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JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
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Fluorinated Heterometallic β-Diketonates as Volatile Single-Source Precursors for the Synthesis of Low-Valent Mixed-Metal Fluorides

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Supporting Information

ABSTRACT: Hexafluoroacetylacetonates that contain lead and divalent first-row transition metals, PbM(hfac)$_4$ (M = Ni (**1**), Co (**2**), Mn (**3**), Fe (**4**), and Zn (**5**)), have been synthesized. Their heterometallic structures are held together by strong Lewis acid—base interactions between metal atoms and diketonate ligands acting in chelating—bridging fashion. Compounds **1**—**5** are highly volatile and decompose below 350 °C. Fluorinated heterometallic β-diketonates have been used for the first time as volatile single-source precursors for the preparation of mixed-metal fluorides. Complex fluorides of composition Pb_2MF_6 have been obtained by decomposition of **1**—**5** in a two-zone furnace under low-pressure nitrogen flow. Lead—transition metal fluorides conform to orthorhombically distorted Aurivillius-type structure with layers of corner-sharing [MF_6] octahedra separated by α-PbO-type (Pb_2F_2) blocks. Pb_2NiF_6 and Pb_2CoF_6 were found to exhibit magnetic ordering below 80 and 43 K, respectively. The ordering is antiferromagnetic, with a weak, uncompensated moment due to the canting of spins. The Pb_2MF_6 fluorides represent a new class of prospective magnetoelectric materials combining transition metals and lone-pair main-group cations.

The most common application of metal β-diketonates as precursors for the metals and metal oxides[1] is based on their high volatility and clean, low-temperature decomposition pattern. At the same time, there are a few reports[2] on the use of fluorinated homometallic diketonates for the synthesis of metal fluorides and oxyfluorides.

There is a considerable interest in the preparation of mixed-metal fluorides that are known to exhibit exotic magnetic behavior[3] as well as promising electrical (high ionic conductivity)[4] and nonlinear optical[5] properties. Some rare-earth doped complex fluorides show photoluminescence and find applications in the fields of solid-state lasers, low-intensity IR imaging, NIR quantum counting devices, 3D flat-panel displays, and biological labels.[6] Most of these materials were synthesized as microcrystalline powders by conventional high-temperature reactions between corresponding fluorides.[4,7] On the other hand, a multisource precursor approach was developed[8] for the synthesis of alkali-metal-containing fluorides. In this method, a mixture of metal trifluoroacetates is subjected to co-thermolysis in a high-boiling solvent such as octadecene, oleic acid, or trioctylphosphine. To the best of our knowledge, there are only two reports on the use of single-source precursors (SSPs) for the synthesis of mixed-metal fluorides.[9] Hydrothermal decomposition of sodium—yttrium fluorocarbonate, $NaY(CO_3)F_2$, resulted in a mixture of products containing $NaYF_4$.[9a] Recently, the nanocrystals of the latter fluoride were isolated by thermolysis of [$NaY(O_2CCF_3)_4$(diglyme)] precursor in 1-octadecene.[9b] All compounds explored for the synthesis of complex fluorides are nonvolatile. With ongoing miniaturization of electronic devices, there is a great interest in volatile precursors that can be used in metal—organic chemical vapor deposition (MOCVD) for the preparation of high-technological thin films with desired stoichiometry.[10]

For the past few years, our group was focused on the development of heavy main group—transition metal diketonates as SSPs for mixed-metal oxides.[11] Recently, we have shown that thermal decomposition of heterometallic Pb—Mn β-diketonates in air/oxygen results in a variety of mixed-metal oxides, including those that cannot be obtained by conventional solid-state techniques.[11b] Herein, we expand this effective approach to the use of volatile fluorinated heterometallic diketonates, PbM(hfac)$_4$ (M = Ni (**1**), Co (**2**), Mn (**3**), Fe (**4**), and Zn (**5**); hfac = hexafluoroacetylacetonate, Figure 1), as single-source precursors for the synthesis of lead—transition metal fluorides, Pb_2MF_6, by thermolysis in a low-pressure nitrogen atmosphere.

Two major synthetic routes were employed for the preparation of the title fluorinated heterometallic diketonates, PbM(hfac)$_4$: (i) solid-state interaction between unsolvated divalent homometallic diketonates, Pb(hfac)$_2$ and M(hfac)$_2$, where M = Ni (**1**), Mn (**3**), and Fe (**4**); (ii) redox reactions of trivalent diketonates, M(hfac)$_3$, with metallic Pb for the complexes **2** and **4** or of an excess of Pb(hfac)$_2$ with metallic Zn in the case of **5**. All reactions were performed in sealed evacuated ampules at 100—130 °C, and the heterobimetallic diketonates were deposited in the cold end (ca. 5 °C lower) of the container in the form of large crystals (ca. 90% yield for **1**, **3**, and **4** and 70% yield for **2** and **5**) within 3—5 days. The purity of the bulk products has been confirmed in each case by comparison of the powder diffraction pattern with the theoretical one calculated on the basis

Received: October 11, 2010
Published: December 21, 2010

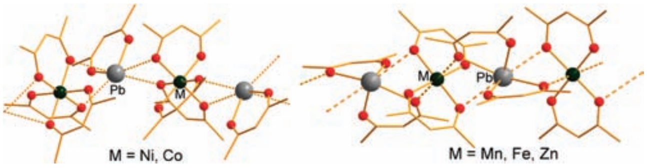

Figure 1. Fragments of the infinite chain structures of heterometallic β-diketonates **1**−**5**. Fluorine and hydrogen atoms are omitted for clarity.

of single-crystal data analysis. All complexes have similar physical properties: (i) readily soluble in coordinating solvents (acetone and THF), while the solubility in noncoordinating solvents (dichloromethane and chloroform) is very limited; (ii) relatively stable in air and can be handled outside the glovebox for a few minutes; (iii) highly volatile and can be quantitatively resublimed at temperatures higher than 100 °C, if needed. The TGA/DTA data showed that the thermal decomposition of complexes **1**−**5** upon heating under nitrogen is accompanied by an apparent loss of β-diketonates to sublimation and is completed around 350 °C.

Single-crystal X-ray analysis revealed that complexes **1**, **2**, **3**, and **5** crystallize in a monoclinic lattice (not isomorphous), while **4** is triclinic. The solid-state structures of heterometallic diketonates consist of infinite zigzag chains (Figure 1) of alternating M(hfac)$_x$ and Pb(hfac)$_y$ (x = 2 or 3, y = 2 or 1) units connected through Lewis acid−base M···O interactions that are significantly shorter than the sum of the corresponding van der Waals radii. In complexes **1** and **2**, the transition-metal atom exhibits octahedral coordination of three chelating β-diketonates, while the lead atom has only one chelating ligand and four additional interactions with diketonate oxygens acting in a chelating−bridging fashion. The Co−O distances in [Co(hfac)$_3$] units (2.04−2.07 Å) are similar to those in the $[\mathrm{Co^{II}(hfac)_3}]^-$ anion[12] (2.04−2.07 Å) but are significantly longer than the corresponding distances in $\mathrm{Co^{III}(hfac)_3}$ (1.88 Å), which indicates the formulation $\{[\mathrm{Co^{II}(hfac)_3}]^-[\mathrm{Pb^{II}(hfac)}]^+\}$ for the complex **2**. In the case of compounds **3**−**5**, each metal center has two chelating β-diketonate ligands and fulfills its coordination by two additional interactions with oxygens from the neighboring units. In the latter complexes, the oxidation state of each metal atom is also +2, which gives the formulation $\{\mathrm{M^{II}(hfac)_2Pb^{II}(hfac)_2}\}$. Such an assignment was confirmed[11b] for compound **3** by magnetic susceptibility measurements.

Thermal decomposition of heterometallic diketonates **1**−**5** has been carried out by the flash vacuum pyrolysis (FVP) method[13] in a two-zone furnace under 1300 mTorr N_2 flow for about 1 h. The temperatures of sublimation and decomposition were set at 100 and 600 °C, respectively. Preliminary analysis of the deposits by X-ray powder diffraction revealed in each case the presence of the phases with a pseudotetragonal unit cell of a = 5.5−5.7 Å and c = 16−17 Å. The powder patterns were found to be similar (though not identical) to those reported in 1969[14] for the lead-containing transition metal fluorides that were assigned a composition of $\mathrm{Pb_2MF_6}$ on the basis of the stoichiometry of the initial reactants mixture. The Ni and Co compounds appeared as microcrystalline materials essentially free of impurities (Figure 2), while those of Mn, Fe, and Zn contained different amounts of divalent metal fluorides and metallic lead. Elemental analysis performed on the Ni sample revealed a composition of $\mathrm{Pb_{2.02}Ni_{0.98}F_{6.00}}$.

The powder patterns of $\mathrm{Pb_2NiF_6}$ and $\mathrm{Pb_2CoF_6}$ were used to establish a tentative structural model of $\mathrm{Pb_2MF_6}$. Both patterns showed reflection splitting that is characteristic of an orthorhombic distortion. The indexing led to a = 5.537(1), b = 5.566(1), and c = 16.124(3) Å and a = 5.588(1), b = 5.606(1), and c = 16.460(3) Å for the Ni and Co phases, respectively. According to the reflection conditions in X-ray and electron diffraction patterns, the likely space groups are *Aemm* (*Cmme*) and *Ae*2*m* (*Aem*2). The similarity to the tetragonal $\mathrm{Ba_2NiF_6}$ (a = 4.054 Å ≈ $5.7/\sqrt{2}$, c = 16.341 Å)[15] suggests the same Aurivillius-type structure for $\mathrm{Pb_2MF_6}$, with two types of layers stacking along the c direction. The layers of the first type comprise corner-sharing $\mathrm{MF_6}$ octahedra, similar to the perovskite structure type. The layers of the second type resemble the structure of α-PbO and contain fluorine atoms in the centers of [$\mathrm{Pb_4}$] tetrahedra (Figure 2, inset). The sequence of ($\mathrm{MF_4}$) and ($\mathrm{Pb_2F_2}$) layers gives rise to the $\mathrm{Pb_2MF_6}$ composition. The lower symmetry of $\mathrm{Pb_2MF_6}$ compared to $\mathrm{Ba_2NiF_6}$ is likely caused by the different size of the $\mathrm{Pb^{2+}}$ cation as well as by its preference for an asymmetric local environment owing to the lone-pair effect.

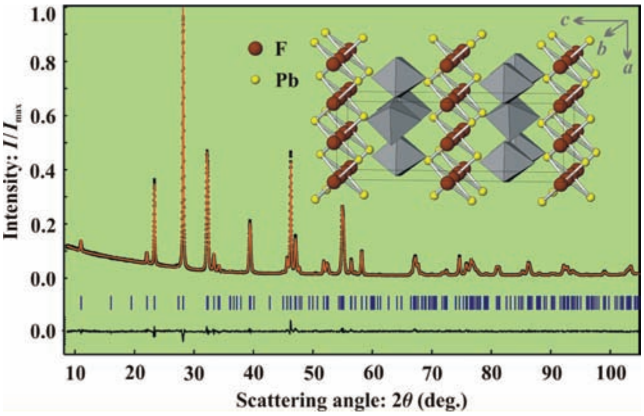

Figure 2. X-ray powder pattern (Cu Kα_1 radiation) of the residues obtained by decomposition of complex **1** and the Le Bail fit for the orthorhombic unit cell specified in the text (space group *Ae*2*m*). The bottom line is the difference curve. The Aurivillius-type structure is inset.

Magnetic susceptibility measurements for $\mathrm{Pb_2MF_6}$ (M = Ni, Co) indicate a canted antiferromagnetic ordering below 80 and 43 K, respectively. The magnetic transitions are reflected by a sharp increase in the magnetic susceptibility and a weak hysteresis of the low-temperature magnetization-vs-field curves. While such a behavior is typical for a ferromagnet, the saturated magnetic moment is well below 0.1 μ_B and suggests a nearly antiparallel alignment of spins. However, slight tilts (spin canting) lead to a small, uncompensated moment. This contrasts with the noncanted antiferromagnetic ordering at 93 K in the tetragonal $\mathrm{Ba_2NiF_6}$ fluoride.[16] The spin canting in lead−transition metal fluorides may be referred to the lower crystal symmetry that leads to anisotropic magnetic interactions. Detailed analysis of the magnetic behavior requires, however, the precise knowledge of the low-temperature crystal structure.

The interest in Pb-containing transition-metal compounds is stimulated by their magnetoelectric properties.[17] The lone pair of $\mathrm{Pb^{2+}}$ drives polar displacements and potential ferroelectricity, whereas transition-metal atoms are responsible for the magnetism.[18] The $\mathrm{Pb_2MF_6}$ compounds are the first transition metal fluorides that reveal such scenario. Compared to $\mathrm{Ba_2NiF_6}$, $\mathrm{Pb_2NiF_6}$ shows lower symmetry and a net magnetic moment that can be coupled to polar displacements. Therefore, we suggest $\mathrm{Pb_2MF_6}$ fluorides as prospective magnetic compounds which are capable of forming polar crystal structures. Recent theoretical studies of magnetoelectric coupling in transition-metal compounds emphasize the crucial role of ligand atoms that control the magnitude of magnetic couplings and polar distortions by changing the charge-tranfer gap between transition-metal d and ligand p states.[19] In this respect, a switch to non-oxide systems, such as halides, requires the preparation of new magnetoelectric compounds. The proposed synthetic approach should help to accomplish this challenging task. The chemical diversity of fluorinated heterometallic Pb−M β-diketonate precursors is beneficial for obtaining further new compounds and tuning the resulting materials to specific applications.

In conclusion, we have shown that fluorinated heterometallic β-diketonates can be used as volatile single-source precursors for the synthesis of mixed-metal fluorides. Further study of the low-temperature crystal structure and magnetic properties of the resulting Pb_2MF_6 fluorides should explore the possible magnetoelectric coupling in these compounds. The preparation of thin films using the title volatile single-source precursors is also underway.

■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Synthetic and characterization details, TGA traces of the thermal decomposition, X-ray powder diffraction analysis of the residues, magnetic measurements, and X-ray structural data for **1**−**5** (CIF, PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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■ ACKNOWLEDGMENT

Financial support from the National Science Foundation (CHE-0718900, E.V.D.) is gratefully acknowledged. A.A.T. was funded by the Alexander von Humboldt Foundation.

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