADECANE-*O,O',O'',O''',O''''*)



Procedure

To a 1-L, round bottomed flask containing 200 mL DMF^\dagger and a magnetic stirring bar is added 14.92 g (0.057 mol) of 99.999% $\text{Ba}(\text{NO}_3)_2$,[‡] 12.69 g (0.057 mol) of 99% 2,5,8,11,14-pentaoxapentadecane (tetraglyme),[†] and 100 mL distilled, deionized water. This mixture is stirred until the barium salt has dissolved. In a separate 500-mL Erlenmeyer flask containing 100 mL DMF and a magnetic stirring bar is added 23.75 g (0.114 mol) distilled 1,1,1,5,5,5-hexafluoro-2,4-pentanedione (Hhfa) [$\text{bp}_{760} = 69\text{--}70^\circ\text{C}$][§] and 6.75 g (0.114 mol) 98% *n*-propylamine[†] with stirring. The Hhfa plus amine solution is added to the stirring Ba^{2+} solution over a period of 30 s. The solvent is then removed using a rotary evaporator until a yellow slurry

* For a 5-mg sample, the checkers found that $T_{50} = 194^\circ\text{C}$ with 1% residue to 350°C.

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[§] Genzyme, Hollands Road, Haverhill Suffolk, CB9 8PU, England.

remains (~ 30 mL volume). Approximately 350 mL deionized, distilled water is then added to the slurry, and the resulting mixture is stirred vigorously for 5 min, at which time the precipitate is collected via suction filtration. This rinse/stir/filtration step is repeated twice. The collected solid is set aside and allowed to dry in air overnight.

Purification

A standard Pyrex sublimator* equipped with a water-cooled cold finger is charged with 29.01 g (0.037 mol) crude pale-yellow solid. The sublimator is evacuated to 4×10^{-3} torr and then heated to 130°C with an oil bath. After 8 h, the white solid on the cold finger is scraped off and subjected to a second sublimation cycle. After the second sublimation cycle, the white solid on the cold finger is collected (scraped off) under ambient conditions, yielding 27.92 g (0.036 mol), 63% Ba(hfa)₂ tetraglyme, based on 14.92 g (0.057 mol) Ba(NO₃)₂.

Anal. Calcd. for C₂₀H₂₄O₉ F₁₂Ba: C, 31.05; H, 3.13. Found: C, 31.19; H, 2.99.

Properties

The colorless crystals (mp 151–152°C) of Ba(hfa)₂·tetraglyme are air-stable and nonhygroscopic. The ¹H NMR spectrum (CDCl₃ solution) exhibits a singlet at δ 3.34 ppm corresponding to the terminal methyl groups of tetraglyme, multiplets at δ 3.45, 3.56, 3.73, and 3.80 ppm corresponding to the internal methylene groups of tetraglyme, and a singlet at δ 5.82 ppm corresponding to the methine proton of the hexafluoroacetylacetonate. A TGA scan (50 mg, N₂ atmosphere; temperature ramp, 10°C/min) gives T₅₀ = 260°C with 16% residue to 350°C.†

Acknowledgment

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* Catalog number CG-2100, Chemglass, 3861 North Mill Road, Vineland, NJ 08360.

† For a 5-mg sample, the checkers found that T₅₀ = 209°C with 2% residue to 350°C.

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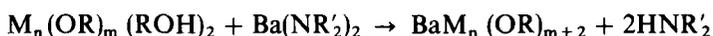
2. BIS(1,1,1,3,3,3-HEXAMETHYLDISILAZANATO)- BIS(TETRAHYDROFURAN)BARIUM

SUBMITTED BY ROGER L. KUHLMAN,* BRIAN A. VAARTSTRA,*
and KENNETH G. CAULTON*

CHECKED BY PAMELA S. TANNER† and TIMOTHY P. HANUSA†



Metal alkoxides are of interest as precursors to oxide materials with ceramic or electronic applications.¹ Barium incorporation in such a precursor is particularly interesting because of the known high- T_c superconductor, $\text{YBa}_2\text{Cu}_3\text{O}_7$. The title compound has vast possibilities for reactions of the type



and has already been used to form the mixed-metal alkoxides $\{\text{BaZr}_2(\text{O}^i\text{Pr})_{10}\}_2$ and $\text{BaZr}_4(\text{O}^i\text{Pr})_{18}$ in a reaction with $\text{Zr}_2(\text{O}^i\text{Pr})_8(\text{O}^i\text{PrOH})_2$.² This source of Ba^{2+} is ideal for these reactions, and generally in organometallic chemistry where an anhydrous, hydrocarbon-soluble reagent is required. The bulky disilazanide group was chosen to help stabilize barium in its atypically low coordination number. This ligand has been used successfully to stabilize other metals with low coordination number.³ The $\text{NH}_3(\text{g})$ catalyst apparently oxidizes the barium to Ba^{2+} , and the resulting barium amide is more finely divided than $\text{Ba}(\text{s})$, and is perhaps soluble in tetrahydrofuran (THF). A subsequent acid-base reaction with the silylamine regenerates $\text{NH}_3(\text{g})$, as the product forms, completing the catalytic cycle. The original report of this synthesis contains a more detailed description of this catalysis.⁴ Alternative syntheses involve transmetallation⁵ (a redox reaction between Ba^0 and $\text{Sn}[\text{N}(\text{SiMe}_3)_2]_2$) and preactivation of the elemental alkaline earth by its formation as a finely divided powder from BaI_2 and K .⁶ Subsequently, it has been reported that even the halide metathesis reaction $[\text{BaCl}_2$ and $\text{NaN}(\text{SiMe}_3)_2]$ succeeds in good yield, although this product was reported to be only slightly soluble in hydrocarbon solvents.⁷ The synthesis reported here is generally the most cost-effective, because it uses hexamethyldisilazane as starting material, which is much cheaper than commercially available silazides.

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Procedure

All manipulations are done under a nitrogen atmosphere using standard Schlenk techniques unless otherwise noted.⁸ Tetrahydrofuran is dried and distilled before use. Barium granules (Alfa, up to ~0.8 cm on an edge), and 1,1,1,3,3,3-hexamethyldisilazane (Aldrich) are used as received without further purification. In a dry box, 4.00 g (29.1 mmol) of barium granules are added to a 300-mL, round-bottomed, 3-neck flask equipped with stir bar, vacuum adapter, and rubber septum. The flask is then removed from the dry box and attached to a Schlenk line in a well-ventilated hood. The barium is then covered with 24 mL (113.8 mmol) of $\text{HN}(\text{SiMe}_3)_2$ via syringe, followed by 24 mL of THF. Access to nitrogen is closed off, and $\text{NH}_3(\text{g})$ ■ (**Caution! Use an efficient hood!**) is bubbled into the liquid via a syringe needle through the septum for 5 min with constant stirring. The flow of $\text{NH}_3(\text{g})$ is monitored by allowing it to escape into the hood through a bubbler filled with Nujol. The evolution of bubbles at the surface of the barium indicates that the reaction is initiated, and the $\text{NH}_3(\text{g})$ flow is no longer needed. In the event that no H_2 bubbles evolve, the treatment with $\text{NH}_3(\text{g})$ can be repeated. The $\text{NH}_3(\text{g})$ flow is then reduced to a slow trickle, and the mixture is stirred for 18 h. The mixture typically turns a dark purple color within 30 min of beginning the $\text{NH}_3(\text{g})$ flow. The mixture is again treated with a more rapid flow of $\text{NH}_3(\text{g})$, at 5-min intervals, until no more bubbles evolve (i.e., until the reaction is complete). Typically, four or five of these final $\text{NH}_3(\text{g})$ treatments are employed, at 20-min intervals. The volume is then reduced to about 10 mL in vacuo, and 100 mL of pentane (or hexanes) is added. The mixture is warmed and stirred to aid dissolution. At this point the reaction mixture is a light yellow solution, with insoluble purple Ba and $\text{Ba}(\text{NH}_2)_2$ impurities. These impurities are removed by filtration into a flame-dried Schlenk flask that is fitted with a filter frit. The mixture is transferred via cannula through a septum fitted to the top of a sintered glass filter stick. The residue is then disposed of appropriately ■ (**Caution! Barium is toxic! Wear gloves!**). The solvent of the filtrate is removed in vacuo, leaving 14.1 g (80.2%) of a white powder which is the title compound. If necessary, the product can be recrystallized from cold pentane with only minimal loss in yield.

Properties

The product is a white powder, soluble in benzene, toluene, pentane, and hexane. It is most conveniently recognized by its ^1H NMR spectrum (toluene- d_8): δ 3.52 (m, 8 H), 1.40 (m, 8 H), 0.28 (s, 36 H).⁹ The product also shows three peaks in its $^{13}\text{C}\{^1\text{H}\}$ NMR (toluene- d_8): δ 68.62(s), 25.46(s),

5.60(s). When redissolved in toluene (the solvent must have a higher boiling point than THF) and stripped to dryness, the compound loses one coordinated THF molecule to yield the dimer $\{\text{Ba}[\text{N}(\text{SiMe}_3)_2]_2(\text{THF})\}_2$. ^1H NMR (toluene- d_8): δ 3.49 (m, 4 H), 1.38 (m, 4 H), 0.26 (s, 36 H). $^{13}\text{C}\{^1\text{H}\}$ NMR (toluene- d_8): δ 68.61 (s), 25.35(s), 5.52(s). Alternately, the product can be isolated with no coordinated THF by sublimation onto a water-cooled cold finger, using heat from an IR lamp⁸ and a vacuum of about 50 mtorr. This product is also a dimer, $\{\text{Ba}[\text{N}(\text{SiMe}_3)_2]_2\}_2$. ^1H NMR (toluene- d_8): δ 0.19(s). ^{13}C NMR (toluene- d_8): δ 5.39(s). The structures of all three compounds,⁴ variable temperature and multinuclear NMR, and vibrational and mass spectra⁵ have been reported. The title compound is perhaps the most convenient in terms of "shelf life," since progressive removal of solvent molecules makes subsequent products increasingly susceptible to decomposition by air and moisture. This variable solvent loss and extreme hydrolytic sensitivity have frustrated the use of elemental analysis as a proof of purity.

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9. Integration of the ^1H NMR spectrum by the checkers showed 1.92 THF molecules per barium.

3. AMMONIUM AND BARIUM SALTS OF THE TRIS[1, 2-BENZENEDIOLATE(2-)-O,O']TITANIUM(IV) DIANION

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CHECKED BY CORTLANDT G. PIERPONT‡

Alkaline earth metal salts of the tris(catecholate)titanium(IV)[§] dianion have been used as precursors to titanate ceramics with controlled stoichiometries.^{1, 2} The acid, $H_2[Ti(cat)_3]$ (cat = dianion of catechol)[§], has been prepared from titanium tetrachloride in a nonaqueous medium and has been shown¹ to react with barium carbonate to generate $Ba[Ti(cat)_3]$, which is a precursor to $BaTiO_3$. Other salts of the tris(catecholate)titanium(IV) dianion (e.g., Sr, Ca, and Pb) have also been used as precursors to the corresponding titanate ceramics. The patent literature² contains a description of the synthesis of $[NH_4]_2[Ti(cat)_3]$ from tetraisopropoxytitanium(IV) and the subsequent formation of $BaTiO_3$ via generation and pyrolysis of the barium salt. Syntheses of the complex $[NH_4]_2[Ti(cat)_3]$ (and closely related hydrates) have been described where both "hydrous titanium dioxide" [formally $Ti(OH)_4$] and $TiCl_4$ have been employed as starting materials.^{3, 4} The source of titanium for the syntheses described here is titanium dioxide, which is depolymerized by acid digestion. Acid-digestion techniques are routinely used by ceramists and present less of an obstacle than the use of a volatile, reactive material such as $TiCl_4$. The following procedures for the preparation of $[NH_4]_2[Ti(cat)_3] \cdot 2H_2O$ and its conversion to $Ba[Ti(cat)_3] \cdot 3H_2O$ have been developed^{5, 6} to provide the ceramist with a route to these ceramic precursors that employs no organic solvents and that avoids the use of ill-defined reagents such as hydrous titanium oxide or volatile reagents such as $TiCl_4$ and $Ti(O-i-Pr)_4$. The precursors described here are air-stable solids under normal conditions and require no special handling techniques. Similar methods to those described may be employed⁷ to generate other salts of the $[Ti(cat)_3]^{2-}$ ion and related strategies lead to catecholate precursors of ceramics based on Zr, Bi, Sn, and so on.⁶

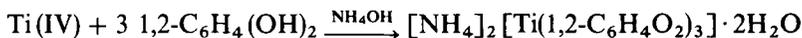
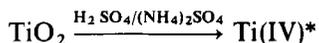
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§ Throughout this manuscript catechol = 1,2-benzenediol and catecholate = 1,2-benzenediolate (2-)-O,O'.

**A. AMMONIUM TRIS[1, 2-BENZENEDIOLATE(2-)-O,O']
TITANIUM(IV) DIHYDRATE**



Procedure

Titanium dioxide (1.04 g, 13 mmol), ammonium sulfate (16.8 g, 127 mmol), and concentrated sulfuric acid (43 mL; 95.6% w/w; 35.87 N) are loaded into a 100-mL round-bottomed flask equipped with an air condenser and heated using a sand bath and Bunsen burner until a clear, yellow solution is obtained (note that appropriate safety measures must be employed when handling sulfuric acid at high temperatures). The addition of ammonium sulfate to elevate the boiling point of the sulfuric acid solvent is critical for effective dissolution of the titanium dioxide reagent. With a sand bath temperature of about 500°C, dissolution takes 4–8 h depending upon the nature of the TiO₂ employed. Anatase, rutile, and mixtures of anatase and rutile may be depolymerized effectively by this method. The solution is then allowed to cool to room temperature, at which point it is clear and colorless. The concentrated acid solution is then added carefully to distilled water (130 mL) and the diluted solution is transferred to a 250-mL bypass-dropping funnel.

Separately, concentrated ammonium hydroxide solution (400 mL) is taken in a 1-L, three-necked, round-bottomed flask equipped with the bypass-dropping funnel, a nitrogen inlet, and a glass stopper, and containing a magnetic stirrer bar. The ammonium hydroxide solution is deaerated by bubbling with nitrogen for 1 h. Catechol (4.31 g, 39 mmol) is added and the contents are stirred under nitrogen until a clear solution results. The acid solution is then added from the bypass-dropping funnel over a period of 5 min while the contents of the flask are stirred under nitrogen. During the addition, a red suspension is produced and this is stirred for an additional 4 h at room temperature. Stirring is then discontinued and the precipitate is allowed to settle. The solid product is isolated by filtration at a water pump and is allowed to air dry. The yield is 5.22 g (90%). If trace amounts of sulfate are present, they can be removed by washing the solid with cold isopropyl alcohol.

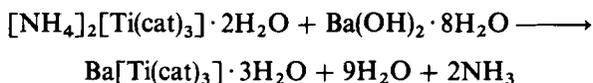
Anal. Calcd. for C₁₈H₂₄O₈N₂Ti: C, 48.66; H, 5.54; N, 6.31; Ti, 10.78; S, 0.0. Found: C, 47.80, 47.89; H, 5.35, 5.39; N, 6.60, 6.62; Ti, 11.01; S, 0.0%.

* Ti(IV) is presumably present as a sulfate complex such as [Ti(SO₄)₃]²⁻.

Properties

Ammonium tris(catecholate)titanium(IV) dihydrate is a rust-red solid that is soluble in water and in dimethyl sulfoxide. It is air-stable as a solid but requires storage under an inert atmosphere when in solution. It is insoluble in hexane, diethyl ether, and other nonpolar organic solvents. Identification of the product as a dihydrate is based upon thermogravimetric analysis where the complex is converted to titanium dioxide (identified by X-ray powder diffraction) by heating in air at 800°C for 12 h. The ^1H NMR spectrum of a DMSO- d_6 solution exhibits resonances due to the aromatic protons of the catecholate ligands (6.0–6.4 ppm; multiplet), the ammonium ion protons (7.2 ppm, singlet, broad), and the protons of the water of crystallization (3.3 ppm, singlet, broad). The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum in the same solvent exhibits three resonances at 109.8, 115.8, and 160.0 ppm due to the carbon atoms of the coordinated catecholate ligands. The IR spectrum⁴ exhibits broad features due to the ammonium ion and the water of crystallization at about 3700–2800 cm^{-1} and sharp bands due to the catecholate ligands in the region below 1600 cm^{-1} . A cyclic voltammogram of the complex measured in aqueous 1M KCl exhibits a single reversible wave at -1.38 V (vs. Ag/AgCl), indicating the absence of detectable dinuclear species in solution.⁴

**B. BARIUM TRIS[1,2-BENZENEDIOLATE(2-)-
O,O']TITANIUM(IV) TRIHYDRATE**

*Procedure*

Ammonium tris(catecholate)titanium(IV) dihydrate (0.41 g, 0.92 mmol) is dissolved in distilled water (50 mL) in a 100-mL, round-bottomed flask containing a magnetic stirrer bar. $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ (0.29 g, 0.92 mmol) is added to the flask, which is then fitted with a water-cooled condenser and heated by an oil bath at 60–70°C for 2 h with stirring. The resulting brown suspension is allowed to cool at room temperature and is filtered at a water pump to produce a clear solution. The solution is then evaporated to dryness, at room temperature, using a vacuum-line, producing a brown solid. The yield is 0.37 g (72%).

Anal. Calcd. for $\text{C}_{18}\text{H}_{18}\text{O}_9\text{TiBa}$: C, 38.36; H, 3.22; N, 0.00; Ti, 8.50. Found: C, 38.34; H, 3.01; N, 0.50; Ti, 8.39%.

Properties

Barium tris(catecholate)titanium(IV) trihydrate is a brown solid that is soluble in water and in dimethyl sulfoxide. It is air-stable as a solid but requires storage under an inert atmosphere when in solution. It is insoluble in hexane, diethyl ether, and other nonpolar organic solvents. Identification of the product as a trihydrate is based upon thermogravimetric analysis where the complex is converted to barium titanate (identified by X-ray powder diffraction) by heating in air at 800°C for 12 h. Despite variable, low levels of nitrogen in the combustion analysis of the barium salt, the X-ray powder diffraction pattern of the calcined material conforms exactly to that of tetragonal BaTiO₃. No other phases such as BaO, TiO₂, or other compounds in the BaO/TiO₂ system were detected. The presence of low levels of nitrogen in the combustion analyses of the barium salt thus does not interfere with its use as a precursor to BaTiO₃. The ¹H NMR spectrum of a D₂O solution exhibits resonances due to the aromatic protons of the catecholate ligands (6.2–6.4 ppm; multiplet). No resonance due to the ammonium ion protons is observed with either D₂O or DMSO-*d*₆ as the solvent. The ¹³C{¹H} NMR spectrum in D₂O exhibits three resonances at 111.8, 117.4, and 159.8 ppm due to the carbon atoms of the coordinated catecholate ligands. The IR spectrum shows that the broad band at about 3000–2600 cm⁻¹ due to the ammonium ions is no longer present. There is a broad band at about 3500 cm⁻¹ that is attributed to water of crystallization. Sharp bands due to the catecholate ligands appear in the region below 1600 cm⁻¹ (the checkers found that the product sometimes showed a weak band in the 650-cm⁻¹ region that may be associated with a Ba₂[TiO(cat)₂]₂ contaminant present at low level). A cyclic voltammogram of the complex measured in aqueous 1M KCl exhibits a single reversible wave at -1.40 V (vs. Ag/AgCl), indicating the absence of detectable dinuclear or titanyl species in solution.⁴

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