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# Mixed-Ligand Approach to Design of Heterometallic Single-Source Precursors with Discrete Molecular Structure

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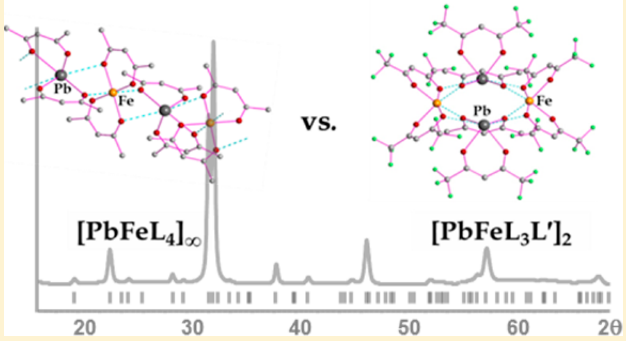
*Supporting Information*



**ABSTRACT:** Heterometallic single-source precursors for the Pb/Fe = 1:1 oxide materials, PbFe(*β*-dik)$_4$ (*β*-dik = hexafluoroacetylacetonate (hfac, **1**), acetylacetonate (acac, **2**), and trifluoroacetylacetonate (tfac, **4**)), have been isolated by three different solid-state synthetic methods. The crystal structures of heterometallic diketonates **1**, **2**, and **4** were found to contain polymeric chains built on alternating [Fe(*β*-dik)$_2$] and [Pb(*β*-dik)$_2$] units that are held together by bridging M−O interactions. Heterometallic precursors are highly volatile, but soluble only in coordinating solvents, in which they dissociate into solvated homometallic fragments. In order to design the heterometallic precursor with a proper metal/metal ratio and with a discrete molecular structure, we used a combination of two different diketonate ligands. Heteroleptic complex Pb$_2$Fe$_2$(hfac)$_6$(acac)$_2$ (**5**) has been obtained by optimized stoichiometric reaction of an addition of homo-Fe(acac)$_2$ to heterometallic Pb$_2$Fe(hfac)$_6$ (**3**) diketonate that can be run in solution on a high scale. The combination of two ligands with electron-withdrawing and electron-donating groups allows changing the connectivity pattern within the heterometallic assembly and yields the precursor with a discrete tetranuclear structure. In accord with its molecular structure, heteroleptic complex **5** is soluble even in noncoordinating solvents and was found to retain its heterometallic structure in solution. Thermal decomposition of heterometallic precursors in air at 750 °C resulted in the target Pb$_2$Fe$_2$O$_5$ oxide, a prospective multiferroic material. Prolonging the annealing time or increasing the decomposition temperature leads to another phase-pure lead−iron oxide PbFe$_{12}$O$_{19}$ that is a representative of the important family of magnetic hexaferrites.

## ■ INTRODUCTION

Lead-containing transition-metal oxides play an important role in materials chemistry due to their ferromagnetic,[1] ferroelectric,[2] piezoelectric,[3] pyroelectric,[4] and superconducting[5] properties. Perovskite-based structures composed of the Pb$^{2+}$ cation with a 6s$^2$ lone electron pair in combination with transition metals are of particular interest as prospective candidates for multiferroic materials.[6] The stereochemical effect of the lone pair can lead to a strong distortion of the perovskite lattice and thus to a decrease of the structure symmetry often resulting in ferroelectric properties.[7] The preparation of PbFeO$_3$ perovskite can only be achieved by high-pressure (7 GPa), high-temperature (1100−1200 °C) synthesis. Its structure contains Pb$^{2+}$, Pb$^{4+}$, and Fe$^{3+}$ ions and releases oxygen around 467 °C to yield a new oxide, Pb$_2$Fe$_2$O$_5$.[8] The perovskite-based Pb$_2$Fe$_2$O$_5$ has a complex layered intergrowth structure found to be periodically modulated by crystallographic shear (CS) planes.[9] Recently, it has been reported[10] that Pb$_2$Fe$_2$O$_5$ ceramics exhibit ferroelectric and ferromagnetic properties at room temperature. The simultaneous occurrence of both ferroelectricity and ferromagnetism makes this oxide a prospective candidate for multiferroic materials. Various synthetic methods that do not require high-pressure processes have been suggested to obtain Pb$_2$Fe$_2$O$_5$. Those include the direct annealing of the PbO/Fe$_2$O$_3$ mixture at the temperatures between 700 and 800 °C for up to 500 h, a sol−gel method utilizing lead and iron citrates,[11] and a polymer precursor approach using lead acetate hydrate and ferric acetylacetonate in glycerin.[10]

Certain heterometallic coordination complexes with suitable ligands can be employed as single-source precursors (SSPs), providing a viable alternative to traditional approaches for the low-temperature synthesis of oxide materials.[12] Such SSPs contain all constituent elements of targeted products, and their decomposition usually leads to the formation of desired material in a single processing step. Volatile precursors are particularly interesting since they can be used in metal−organic chemical vapor deposition (MOCVD) processes for the preparation of high-technological oxides.[13] Precursors with discrete molecular (rather than polymeric) structures are ideal to enhance solubility as well as to ensure the retention of the heterometallic structure in solution. The latter is important for practical applications of precursors in the direct liquid injection CVD technique for thin film growth, a very attractive

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deposition method that is applicable to a wide range of materials.[14]

The application of heterometallic single-source precursors to obtain $Pb_2Fe_2O_5$ material upon thermal decomposition is currently limited by two reported examples. Heating of the heterometallic complex $Pb_2[Fe(CN)_6]\cdot 4H_2O$ at 700 °C in air resulted in a mixture of $Pb_2Fe_2O_5$, PbO, and $Fe_2O_3$ oxide phases.[15] More recent work[16] describes the use of a lead nitroprusside complex $Pb[Fe(CN)_5NO]$ to produce pure $Pb_2Fe_2O_5$ upon heating at 750 °C in air. Metal $\beta$-diketonate complexes represent an important class of heterometallic precursors due to their unique properties, such as high volatility with a sufficient vapor pressure and mass transport at reasonable temperatures (~100 °C), stable composition of the vapor phase during the evaporation process, solubility in a variety of common solvents, clean low-temperature decomposition, and the absence of stable intermediate (residues) formation upon pyrolysis.[17,18] A number of studies have been devoted to homometallic $\beta$-diketonate complexes of the general formula $M(hfac)_2\cdot TMEDA$ (M = Fe, Co, Cu) and their application for the preparation of nanostructured thin films by the CVD technique.[19] Our group has already demonstrated the successful use of heterometallic $\beta$-diketonates as single-source precursors for the synthesis of main group−transition-metal oxide materials.[20] Herein, we report the preparation, characterization, and decomposition study of volatile heterometallic precursors with a proper Pb/Fe = 1:1 metal ratio for the synthesis of the prospective multiferroic material $Pb_2Fe_2O_5$. By using a mixed-ligand combination approach, we were able to effectively change the connectivity pattern within the heterometallic assembly in order to obtain a precursor with a discrete molecular structure that exhibits the retention of the heterometallic core in a variety of common solvents.

## ■ RESULTS AND DISCUSSION

Heterometallic diketonates with a Pb/Fe ratio of 1:1, $PbFe(hfac)_4$ (**1**, hfac = hexafluoroacetylacetonate) and $PbFe(acac)_4$ (**2**, acac = acetylacetonate), have been obtained by three different methods using solid-state reactions in sealed evacuated ampules. The title compounds were isolated as sole products of the reaction between stoichiometric amounts of unsolvated divalent lead and iron diketonates at 90−110 °C:

$$Pb(\beta\text{-dik})_2 + Fe(\beta\text{-dik})_2 \rightarrow PbFe(\beta\text{-dik})_4 \qquad (1)$$

Crystals of heterometallic precursors can be conveniently collected with ca. 80% yield after 4 days in the cold end of the ampule, where the temperature was kept ca. 5 °C lower. The only drawback of this process is the availability and sensitivity of starting reagents. Whereas lead diketonates are commercially available, the unsolvated iron(II) diketonates require special preparation[21] and handling, especially very moisture- and air-sensitive $Fe(hfac)_2$ that should be used as freshly synthesized only.

Trivalent iron diketonates $Fe(\beta\text{-dik})_3$ demonstrate good oxidative activity toward metallic lead at 80−110 °C and afford the title heterometallic precursors after a few days:

$$2Fe(\beta\text{-dik})_3 + Pb \rightarrow PbFe(\beta\text{-dik})_4 + Fe(\beta\text{-dik})_2 \qquad (2)$$

All starting reagents for this reaction either are commercially available or, in the case of $Fe(hfac)_3$, can be readily obtained by a simple, one-step procedure. The real disadvantage of this approach is the necessity of separating the target materials from the iron(II) diketonate byproducts either manually or by fractional sublimation.

Perhaps, the most convenient approach to obtain the title heterometallic precursors is the reaction between 2 equiv of lead diketonate and anhydrous iron(II) chloride:

$$2Pb(\beta\text{-dik})_2 + FeCl_2 \rightarrow PbFe(\beta\text{-dik})_4 + PbCl_2 \qquad (3)$$

It employs commercially available reagents only and allows an effective separation of target compounds from the second product, $PbCl_2$, which is nonvolatile and thus remains in the hot end of the container during the course of reaction and mass transfer.

It should be noted that the proper stoichiometric reagent ratio is crucial for the above synthetic procedures, especially for reactions 1 and 3. By changing the starting reagent ratio in the latter reactions, we manage to isolate yet another lead−iron heterometallic diketonate with a 2:1 metal ratio, $Pb_2Fe(hfac)_6$ (**3**):

$$2Pb(hfac)_2 + Fe(hfac)_2 \rightarrow Pb_2Fe(hfac)_6 \qquad (4)$$

$$3Pb(hfac)_2 + FeCl_2 \rightarrow Pb_2Fe(hfac)_6 + PbCl_2 \qquad (5)$$

This unusual lead-rich heterometallic compound can most conveniently be obtained by redox reaction of commercially available reagents:

$$3Pb(hfac)_2 + Fe \rightarrow Pb_2Fe(hfac)_6 + Pb \qquad (6)$$

Not surprisingly, heterometallic diketonate **3** can be readily and quantitatively transformed to precursor **1** on addition of $Fe(hfac)_2$ and, vice versa, on addition of $Pb(hfac)_2$:

$$Pb_2Fe(hfac)_6 + Fe(hfac)_2 \rightarrow 2PbFe(hfac)_4 \qquad (7)$$

$$PbFe(hfac)_4 + Pb(hfac)_2 \rightarrow Pb_2Fe(hfac)_6 \qquad (8)$$

Synthetic details for heterometallic diketonates are summarized in the Supporting Information. Purity of the bulk products has been confirmed by X-ray powder diffraction through comparison of the experimental spectra with theoretical patterns calculated from the single-crystal data (Supporting Information, Figures S1−S5). Heterometallic $\beta$-diketonates **1** and **2** are relatively stable in open air and can be handled outside the glovebox for a reasonable period of time in the course of characterization and decomposition studies. Crystals of **3** are sensitive to moisture and lose their crystallinity within minutes in open air. All compounds are volatile and can be quantitatively resublimed at 105 (**1**) or 130 °C (**2**, **3**) in an evacuated ampule. The sublimation starts at ca. 75 (**1**) or 100 °C (**2**, **3**), and the precursors do not show any signs of decomposition until about 115 (**1**) or 135 °C (**2**, **3**). Compounds **1**−**3** are insoluble in noncoordinating solvents ($CH_2Cl_2$, $CHCl_3$, hexanes, benzene) but are readily soluble in coordinating solvents, such as acetone, THF, and DMSO. NMR ($^1H$ and $^{19}F$) spectra of the solutions of **1**−**3** in coordinating solvents indicate the dissociation of the heterometallic structure that is evident by the appearance of a signal corresponding to the solvated homometallic diketonate $Pb(\beta\text{-dik})_2$ (Supporting Information, Figures S12 and S13). Similar behavior has already been reported by us for heterometallic hexafluoroacetylacetonate complexes of Pb with Mn,[20a] Co, and Ni.[22]

Single-crystal X-ray diffraction analysis revealed that the solid-state structures of heterometallic precursors with a Pb/Fe = 1:1 ratio (**1**, **2**) are represented by the infinite zigzag chains of

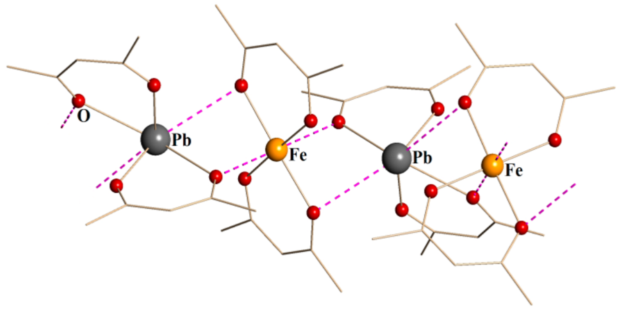

**Figure 1.** Fragment of the polymeric chain structure of heterometallic *β*-diketonate PbFe(acac)$_4$ (**2**). Hydrogen atoms are omitted for clarity. Lead, iron, and oxygen atoms are shown as spheres of arbitrary radii. Bridging interactions to metal atoms are shown as dashed lines. Heterometallic *β*-diketonate PbFe(hfac)$_4$ (**1**) has a similar structure (Supporting Information, Figure S6).

**Table 1. Averaged Bonding Distances (Å) in the Structures of Heterometallic Diketonates 1−5**

| | Pb−O$_c$$^a$ | Pb−O$_{c\text{-}b}$$^a$ | Pb−O$_b$$^a$ | Fe−O$_c$$^a$ | Fe−O$_{c\text{-}b}$$^a$ | Fe−O$_b$$^a$ |
|---|---|---|---|---|---|---|
| (**1**) | 2.348 | 2.582 | 2.812,<br>2.833 | 2.025 | 2.024 | 2.334,<br>2.370 |
| (**2**) | 2.313 | 2.494 | 2.879,<br>2.923 | 2.033 | 2.052 | 2.245,<br>2.272 |
| (**3**) | 2.480 | 2.391 | 2.730,<br>2.879 | 2.033 | 2.004 | 2.209 |
| (**4**) | 2.332 | 2.502 | 2.805,<br>2.858 | 2.042 | 2.046 | 2.237,<br>2.240 |
| (**5**) | 2.393 | 2.436 | 2.871,<br>2.968 | 2.051 | 2.058 | 2.185,<br>2.198 |

$^a$c, chelating; c-b, chelating-bridging; b, bridging.

alternating [Fe(*β*-dik)$_2$] and [Pb(*β*-dik)$_2$] units (Figure 1). The units are connected through Lewis acid−base M−O interactions (Table 1). Each metal center has two chelating *β*-diketonate ligands and fulfills its coordination by two additional contacts with oxygen atoms that are chelating to the neighboring metals. These bridging contacts are longer than related chelating M−O bonds, but still significantly shorter than the sum of the corresponding van der Waals radii. Iron atoms have two chelating ligands located in a plane, and their coordination can be described as a slightly distorted octahedral. Both diketonate ligands chelating to the metal center provide bridging interactions to the neighboring metal atoms. The real significant difference between the structures of **1** and **2** is the bridging Fe−O contacts that are ca. 0.1 Å shorter for more electron-donating oxygen atoms of the smaller acac ligands.

The solid-state structure of a lead-rich heterometallic diketonate Pb$_2$Fe(hfac)$_6$ (**3**) is also polymeric and contains infinite zigzag chains of trinuclear [Pb$_2$Fe(hfac)$_6$] units, in which a planar [Fe(hfac)$_2$] fragment is sandwiched between two [Pb(hfac)$_2$] groups (Figure 2). The additional Fe−O contacts that make iron octahedrally coordinated are even shorter (Table 1) than those in the structure of **2**. The trinuclear units are connected between each other through a couple of Pb−O bridging interactions. Each Pb atom has a second bridging contact to the diketonate oxygen of the [Fe(hfac)$_2$] unit and maintains a very similar coordination to that found in **1** and **2**. The arrangement of trinuclear units in this compound resembles one in the structure of Bi$_2$Fe(hfac)$_8$ heterometallic diketonate,[23] except that the latter does not exhibit strong interactions between the trimetallic fragments.

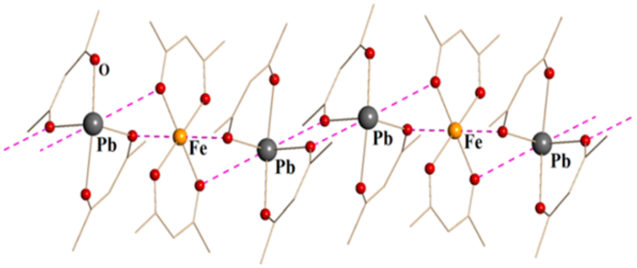

**Figure 2.** Fragment of the polymeric structure of heterometallic *β*-diketonate Pb$_2$Fe(hfac)$_6$ (**3**). Fluorine and hydrogen atoms are omitted for clarity. Bridging interactions to metal atoms are shown as dashed lines.

Heterometallic diketonates **1** and **2** are highly volatile and can be used as single-source precursors in the CVD technique of thin film growth. Moreover, heterometallic fragments are likely present in the vapor phase of those compounds since they can be resublimed quantitatively at the temperatures at which one of the possible homometallic dissociation species, Pb(*β*-dik)$_2$, is not volatile. However, diketonates **1** and **2**, having polymeric structures, are not soluble in noncoordinating solvents, whereas they dissociate into homometallic fragments in coordinating solvents. Thus, these single-source precursors cannot be explored for the direct liquid injection MOCVD technique. Our goal was to synthesize a heterometallic Pb/Fe = 1:1 diketonate with a discrete molecular structure that is soluble in noncoordinating solvents and retains its heterometallic structure in solution. Recently,[20b] we have demonstrated that application of asymmetric ligands allows one to effectively change the bridging connectivity pattern within the heterometallic assembly and results in isolation of heterometallic molecular precursors.

Trying to achieve our initial goal, we synthesized heterometallic lead−iron diketonate with asymmetric trifluoroacetylacetonate (tfac) ligands using the reaction 2. X-ray investigation revealed that, though the structure of PbFe(tfac)$_4$ (**4**) is still polymeric, the bridging connectivity is clearly altered. As it can be seen from Figure 3, the iron atoms maintain their additional contacts with lead-chelating tfac ligand oxygens that are located next to the electron-donating methyl substituents, and, conversely, Pb atoms have bridging interactions with diketonate oxygens that are close to trifluoromethyl groups.

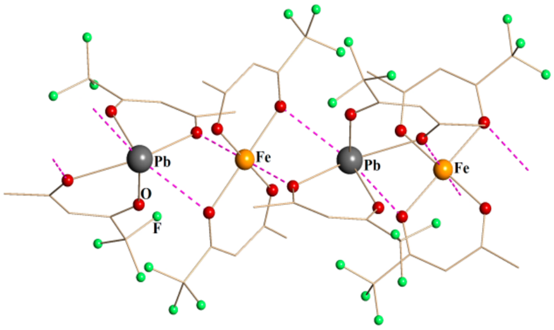

**Figure 3.** Fragment of the polymeric structure of heterometallic *β*-diketonate PbFe(tfac)$_4$ (**4**). Hydrogen atoms are omitted for clarity. Bridging interactions to metal atoms are shown as dashed lines.

Analysis of bridging connectivity in the solid-state structure of **4** offered us an idea for further design of this family of precursors, namely, to change the ratio of $CH_3/CF_3$ substituents in the heterometallic molecule. The latter was achieved by using a mixed-ligand (hfac/acac) approach for the synthesis of heterometallic precursors.

Heterometallic precursor $Pb_2Fe_2(hfac)_6(acac)_2$ (**5**) has been isolated in the course of the synthesis of heteroleptic diketonates. It should be noted that no other Pb/Fe = 1:1 compounds with different ligand ratios have been detected. The optimized method for the synthesis of **5** is based on reaction 7 by addition of homo- to heterometallic diketonate:

$$Pb_2Fe(hfac)_6 + Fe(acac)_2 \rightarrow Pb_2Fe_2(hfac)_6(acac)_2 \qquad (9)$$

The reaction can be performed at room temperature in a solution of dry methylene chloride within a few hours for a high-scale preparation of the product. Upon solvent removal, the dried powder can be further purified by sublimation at 110−115 °C to afford the title compound in ca. 70% yield. The heterometallic reactant was obtained by reaction 6 from commercially available reagents. The second starting material was typically prepared by a simple quantitative reaction between $Fe(acac)_3$ and finely divided metallic iron.

Single-crystal X-ray analysis revealed that the structure of heteroleptic diketonate **5** contains discrete tetranuclear molecules (Figure 4) with a proper 1:1 metal ratio for the desired decomposition product. The tetrameric unit consists of two $[Fe(hfac)_2]$ and two [Pb(acac)(hfac)] fragments. Similar to the structure of tfac compound **4**, each Fe atom features two additional bridging interactions to the oxygens of the acac ligands on both lead atoms, thus maintaining an octahedral coordination. Each Pb atom also has two additional contacts with oxygens of the neighboring $[Fe(hfac)_2]$ units. While the iron atom is chelated by the electron-withdrawing hfac ligands only, the strongest bridging Fe−O interactions, primarily responsible for holding this structure together, involve all of the most electron-rich oxygens of the Pb-chelating acac ligands. The major structural difference between heteroleptic precursor **5** and homoleptic diketonates **1**−**4** is within the octahedral coordination polyhedron of iron atoms. In all the structures of homoleptic compounds **1**−**4**, two Fe-chelating ligands are in the same plane and bridging Fe−O contacts are *trans* to each other. On the contrary, in the structure of **5**, the iron atoms are forced to maintain the bridging contacts at 77.5°, while the angle between the chelating diketonate planes is ca. 75°.

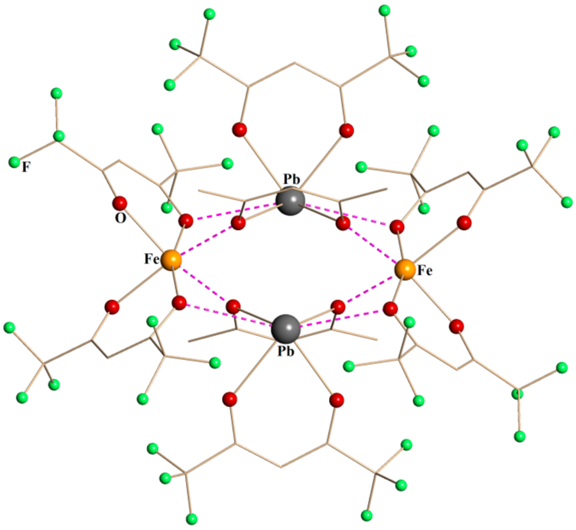

**Figure 4.** View of the tetrameric structure of heterometallic β-diketonate $Pb_2Fe_2(hfac)_6(acac)_2$ (**5**). Hydrogen atoms are omitted for clarity. Bridging interactions to metal atoms are shown as dashed lines.

In accord with its discrete molecular structure, heterometallic diketonate $Pb_2Fe_2(hfac)_6(acac)_2$ (**5**) is readily soluble in both coordinating and noncoordinating solvents. Importantly, the solutions of **5** are NMR ($^1$H and $^{19}$F) silent not only in the solvents such as dichloromethane and chloroform but also in coordinating solvents such as acetone. These observations sharply contrast the behavior of precursors **1**−**4** that have polymeric structures. The absence of NMR signals indicates that the heterometallic molecules **5** remain intact in solution as we have already demonstrated for a variety of main group−transition-metal β-diketonates.[20] A number of heterometallic precursors with discrete molecular structures, ($PbMn_2(hfac)_6$, $Li_2Co_2(tbaoac)_6$, and $LiMn_2(thd)_5$), have been reported to be NMR ($^1$H, $^7$Li, and $^{19}$F) silent. The retention of heterometallic structures in solutions of the above complexes was also confirmed by IR spectroscopy and mass spectrometry data. Heterometallic precursor **5** is highly volatile and can be resublimed quantitatively at 115 °C within several hours. It can be handled outside the glovebox in the course of decomposition studies. The purity of the bulk synthetic product was confirmed by the Le Bail fit of its powder X-ray diffraction pattern (Supporting Information, Figure S5).

According to the TGA data, heterometallic precursors exhibit a complex decomposition that proceeds in multiple steps between 80−90 °C and 350−450 °C and features a partial loss of β-diketonates to sublimation (Supporting Information, Figures S15−S17). Thermal decomposition of heterometallic precursors with the Pb/Fe = 1:1 ratio has been studied at different temperatures in an air atmosphere oven using high-alumina crucibles. Analysis of decomposition products by X-ray powder diffraction revealed that the presence of crystalline $Pb_2Fe_2O_5$ oxide can be detected at as low as 700 °C. Decomposition and annealing of the precursors between 700 and 750 °C result in very close phase compositions for different samples. While $Pb_2Fe_2O_5$ constitutes the major phase, impurities such as PbO can clearly be detected (Supporting Information, Figure S18), and an elongation of the annealing time only changes their mutual ratio. The best results for the preparation of target $Pb_2Fe_2O_5$ oxide have been achieved by carrying out the decomposition at 750 °C for a short period of time (Figure 5). Unit cell parameters for the perovskite-based lead−iron oxide phase derived from the Le Bail fit correspond well with the literature data (Table 2).

Prolonging annealing of the samples at 750 °C for several days or increasing the decomposition temperature results in phase-pure oxide, $PbFe_{12}O_{19}$ (Figure 6 and Supporting Information, Figure S19), that has a Pb/Fe ratio very different from the one in starting precursors due to PbO volatility above 700 °C.[24] We have already observed[20a] a similar effect when studying thermal decomposition of the Pb/Mn = 1:1 heterometallic precursor that yielded manganese-rich $Pb_3Mn_7O_{15}$ oxide at high temperatures. It is noteworthy that the title heterometallic complexes behave as prospective volatile single-source precursors for the preparation of iron-rich $PbFe_{12}O_{19}$ oxide in the form of thin films and nanocrystals. One can envision a similar application of the corresponding heterometallic precursors for the synthesis of other members of

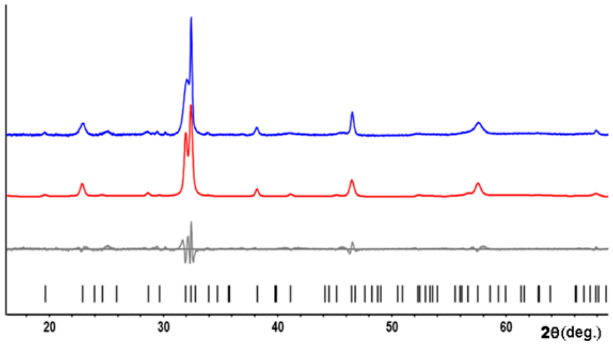

**Figure 5.** X-ray powder pattern of $Pb_2Fe_2O_5$ obtained by decomposition of heterometallic precursors in air at 750 °C for 2 h, and the Le Bail fit. The blue and red curves are the experimental and calculated patterns, respectively. The gray line is the difference curve. Theoretical peak positions are shown at the bottom as black lines.

**Table 2. Comparison of the Unit Cell Parameters for Lead−Iron Oxides Obtained by Decomposition of Heterometallic *β*-Diketonate Precursors with the Literature Data**

| Pb−Fe oxide | space group | literature data | Le Bail fit results |
|---|---|---|---|
| $Pb_2Fe_2O_5$[26] | *I*4/*mmm* | *a* = 3.9047(2) Å | *a* = 3.9039(2) Å |
| | | *c* = 36.000(3) Å | *c* = 36.114(5) Å |
| | | *V* = 548.60 Å$^3$ | *V* = 550.39 Å$^3$ |
| $PbFe_{12}O_{19}$[27] | *P*6$_3$/*mmc* | *a* = 5.8915(1) Å | *a* = 5.8831(8) Å |
| | | *c* = 23.0971(6) Å | *c* = 23.067(3) Å |
| | | *V* = 694.28 Å$^3$ | *V* = 691.41 Å$^3$ |

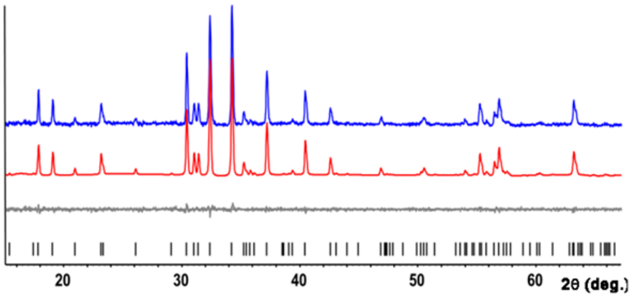

**Figure 6.** X-ray powder pattern of $PbFe_{12}O_{19}$ obtained by decomposition of heterometallic precursor in air at 750 °C for 5 days, and the Le Bail fit. The blue and red curves are the experimental and calculated patterns, respectively. The gray line is the difference curve. Theoretical peak positions are shown at the bottom as black lines.

the hexaferrite $MFe_{12}O_{19}$ family (M = Sr, Ba) that constitutes a class of important magnetic materials.[25]

## CONCLUSIONS

In conclusion, new heterometallic single-source precursors for the preparation of lead−iron oxides have been reported. This work primarily targeted the synthesis of diketonate precursors with the Pb/Fe = 1:1 metal ratio. The successful isolation of heteroleptic molecular precursor $Pb_2Fe_2(hfac)_6(acac)_2$ (**5**) was a result of a mixed-ligand approach that allows one to obtain the target product with a discrete molecular structure and a proper metal/metal ratio. The combination of two different diketonate ligands with electron-withdrawing and electron-donating groups, respectively, brings about changes in the connectivity pattern within the heterometallic assembly and yields the precursor with a molecular structure, even though both homoleptic counterparts were found to be coordination polymers. The retention of heterometallic structure **5** in solution makes the title precursor attractive for applications in the direct liquid injection chemical vapor deposition technique. The work also underlines the need to optimize the heteroleptic precursor preparation procedure that was achieved by introducing a new synthetic technique based on addition of homo- to heterometallic diketonate. The mixed-ligand approach developed in this work for the isolation of $Pb_2Fe_2(hfac)_6(acac)_2$ (**5**) opens broad opportunities to design new heterometallic precursors, especially in the cases when corresponding homoleptic complexes do not afford a proper metal/metal ratio and/or a discrete molecular structure.

## ASSOCIATED CONTENT

### Ⓢ Supporting Information

Experimental procedures, IR and NMR spectra, powder X-ray diffraction patterns, and phase analysis of thermal decomposition products for precursors **1**−**5**, and CIF files providing crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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### Notes

The authors declare no competing financial interests.

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