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(54) Title: LEWIS BASE ADDUCTS OF ANHYDROUS MONONUCLEAR TRIS(BETA-DIKETONATE) BISMUTH COMPOSITIONS FOR DEPOSITION OF BISMUTH-CONTAINING FILMS, AND METHOD OF MAKING THE SAME

(57) Abstract

Anhydrous mononuclear Lewis base adducted tris(β-diketonato) bismuth complexes, useful as precursors for chemical vapor deposition of bismuth, for producing Bi-containing films of significantly improved stoichiometry, morphology and functional character, as compared to films obtained from dinuclear tris(β-diketonato) bismuth complexes of the prior art.

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# LEWIS BASE ADDUCTS OF ANHYDROUS MONONUCLEAR TRIS(BETA-DIKETONATE) BISMUTH COMPOSITIONS FOR DEPOSITION OF BISMUTH-CONTAINING FILMS, AND METHOD OF MAKING THE SAME

## BACKGROUND OF THE INVENTION

### Field Of The Invention

This invention relates to the synthesis and production of Lewis base adducts of anhydrous mononuclear tris(β-diketonate) bismuth compositions e.g., anhydrous mononuclear tris-(2,2,6,6-tetramethyl-3,5-heptanedionato) bismuth *N,N,N'N'*-tetramethylethylenediamine adduct. Such bismuth-containing compositions have utility as precursors for chemical vapor deposition of bismuth, bismuth oxide, bismuth-containing oxides and bismuth-containing chalcogonides.

### Description of the Related Art

Ferroelectric random access memories (FRAMs) rely on high-integrity ferroelectric thin-films as critical components of memory cell architecture.

Electrical performance of ferroelectric oxides such as $SrBi_2Ta_2O_9$ (SBT) show a strong dependence on the identity of the precursor used in depositing the Bi component in the ferroelectric material. For example, the use of a Bi precursor such as triphenyl bismuth results in poor stoichiometric control, high substrate temperatures to decompose the precursor, strong surface dependence, and extreme dependence of the precursor incorporation efficiency on reactor pressure and partial pressure of oxygen during deposition.

To ameliorate the foregoing deficiencies, the art has continued to seek other bismuth precursors.

One such bismuth-containing precursor candidate is tris(2,2,6,6-tetramethyl-3,5-heptanedionato) bismuth tetramethylethylenediamine adduct. As used hereinafter, the ligand "2,2,6,6-tetramethyl-3,5-heptanedionato" is sometimes referred to by the designation "thd" and the tetramethylethylenediamine adduct is sometimes referred to by the designation "tmeda."

It is an object of the present invention to provide an improved class of bismuth precursors for deposition of Bi for applications such as ferroelectric thin film devices, chalcogonides and thermoelectric films.

Other objects and advantages of the present invention will be more fully apparent from the ensuing disclosure and appended claims.

## SUMMARY OF THE INVENTION

The present invention relates to Lewis base adducts of anhydrous mononuclear tris(β-diketonate) bismuth compositions, and to a method of synthesis thereof. Such adducts of anhydrous mononuclear bismuth precursors have been discovered as novel compositions having unexpectedly superior properties in relation to dinuclear (β-diketonate) bismuth compositions of the prior art, in respect of their volatilization and deposition characteristics, which render the adducts of anhydrous mononuclear bismuth precursors of the present invention particularly suitable as CVD precursors. The adducts of anhydrous mononuclear bismuth compositions of the present invention therefore constitute a substantial advance in the art over the dinuclear tris(β-diketonate) bismuth precursors heretofore available.

The β-diketonato ligand of the anhydrous mononuclear tris(β-diketonate) bismuth compositions of the present invention may be any suitable type, including the illustrative β-diketonato ligand species set out in Table I below:

TABLE I

| β-diketonato ligand | Abbreviation |
|---|---|
| 2,2,6,6-tetramethyl-3,5-heptanedionato | thd |
| 1,1,1-trifluoro-2,4-pentanedionato | tfac |
| 1,1,1,5,5,5-hexafluoro-2,4-pentanedionato | hfac |
| 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionato | fod |
| 2,2,7-trimethyl-3,5-octanedionato | tod |
| 1,1,1,5,5,6,6,7,7,7-decafluoro-2,4-heptanedionato | dfhd |
| 1,1,1-trifluoro-6-methyl-2,4-heptanedionato | tfmhd |

The Lewis base adducts of the anhydrous mononuclear tris(β-diketonate) bismuth compositions of the present invention may be any suitable type, including at least one adduct ligand selected from the group consisting of: amines, ethers, glymes, aryls and aryl amines, more specifically, NH3, primary amines, secondary amines, tertiary amines, polyamines, monoglymes, diglymes, triglymes, tetraglymes, polyethers, aliphatic ethers, cyclic ethers, and more specifically, pyridine, toluene, tetrahydrofuran, *N,N,N',N'*-tetramethylethylenediamine and *N,N,N',N',N''*-pentamethyldiethylenetriamine.

The Lewis base adducts of the anhydrous mononuclear tris(β-diketonato) bismuth compositions of the invention have utility as precursors for the vapor-phase deposition of bismuth, as for example in the formation of ferroelectric thin films of $SrBi_2Ta_2O_9$ (SBT), or in the formation of superconducting films containing Bi. In such applications, the use of the adducted anhydrous mononuclear Bi source material provides for better

thermal transport and flash vaporization leading to Bi-containing films of significantly improved stoichiometry, morphology and ferroelectric/superconducting character. These same issues are important to chalcogonides, skutterudites and other Bi-containing materials.

The synthesis of Lewis base adducted anhydrous mononuclear tris(β-diketonato) bismuth complexes of the present invention may be prepared by reacting at least one equivalent of the Lewis base adduct compound with the mononuclear tris(β-diketonato) bismuth of the current art or the dinuclear tris(β-diketonato) bismuth of the prior art in an aprotic solvent medium, under anaerobic conditions followed by removal of the aprotic solvent medium. Purification of the isolated reaction product bismuth complex, e.g., by recrystallization, should also be carried out in an aprotic medium under anaerobic conditions.

In one aspect, the invention relates to an anhydrous mononuclear Lewis base adducted bismuth complex, comprising the formula:

$$Bi(A)_3 \cdot X$$

wherein:

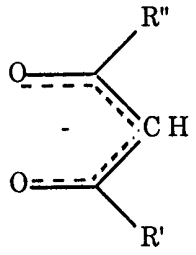
A comprises a β-diketonato ligand and X comprises a Lewis base adduct.

In another aspect the present invention relates to an anhydrous mononuclear Lewis base adducted bismuth complex, comprising the formula:

$$Bi(A)_3 \cdot X$$

wherein:

A comprises a β-diketonato ligand having the formula:



wherein:

R' and R" may be the same or different and are independently selected from H, $C_6$ - $C_{10}$ aryl, $C_6$ - $C_{10}$ fluoroaryl, $C_6$ - $C_{10}$ perfluoroaryl, $C_1$ - $C_6$ alkyl, $C_1$ - $C_6$ fluoroalkyl, and $C_1$ - $C_6$ perfluoroalkyl; and

X comprises at least one Lewis base adduct.

In another aspect the present invention relates to an anhydrous mononuclear Lewis base adducted bismuth complex, comprising the formula:

$$Bi(A)_3 \cdot X$$

wherein:

A comprises a β-diketonato ligand selected from the group consisting of: thd, tfac, hfac, fod, tod, dfhd, tfmhd; and

X comprises at least one Lewis base adduct selected from the group consisting of: amines, ethers, glymes, aryls and aryl amines, more specifically, NH3, primary amines, secondary amines, tertiary amines, polyamines, monoglymes, diglymes, triglymes, tetraglymes, polyethers, aliphatic ethers, cyclic ethers, and more specifically, pyridine, toluene, tetrahydrofuran, *N,N,N',N'*-tetramethylethylenediamine and *N,N,N',N',N"*-pentamethyldiethylenetriamine.

In one specific method aspect, the present invention relates to a method of synthesis of *N,N,N'N'*-tetramethylethylenediamine adducted anhydrous mononuclear tris(2,2,6,6-tetramethyl-3,5-heptanedionato) bismuth , by reaction of dinuclear tris(2,2,6,6-tetramethyl-3,5-heptanedionato) bismuth complex and *N,N,N'N'*-tetramethylethylenediamine in an aprotic solvent under anaerobic conditions.

In another specific method aspect, the present invention relates to a method of synthesis of *N,N,N',N','N''*-pentamethyldiethylenetriamine adducted anhydrous mononuclear tris(2,2,6,6-tetramethyl-3,5-heptanedionato) bismuth, by reaction of dinuclear tris(2,2,6,6-tetramethyl-3,5-heptanedionato) bismuth complex and *N,N,N',N','N''*-pentamethyldiethylenetriamine in an aprotic solvent under anaerobic conditions.

In another specific method aspect, the present invention relates to a method of synthesis of *N,N,N',N','N''*-pentamethyldiethylenetriamine adducted anhydrous mononuclear tris(2,2,6,6-tetramethyl-3,5-heptanedionato) bismuth, by reaction of anhydrous mononuclear tris(2,2,6,6-tetramethyl-3,5-heptanedionato) bismuth and *N,N,N',N','N''*-pentamethyldiethylenetriamine in an aprotic solvent under anaerobic conditions.

The *N,N,N'N'*-tetramethylethylenediamine adducted anhydrous mononuclear tris(2,2,6,6-tetramethyl-3,5-heptanedionato) bismuth precursor of the invention may be usefully employed for depositing bismuth or a bismuth-containing film on a substrate, by vaporizing the Lewis base adducted anhydrous mononuclear tris(β-diketonato) bismuth to form a vaporized precursor, and contacting the vaporized precursor with the substrate to deposit bismuth or a bismuth-containing film thereon.

Such deposition may employ liquid delivery and flash vaporization of the Lewis base adducted anhydrous mononuclear tris(β-diketonato) bismuth precursor to form the precursor vapor, and the deposition may be effected by various techniques such as chemical vapor deposition (CVD), including any of various assisted (e.g., plasma-assisted, photoactivated, ion beam-assisted, etc.) CVD methods.

Other aspects, features and embodiments of the invention will be more fully apparent from the ensuing disclosure and appended claims.

## BRIEF DESCRIPTION OF THE DRAWINGS

Figures 1 and 2 are x-ray crystallographic structural depictions reported in the literature (PRIOR ART) for the dinuclear bismuth complex [Bi(thd)3]2, which is a crystalline white solid with a melting point of 117 °C.

Figure 3 is a plot of precursor transport (TGA) and melting point (DSC) curves for a representative dinuclear bismuth complex [Bi(thd)3]2 of the prior art.

Figure 4 is a crystal structure determined from a single crystal diffraction analysis of solid *N,N,N'N'*-tetramethylethylenediamine adducted anhydrous mononuclear tris(2,2,6,6-tetramethyl-3,5-heptanedionato) bismuth of the present invention.

Figure 5 is a plot of precursor transport (TGA) and melting point (DSC) curves of single crystalline solid, *N,N,N'N'*-tetramethylethylenediamine adducted anhydrous mononuclear tris(2,2,6,6-tetramethyl-3,5-heptanedionato) bismuth prepared from dinuclear tris(2,2,6,6-tetramethyl-3,5-heptanedionato) bismuth.

Figure 6 is a plot of precursor transport (TGA) and melting point (DSC) curves of solid *N,N,N',N','N''*-pentamethyldiethylenetriamine adducted anhydrous mononuclear tris(2,2,6,6-tetramethyl-3,5-heptanedionato) bismuth prepared from dinuclear tris(2,2,6,6-tetramethyl-3,5-heptanedionato) bismuth.

Figure 7 is a plot of precursor transport (TGA) and melting point (DSC) curves of solid *N,N,N',N','N''*-pentamethyldiethylenetriamine adducted anhydrous mononuclear tris(2,2,6,6-tetramethyl-3,5-heptanedionato) bismuth prepared from mononuclear tris(2,2,6,6-tetramethyl-3,5-heptanedionato) bismuth.

## DETAILED DESCRIPTION OF THE INVENTION, AND PREFERRED EMBODIMENTS THEREOF

The present invention relates to the discovery of Lewis base adducts of anhydrous mononuclear forms of tris(β-diketonato) bismuth compositions, e.g., tris(2,2,6,6-tetramethyl-3,5-heptanedionato) bismuth *N,N,N'N'*-tetramethylethylenediamine, which overcome deficiencies of the prior art dinuclear bismuth complex $[Bi(thd)_3]_2$.

As a result of its mononuclear form, the Lewis base adduct bismuth complex of the present invention provides improved thermal transport and more controlled and reproducible gas-phase concentrations than are possible with the prior art dinuclear complexes. These characteristics provide the mononuclear bismuth complexes of the present invention with the ability to form Bi-containing films of superior stoichiometry, morphology and functional performance characteristics, in relation to the films of the prior art formed from the aforementioned dinuclear bismuth complex $[Bi(thd)_3]_2$.

As a precursor for the deposition of Bi or Bi-containing films, the previously commercially available dinuclear Bi-thd complex is markedly inferior in respect of its volatility, transport and vaporization properties, being less volatile and more easily decomposed during transport and flash vaporization than desired, and producing higher levels of residue in process equipment upstream of the deposition chamber. The ready susceptibility of the prior art dinuclear bismuth complex $[Bi(thd)_3]_2$ to decomposition of the precursor is severely detrimental in a liquid delivery flash vaporization process, where such decomposition leads to premature clogging of the vaporizer as well as undesirable changes in gas-phase concentrations during the deposition process. Such gas-phase concentration variations in turn yield undesirable gradients in deposited film thickness, and in film stoichiometry where the bismuth component is deposited in a multicomponent film.

Unexpectedly, the discovery of the Lewis base adducted mononuclear Bi(β-diketonate)$_3$ complexes of the present invention has provided a solution to such deficiencies of the prior art Bi(thd)$_3$ precursor material. The Lewis base adducted mononuclear Bi(β-diketonate)$_3$ complexes of the present invention are markedly superior to the corresponding dinuclear species, providing improved vaporizer performance, extended vaporizer lifetimes and better control of the Bi-containing film stoichiometry than [Bi(thd)$_3$]$_2$. As a result, the Lewis base adducted Bi(β-diketonate)$_3$ mononuclear complexes of the present invention lead to a more highly reproducible CVD process and improved quality of the deposited film, based on film stoichiometry and uniformity.

While the Lewis base adducted anhydrous mononuclear tris(β-diketonato) bismuth complexes of the present invention are usefully employed in a wide variety of chemical vapor deposition processes for the formation of bismuth-containing films, the complexes have particular utility as a precursor for the vapor-phase deposition of bismuth or bismuth oxide in the formation of ferroelectric thin films and Bi-based superconducting thin film materials. A most preferred use of such Lewis base adducted mononuclear tris(β-diketonato) bismuth complexes is in the formation of ferroelectric Bi-containing thin films for the manufacture of devices such as ferroelectric random access memories. The same materials may be used to deposit bismuth-containing chalcogonides and skutterudites.

The Lewis base adducted mononuclear tris(β-diketonato) bismuth complexes of the invention may be deposited in any suitable manner. For example, the bismuth deposition process may employ liquid delivery and flash vaporization of the Lewis base adducted anhydrous mononuclear tris(β-diketonato) bismuth precursor to form the precursor vapor, and the deposition itself may be effected by chemical vapor deposition (CVD), including any of various assisted (e.g., plasma-assisted) CVD methods, or in any other suitable manner. For purposes of liquid delivery, the Lewis base adducted anhydrous mononuclear tris(β-diketonato) bismuth may be dissolved in any suitable

solvent medium, e.g., a single solvent or a multicomponent solvent mixture, compatible with such bismuth reagent.

A suitable multicomponent solvent mixture for such purpose is a solvent composition comprising solvent species A, B and C, wherein A is a $C_6$-$C_8$ alkane, $C_6$-$C_{10}$ aryl, ether or cyclic ether, B is a $C_8$-$C_{12}$ alkane, and C is a glyme-based solvent (glyme, diglyme, tetraglyme, etc.), polyamine or arylamine in the proportion A:B:C wherein A is from about 2 to about 10 parts by volume, B is from about 0 to about 6 parts by volume, and C is from 0 to about 3 parts by volume. Preferred compositions of A include tetrahydrofuran, toluene and octane and C is often common to the Lewis base adduct of the tris(β-diketonato) bismuth species.

A highly preferred solvent composition of such type comprises octane, decane and a polyamine in approximately 5:4:1 proportion by volume.

Another highly preferred solvent system of such type comprises tetrahydrofuran and a polyamine in approximately 8:2 proportion by volume.

Polyamine species potentially useful as component C in the above-described solvent composition include *N,N,N',N'*-tetramethylethylenediamine, *N,N,N',N',N"*-pentamethyldiethylenetriamine, *N, N, N', N", N''', N'''*-hexamethyltriethylenetetramine, pyridine or other suitable polyamine component.

The composition of the present invention relates to an anhydrous mononuclear Lewis base adducted bismuth complex, comprising the formula:

$$Bi(A)_3 \cdot X$$

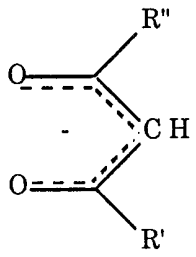
wherein A comprises a β-diketonato ligand and X comprises at least one Lewis base adduct.

More specifically the composition of the present invention relates to an anhydrous mononuclear Lewis base adducted bismuth complex, comprising the formula:

$$Bi(A)_3 \cdot X$$

wherein:

A comprises a β-diketonato ligand having the formula:




wherein:

R' and R" may be the same or different and are independently selected from H, $C_6$ - $C_{10}$ aryl, $C_6$ - $C_{10}$ fluoroaryl, $C_6$ - $C_{10}$ perfluoroaryl, $C_1$ - $C_6$ alkyl, $C_1$ - $C_6$ fluoroalkyl, and $C_1$ - $C_6$ perfluoroalkyl; and

X comprises at least one Lewis base adduct.

More specifically the composition of the present invention relates to an anhydrous mononuclear Lewis base adducted bismuth complex, comprising the formula:

$$Bi(A)_3 \cdot X$$

wherein:

A comprises a β-diketonato ligand selected from the group consisting of:

| | |
|---|---|
| 2,2,6,6-tetramethyl-3,5-heptanedionato | thd |
| 1,1,1-trifluoro-2,4-pentanedionato | tfac |
| 1,1,1,5,5,5-hexafluoro-2,4-pentanedionato | hfac |
| 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionato | fod |
| 2,2,7-trimethyl-3,5-octanedionato | tod |

| | |
|---|---|
| 1,1,1,5,5,6,6,7,7,7-decafluoro-2,4-heptanedionato | dfhd |
| 1,1,1-trifluoro-6-methyl-2,4-heptanedionato | tfmhd |

and X comprises at least one Lewis base adduct selected from the group consisting of: amines, ethers, glymes, aryls and aryl amines, more specifically, NH3, primary amines, secondary amines, tertiary amines, polyamines, monoglymes, diglymes, triglymes, tetraglymes, polyethers, aliphatic ethers, cyclic ethers, and more specifically, pyridine, toluene, tetrahydrofuran, *N,N,N',N'*-tetramethylethylenediamine and *N,N,N',N',N''*-pentamethyldiethylenetriamine.

In one specific method aspect, the present invention relates to a method of synthesis of *N,N,N'N'*-tetramethylethylenediamine adducted anhydrous mononuclear tris(2,2,6,6-tetramethyl-3,5-heptanedionato) bismuth , by reaction of dinuclear tris(2,2,6,6-tetramethyl-3,5-heptanedionato) bismuth complex and *N,N,N'N'*-tetramethylethylenediamine in an aprotic solvent under anaerobic conditions.

In another specific method aspect, the present invention relates to a method of synthesis of *N,N,N',N','N''*-pentamethyldiethylenetriamine adducted anhydrous mononuclear tris(2,2,6,6-tetramethyl-3,5-heptanedionato) bismuth, by reaction of dinuclear tris(2,2,6,6-tetramethyl-3,5-heptanedionato) bismuth complex and *N,N,N',N','N''*-pentamethyldiethylenetriamine in an aprotic solvent under anaerobic conditions.

In another specific method aspect, the present invention relates to a method of synthesis of *N,N,N',N','N''*-pentamethyldiethylenetriamine adducted anhydrous mononuclear tris(2,2,6,6-tetramethyl-3,5-heptanedionato) bismuth, by reaction of anhydrous mononuclear tris(2,2,6,6-tetramethyl-3,5-heptanedionato) bismuth and *N,N,N',N','N''*-pentamethyldiethylenetriamine in an aprotic solvent under anaerobic conditions.

The *N,N,N'N'*-tetramethylethylenediamine adducted anhydrous mononuclear tris(2,2,6,6-tetramethyl-3,5-heptanedionato) bismuth precursor of the invention may be usefully employed for depositing bismuth or a bismuth-containing film on a substrate, by vaporizing the Lewis base adducted anhydrous mononuclear tris(β-diketonato) bismuth to form a vaporized precursor, and contacting the vaporized precursor with the substrate to deposit bismuth or a bismuth-containing film thereon.

The synthesis of Lewis base adducted anhydrous mononuclear tris(β-diketonato) bismuth complexes of the present invention may be readily carried out in an aprotic solvent medium under anaerobic conditions, and at room temperature and pressure, by reacting at least one equivalent of the Lewis base adduct compound with the mononuclear tris(β-diketonato) bismuth of the current art or the dinuclear tris(β-diketonato) bismuth of the prior art in an aprotic solvent medium under anaerobic conditions for sufficient time and at sufficient temperature with subsequent removal of the aprotic solvent medium to yield said anhydrous mononuclear Lewis base adducted tris(β-diketonato) bismuth complex as a reaction product thereof. Purification of the isolated reaction product Lewis base adducted bismuth complex, e.g., by recrystallization, is also advantageously performed in an aprotic medium under anaerobic conditions.

The aprotic solvent may suitably comprise one or more alkanes such as pentane, hexanes, octane, or decane, aryl solvent species such as benzene or toluene, and/or any other suitable aprotic solvent(s) for solution of the mononuclear tris (β-diketonato) bismuth of the current art or the dinuclear tris (β-diketonato) bismuth of the prior art and Lewis base adduct starting materials, wherein such solvents do not preclude the reaction of such starting materials to form the Lewis base adducted mononuclear (β-diketonato) bismuth product.

The foregoing synthesis reaction is carried out under anaerobic conditions, i.e., in the substantial absence, and preferably substantially complete absence, of oxygen. Such

anaerobic conditions may for example comprise carrying out the reaction under inert or oxygen-free atmosphere, such as under a nitrogen or argon blanket over the reaction vessel containing the reactants and the aprotic solvent medium. Similarly, the solvents and reactants should be dry and free from water and other protic source constituents.

As an illustrative example of the foregoing synthesis, anhydrous mononuclear tris (2,2,6,6-tetramethyl-3,5-heptanedionato)bismuth *N,N,N'N'*-tetramethylethylenediamine adduct may be synthesized in accordance with the present invention by reaction of dinuclear tris (2,2,6,6-tetramethyl-3,5-heptanedionato)bismuth complex and *N,N,N'N'*-tetramethylethylenediamine in hexanes under a nitrogen gas environment.

Referring now to the drawings, Figures 1 and 2 are x-ray crystallographic structural depictions reported in the literature for the dinuclear bismuth complex $[Bi(thd)_3]_2$, which is a crystalline white solid with a melting point of 117°C. (Prior Art)

Figure 3 is a plot of precursor transport (TGA) and melting point (DSC) curves for a representative dinuclear bismuth complex [Bi(thd)3]2 of the prior art, having a melting point of 117°C. The literature has variously reported the melting point of such material as being in the range of 112-115°C. This material is inferior in precursor transport properties, as reflected by the TGA plot, showing a gradual weight loss over a wide temperature range during the STA examination.

Figure 4 is a crystal structure determined from a single crystal diffraction analysis of solid *N,N,N'N'*-tetramethylethylenediamine adducted anhydrous mononuclear tris(2,2,6,6-tetramethyl-3,5-heptanedionato) bismuth of the present invention.

Figure 5 is a plot of precursor transport (TGA) and melting point (DSC) curves of single crystalline solid, *N,N,N'N'*-tetramethylethylenediamine adducted anhydrous mononuclear tris(2,2,6,6-tetramethyl-3,5-heptanedionato) bismuth prepared from

dinuclear tris(2,2,6,6-tetramethyl-3,5-heptanedionato) bismuth. The material exhibits a melting point of about 136 °C.

Figure 6 is a plot of precursor transport (TGA) and melting point (DSC) curves of solid *N,N,N',N','N''*-pentamethyldiethylenetriamine adducted anhydrous mononuclear tris(2,2,6,6-tetramethyl-3,5-heptanedionato) bismuth prepared from dinuclear tris(2,2,6,6-tetramethyl-3,5-heptanedionato) bismuth. The material exhibits a melting point of about 73°C.

Figure 7 is a plot of precursor transport (TGA) and melting point (DSC) curves of solid *N,N,N',N','N''*-pentamethyldiethylenetriamine adducted anhydrous mononuclear tris(2,2,6,6-tetramethyl-3,5-heptanedionato) bismuth prepared from mononuclear tris(2,2,6,6-tetramethyl-3,5-heptanedionato) bismuth. The material exhibits a melting point of about 73°C.

Single crystal x-ray diffraction structural determination conclusively shows the Lewis base adducted $Bi(thd)_3$ material of the present invention to be of mononuclear form. Such material is prepared by addition of the mononuclear tris(β-diketonato) bismuth of the current art or the dinuclear tris(β-diketonato) bismuth of the prior art and Lewis base adduct starting materials, as shown in the plots of Figures 6 & 7 wherein both materials exhibit a melting point of about 73°C. The prior art literature reports an x-ray crystal structure which is a dinuclear complex, $[Bi(thd)_3]_2$, with excess H(thd) ligand in the crystal lattice.

The Lewis base adducted $Bi(thd)_3$ material of the present invention thus is a mononuclear complex heretofore unknown, and represents a significant advance in the art in the provision of a precursor material having highly attractive characteristics for vaporization, vapor-phase transport, and bismuth deposition, in a wide variety of applications in which bismuth or bismuth-containing films are employed in the fabrication of microelectronic, ferroelectric and superconducting devices or structures.

Although the invention has been variously disclosed herein with reference to illustrative embodiments and features, it will be appreciated that the embodiments and features described hereinabove are not intended to limit the invention, and that other variations, modifications and other embodiments will suggest themselves to those of ordinary skill in the art. The invention therefore is to be broadly construed, consistent with the claims hereafter set forth.

**What Is Claimed Is:**

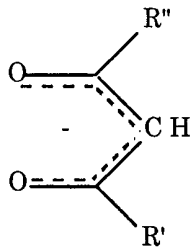
1. Anhydrous mononuclear Lewis base adducted tris(β-diketonato) bismuth.

2. An anhydrous mononuclear Lewis base adducted bismuth complex, comprising the composition:

$$Bi(A)_3 \cdot X$$

wherein A comprises a β-diketonato ligand and X comprises at least one Lewis base adduct.

3. The β-diketonato ligand according to claim 2 comprising the composition:




wherein R' and R" may be same or different and are independently selected from the group consisting of H, H, $C_6$ - $C_{10}$ aryl, $C_6$ - $C_{10}$ fluoroaryl, $C_6$ - $C_{10}$ perfluoroaryl, $C_1$-$C_6$ alkyl $C_1$-$C_6$ perfluoroalkyl and $C_1$-$C_6$ perfluoroalkyl.

4. The anhydrous mononuclear Lewis base adducted bismuth complex according to claim 2 wherein the β-diketonato ligand is selected from the group consisting of:

2,2,6,6-tetramethyl-3,5-heptanedionato;
1,1,1-trifluoro-2,4-pentanedionato;
1,1,1,5,5,5-hexafluoro-2,4-pentanedionato;
6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionato;
2,2,7-trimethyl-3,5-octanedionato;

1,1,1,5,5,6,6,7,7,7-decafluoro-2,4-heptanedionato; and
1,1,1-trifluoro-6-methyl-2,4-heptanedionato.

5. The anhydrous mononuclear Lewis base adducted bismuth complex according to claim 2 wherein the Lewis base adduct is selected from the group consisting of: amines, ethers, glymes, aryls and aryl amines.

6. The anhydrous mononuclear Lewis base adducted bismuth complex according to claim 2 wherein the Lewis base adduct is selected from the group consisting of: NH3, primary amines, secondary amines, tertiary amines and polyamines.

7. The anhydrous mononuclear Lewis base adducted bismuth complex according to claim 2 wherein the Lewis base adduct is selected from the group consisting of: monoglymes, diglymes, triglymes, tetraglymes, aliphatic ethers, polyethers, and cyclic ethers.

8. The anhydrous mononuclear Lewis base adducted bismuth complex according to claim 2 wherein the Lewis base adduct is tetrahydrofuran.

9. The anhydrous mononuclear Lewis base adducted bismuth complex according to claim 2 wherein the Lewis base adduct is selected from the group consisting of toluene and pyridine.

10. The anhydrous mononuclear Lewis base adducted bismuth complex according to claim 2 wherein the Lewis base adduct is selected from the group consisting of: *N,N,N',N'*-tetramethylethylenediamine and *N,N,N',N',N"*-pentamethyldiethylenetriamine.

11. Anhydrous mononuclear Lewis base adducted tris(2,2,6,6-tetramethyl-3,5-heptanedionato) bismuth.

12. *N,N,N'N'*-tetramethylethylenediamine adducted anhydrous mononuclear tris(2,2,6,6-tetramethyl-3,5-heptanedionato) bismuth having a melting point of about 136°C.

13. *N,N,N'N'*-tetramethylethylenediamine adducted anhydrous mononuclear tris(2,2,6,6-tetramethyl-3,5-heptanedionato) bismuth having the x-ray crystallographic structure shown in Figure 4.

14. A method of synthesis of an anhydrous mononuclear Lewis base adducted tris(β-diketonato) bismuth complex comprising reacting at least one equivalent of a Lewis base adduct compound with a mononuclear tris (β-diketonato) bismuth compound or a dinuclear tris (β-diketonato) bismuth compound in an aprotic solvent medium under anaerobic conditions at sufficient temperature for sufficient time with subsequent removal of the aprotic solvent medium to yield said anhydrous mononuclear Lewis base adducted tris(β-diketonato) bismuth complex as a reaction product thereof.

15. The method according to claim 14, wherein the aprotic solvent medium comprises a solvent selected from the group consisting of aryl ethers and aryl amines.

16. The method according to claim 14, wherein the aprotic solvent medium comprises a solvent selected from the group consisting of pentane, hexane, octane, decane, tetrahydrofuran, benzene, toluene and pyridine.

17. The method according to claim 14, wherein the mononuclear tris (β-diketonato) bismuth compound comprises a β-diketonato composition selected from the group consisting of:

2,2,6,6-tetramethyl-3,5-heptanedionato;
1,1,1-trifluoro-2,4-pentanedionato;

1,1,1,5,5,5-hexafluoro-2,4-pentanedionato;
6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionato;
2,2,7-trimethyl-3,5-octanedionato;
1,1,1,5,5,6,6,7,7,7-decafluoro-2,4-heptanedionato; and
1,1,1-trifluoro-6-methyl-2,4-heptanedionato.

18. The method according to claim 14, wherein the dinuclear tris (β-diketonato) bismuth compound comprises a β-diketonato composition selected from the group consisting of:

2,2,6,6-tetramethyl-3,5-heptanedionato;
1,1,1-trifluoro-2,4-pentanedionato;
1,1,1,5,5,5-hexafluoro-2,4-pentanedionato;
6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionato;
2,2,7-trimethyl-3,5-octanedionato;
1,1,1,5,5,6,6,7,7,7-decafluoro-2,4-heptanedionato; and
1,1,1-trifluoro-6-methyl-2,4-heptanedionato.

19. The method according to claim 14, wherein the Lewis base adduct compound is selected from the group consisting of: amines, ethers, glymes and aryls.

20. The method according to claim 14, wherein the Lewis base adduct compound is selected from the group consisting of: $NH_3$, primary amines, secondary amines, tertiary amines and polyamines.

21. The method according to claim 14, wherein the Lewis base adduct compound is selected from the group consisting of: monoglymes, diglymes, triglymes, tetraglymes, aliphatic ethers, polyethers, and cyclic ethers.

22. The method according to claim 14, wherein the Lewis base adduct compound is tetrahydrofuran.

23. The method according to claim 14, wherein the Lewis base adduct compound is toluene.

24. The method according to claim 14, wherein the Lewis base adduct compound is selected from the group consisting of: *N,N,N',N'*-tetramethylethylenediamine and *N,N,N',N',N''*-pentamethyldiethylenetriamine.

25. A method of synthesis of Lewis base adducted anhydrous mononuclear tris(2,2,6,6-tetramethyl-3,5-heptanedionato) bismuth, comprising reaction of anhydrous mononuclear tris (2,2,6,6-tetramethyl-3,5-heptanedionato)bismuth and *N,N,N'N'*-tetramethylethylenediamine in hexanes under a nitrogen gas environment in an aprotic solvent medium under anaerobic conditions.

26. A method of synthesis of Lewis base adducted anhydrous mononuclear tris(2,2,6,6-tetramethyl-3,5-heptanedionato) bismuth, comprising reaction of dinuclear tris(2,2,6,6-tetramethyl-3,5-heptanedionato) bismuth and *N,N,N'N'*-tetramethylethylenediamine in hexanes under a nitrogen gas environment in an aprotic solvent medium under anaerobic conditions.

27. The method according to claim 25, wherein the aprotic solvent medium comprises a solvent selected from the group consisting of alkanes, aliphatic ethers, cyclic ethers, and aryl compounds.

28. The method according to claim 26, wherein the aprotic solvent medium comprises a solvent selected from the group consisting of alkanes, aliphatic ethers, cyclic ethers, and aryl compounds.

29. The method according to claim 25, wherein the aprotic solvent medium comprises a solvent selected from the group consisting of pentane, hexanes, octane, decane, tetrahydrofuran, benzene and toluene.

30. The method according to claim 26, wherein the aprotic solvent medium comprises a solvent selected from the group consisting of pentane, hexanes, octane, decane, tetrahydrofuran, benzene and toluene.

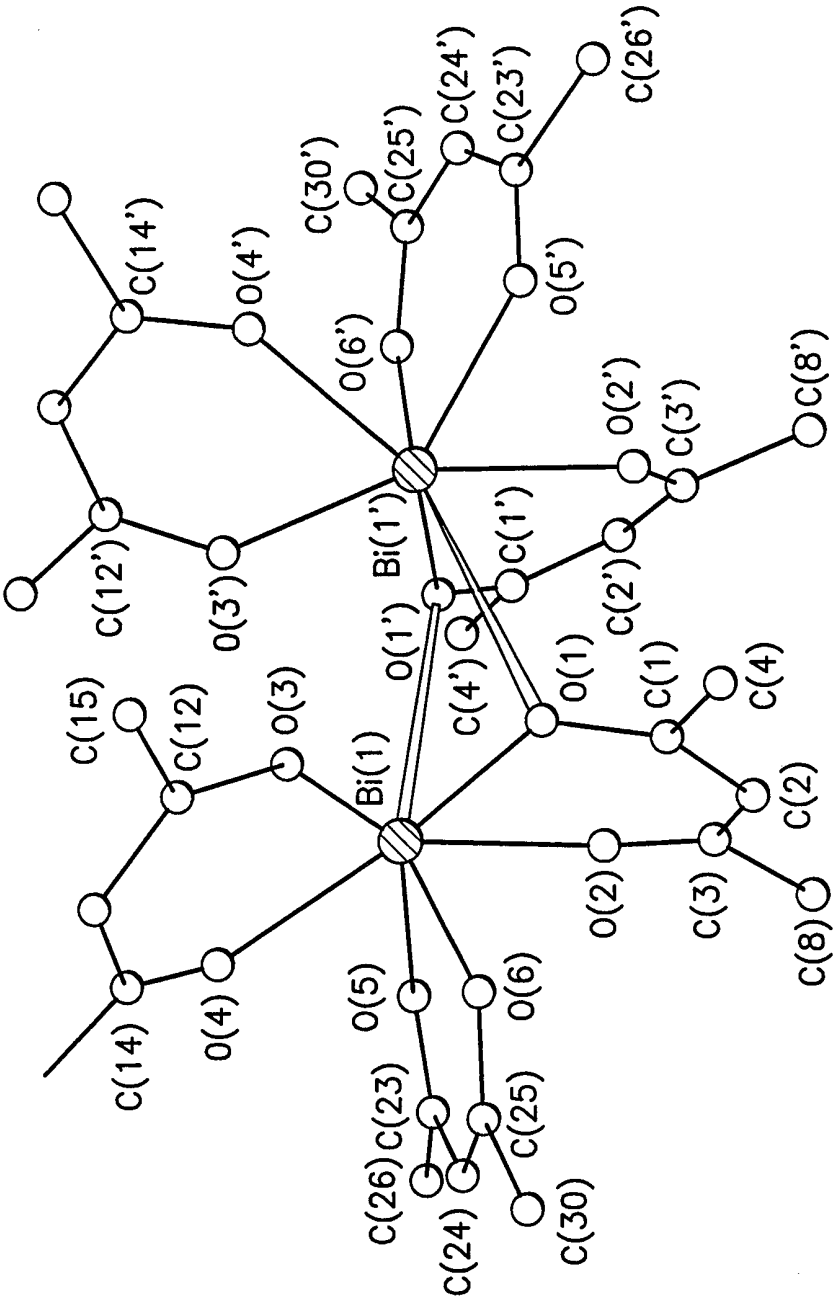



FIG. 1
PRIOR ART

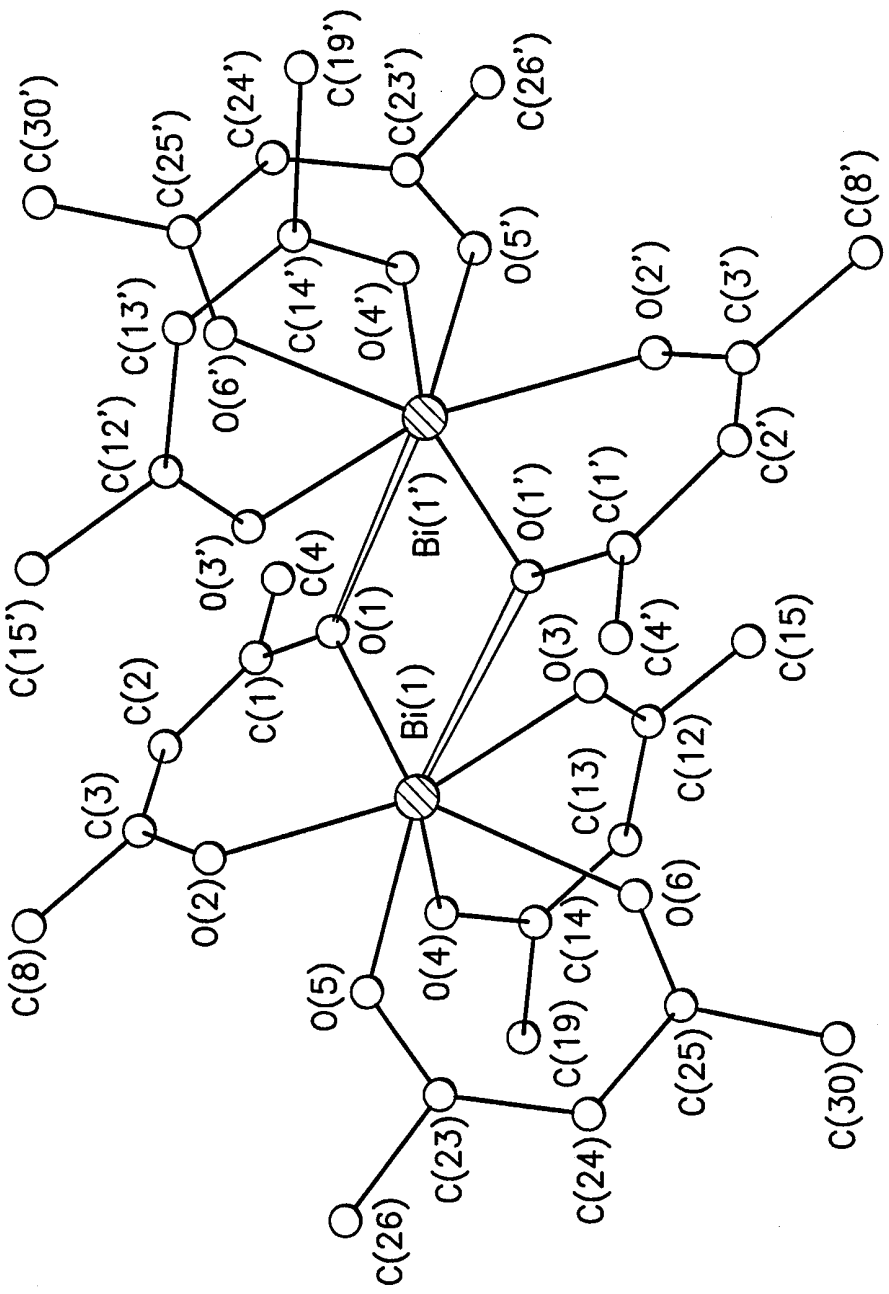



FIG.2
PRIOR ART

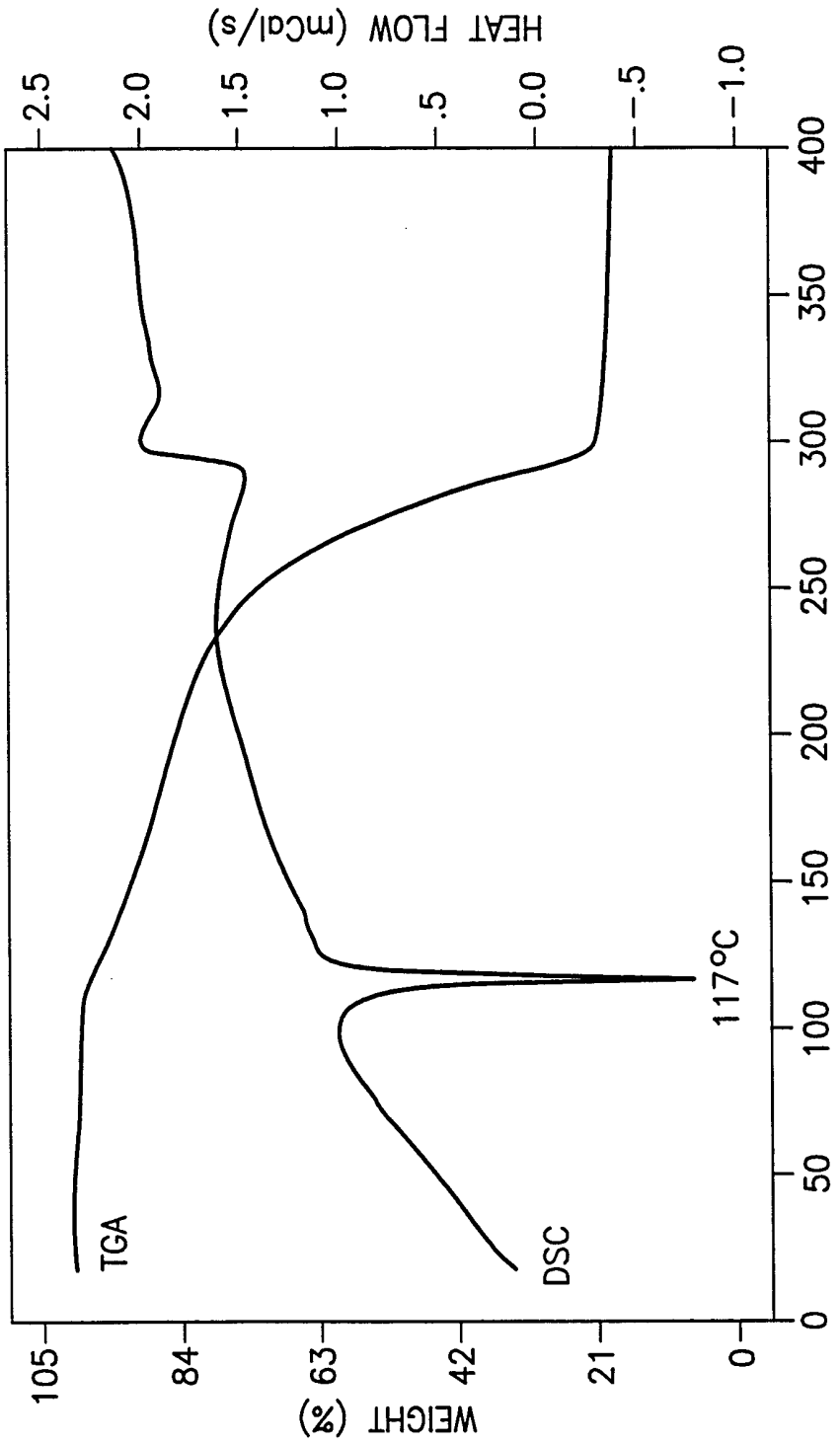
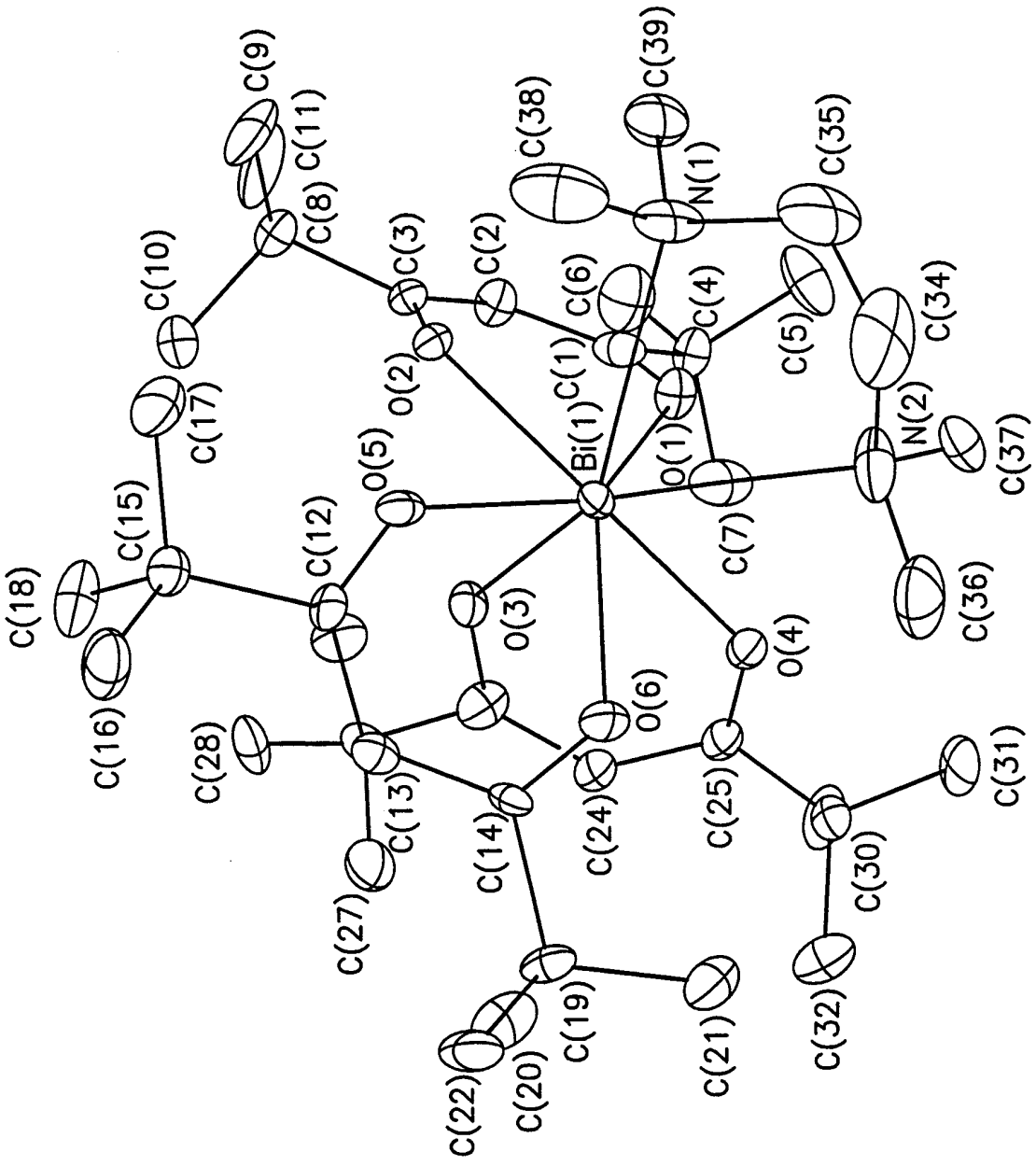



FIG.3
PRIOR ART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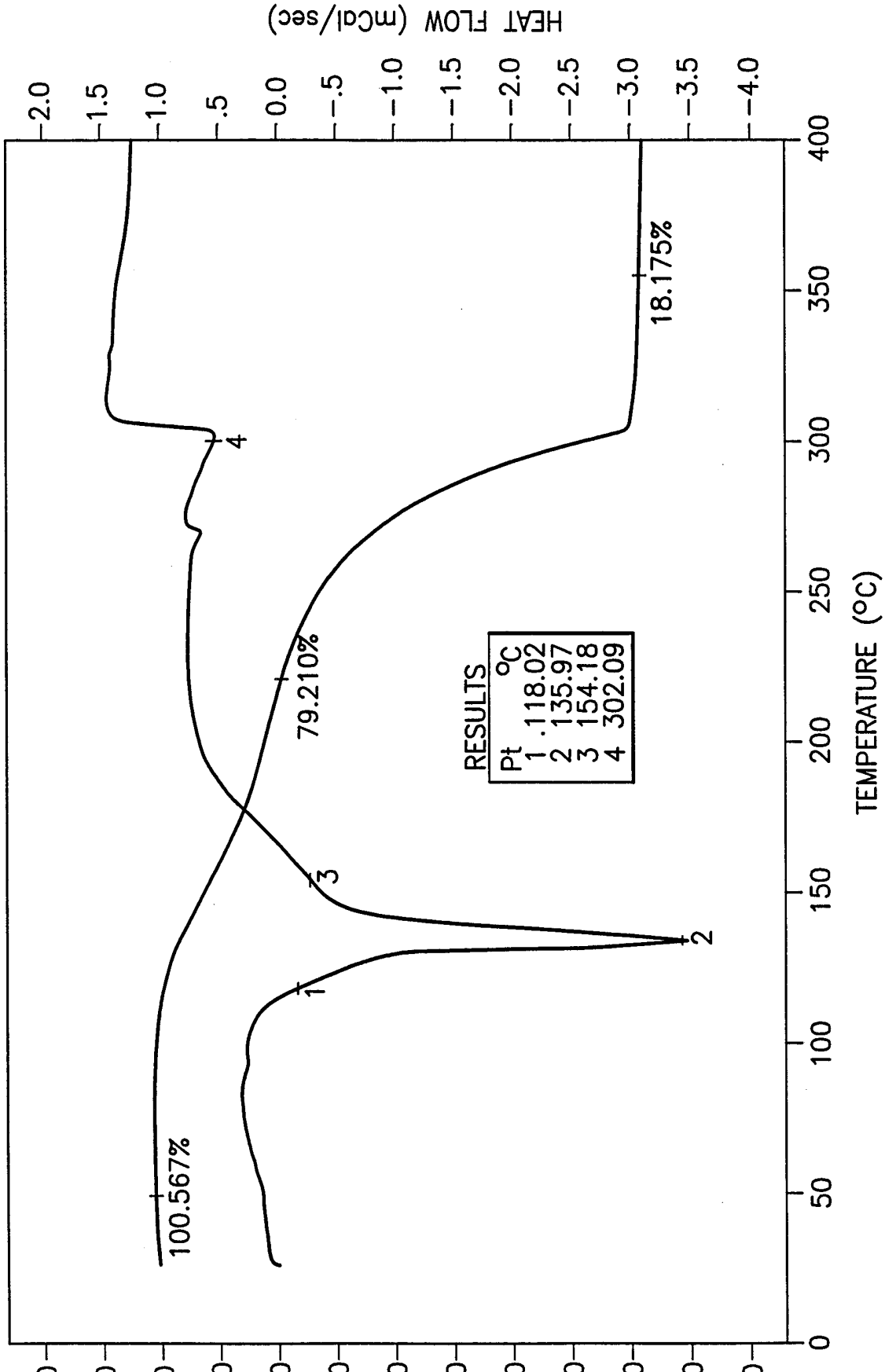
C(21)

FIG.4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-3.0
-3.5
-4.0
400
350
300
250
200
150
100
50
0
TEMPERATURE (°C)
WEIGHT (%)
120
110
100
90
80
70
60
50
40
30
20
10
0
100.567%
79.210%
18.175%
RESULTS
Pt °C
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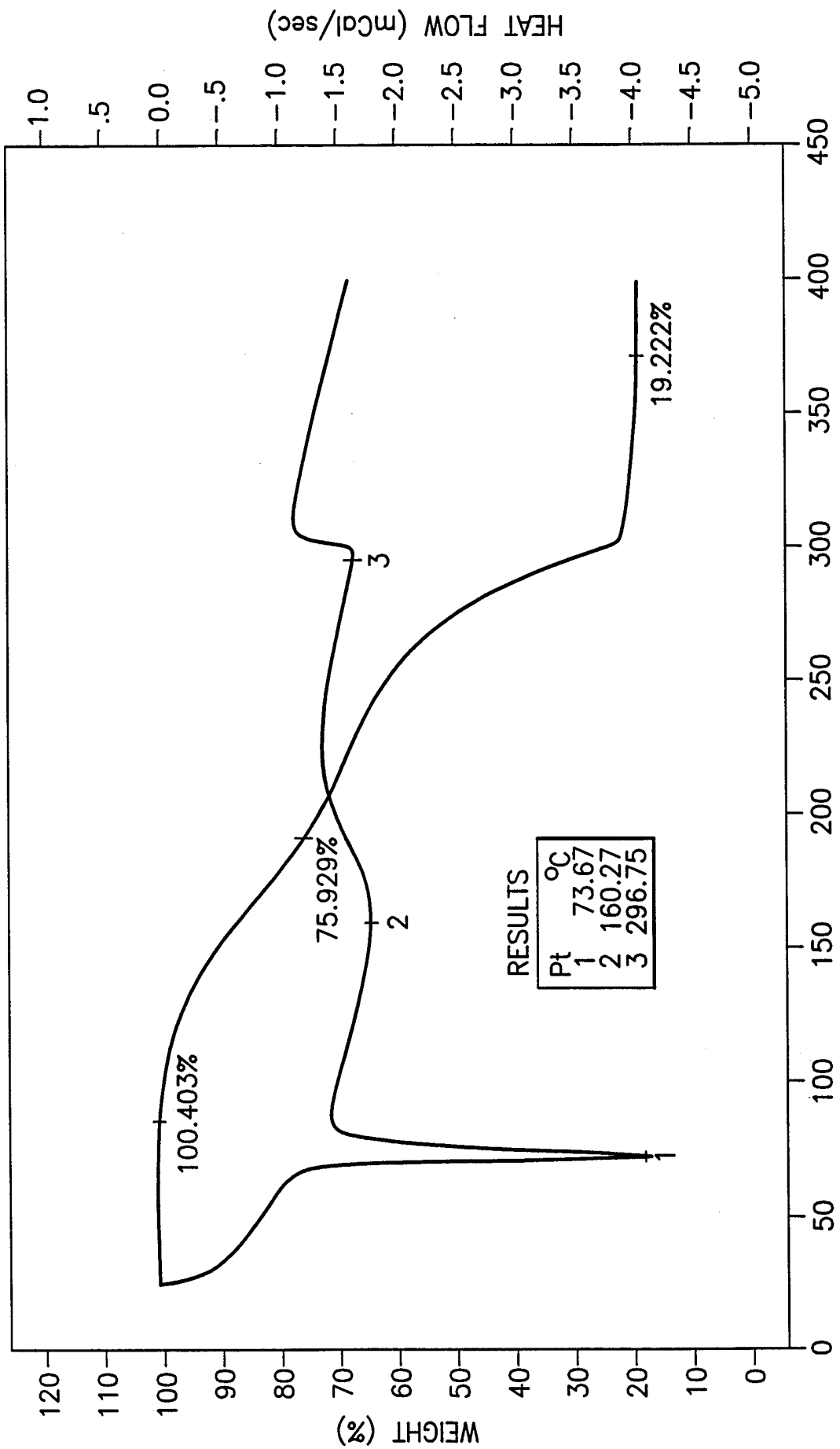
2 135.97
3 154.18
4 302.09
1
2
3
4

FIG.5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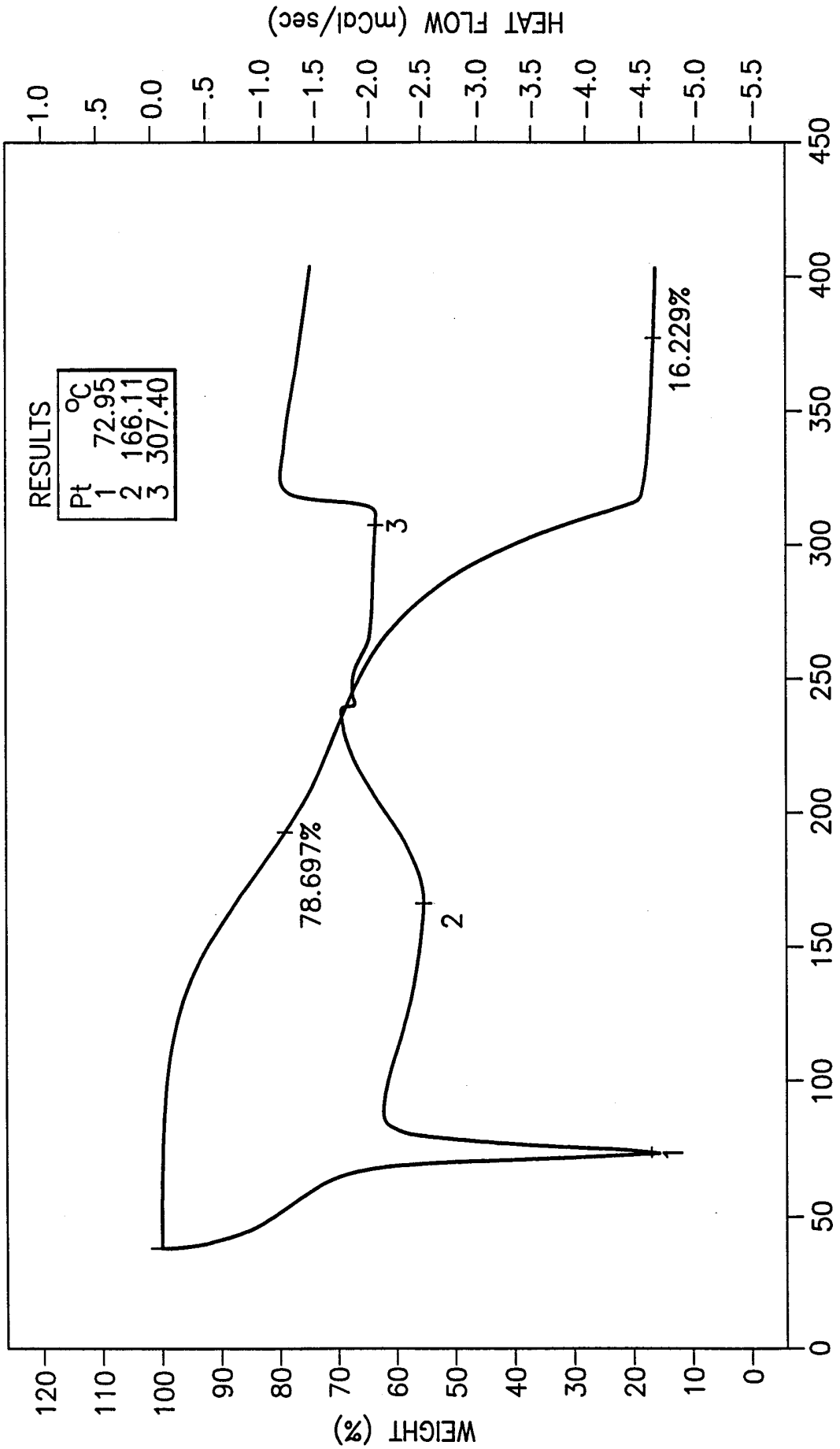
-4.5
-5.0
450
400
350
300
250
200
150
100
50
0
TEMPERATURE (°C)
WEIGHT (%)
120
110
100
90
80
70
60
50
40
30
20
10
0
100.403%
75.929%
19.222%
1
2
3
RESULTS
Pt °C
1 73.67
2 160.27
3 296.75

FIG.6


HEAT FLOW (mCal/sec)
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0.0
-.5
-1.0
-1.5
-2.0
-2.5
-3.0
-3.5
-4.0
-4.5
-5.0
-5.5
RESULTS
Pt °C
1 72.95
2 166.11
3 307.40
78.697%
16.229%
1
2
3
WEIGHT (%)
120
110
100
90
80
70
60
50
40
30
20
10
0
0
50
100
150
200
250
300
350
400
450
TEMPERATURE (°C)

FIG.7

# INTERNATIONAL SEARCH REPORT

International application No.
PCT/US99/23034

**A. CLASSIFICATION OF SUBJECT MATTER**

IPC(6) :C07F 9/94
US CL :556/76, 64

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 556/76, 64

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

Please See Extra Sheet.

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| P, X<br>----<br>A | US 5,859,274 A (BAUM et al) 12 January 1999, whole patent, especially columns 1 - 2 and examples. | 1<br>----<br>2-30 |
| A | Database Caplus on STN, Chem Abstracts, (Columbus, OH, USA) No. 120:42314 Fukin, G. K. et al 'The crystal and molecular structures of bismuth dipivaloylmethanes' , abstract Zh. Neorg. Khim. Vol. 38, No. 7, pp 1205-1211, July 1997. | 1-30 |
| A | Database caplus on STN, Chem Abstracts, (Columbus OH, USA) No. 121:147729 Zharkova, G. I. et al 'Complexes of bismuth(III) with fluorinated beta-diketones' abstract Koord. Khim. Vol. 20, No. 2 pp 101-115. | 1-30 |

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

| | | | |
|---|---|---|---|
| * | Special categories of cited documents: | "T" | later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention |
| "A" | document defining the general state of the art which is not considered to be of particular relevance | "X" | document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone |
| "E" | earlier document published on or after the international filing date | "Y" | document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art |
| "L" | document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) | "&" | document member of the same patent family |
| "O" | document referring to an oral disclosure, use, exhibition or other means | | |
| "P" | document published prior to the international filing date but later than the priority date claimed | | |

Date of the actual completion of the international search
04 DECEMBER 1999

Date of mailing of the international search report
19 JAN 2000

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Telephone No. (703) 308-1235

Form PCT/ISA 210 (second sheet)(July 1992)★

B. FIELDS SEARCHED
Electronic data bases consulted (Name of data base and where practicable terms used):

CAS ONLINE

search terms: bismuth diketonato, mononuclear tris heptanedionato, structure drawing, base adduct